Risk assessment of arsenic in ground water of Larkana city

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Abstract

Water is an essential component for the survival of humans and animals. Due to industrialization, water is being contaminated with varying polluting agents, arsenic (As) contamination is one of them. An exclusive study was carried out for the determination of As in groundwater of Larkana city using microwave-assisted digestion followed by atomic absorption spectrometry (AAS). For that purpose, a total of 110 groundwater samples were collected from 10 union councils (UCs) of the city based on global position system (GPS) method. Results revealed that maximum concentration of As was found 17.0 μg/L in UC-6, while in UC-1, UC-2 and UC-10 the concentration of As was found within the permissible limits of WHO. The minimum and maximum mean concentration of As was found 3.59 μg/L and 6.78 μg/L, respectively. Out of 110 ground water samples of Larkana city, 13 samples were found above the permissible limits (~12% of total samples). Hence, water can be used for drinking purpose with caution.

1. Introduction

Water is an essential component and building block to sustain life. Water is considered economical development indicator for third world and developed countries. Water has essential usages of biochemical reactions in body, drinking, and home usage (Braune & Xu, 2008). Fresh water consists of 3% of the total water on earth and very small quantity is used by human beings (Hinrichsen & Tacio, 2002). Water resources have dwindled day by day and showing negative impact on every walk of life due to urbanization, industrialization and agricultural usage (Azizullah, Khattak, Richter, & Häder, 2011; Guven & Akinci, 2011). Recent reports of UNICEF and WHO have revealed 748 million people around the world lacking access to safe water resources and over 2.5 billion people suffering shortage of water supply (Supply & Programme, 2014).

Since water is polluted and contaminated day by day due to anthropogenic activities, waste disposal mismanagement, industrial effluent and usage of pesticides (Soomro, Siyal, Mirjat, & Sial, 2013). Arsenic (As) is major concern for human health due to its presence in ground water that is used for drinking purpose. Mobilization of As in atmosphere has many factors such as natural ways like weathering of rocks, eruption of volcanoes and degradation of biological activities (Mukherjee & Fryar, 2008). The man-made activities like combustion of fuel, coal, coke, using insecticides, herbicides, crop disinfectant medicine and other anthropogenic activates as smelting, mining and an additive usage of As to livestock feed for poultry as well as for wood preservative (Haque, Nabi, Baig, Hayat, & Trefry, 2008; Jadhav et al., 2015). The contamination of As in groundwater has become a grave concern of water purity in large areas of the world, especially in Bengal. In the history of mankind, it has been reported that millions of Bangladeshi peoples suffering from the poison of As in ground water (Kumar & Shah, 2006). In the literature, various countries of world such as Australia, USA, Argentina, Canada, India, Bengal, Mongolia, China as well as Vietnam have highlighted diseases caused by As contamination in water (Jakhrani, Malik, Sahito, & Jakhrani, 2011; Mukherjee & Fryar, 2008). People of Bengal in both parts of India and Bangladesh are exposed to As level up to 4 × 10\textsuperscript{4} μg/L (Kumar & Shah, 2006). In another study, Guo et al. (2001) reported highest concentration of As in the region of Chinese Mongolia up to 4000 μg/L (Guo et al., 2001). Taiwan inhabitants bore hazardous quantities of As in their water samples measured up to 1800 μg/L (Lin, Sung, Chen, & Guo, 2013). Researchers also pointed out high level of As 3100 μg/L in Vietnam’s water (Berg et al., 2001). Bleak health problems were encountered by Pakistani community of infested water of As. Unfortunately, in different parts of Pakistan, high quantity of As was spotted in water (Edition, 2011). Water management is poor throughout

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the country, so public health has major threats of water pollution. Pakistan stood at number 80 among 122 countries regarding water quality. Potable water sources either ground or surface are contaminated and violates WHO set standards (Azizullah et al., 2011). People of Sindh bear more burden of As contamination in water, almost 36% common people exposed to higher quantities as reported by Azizullah et al. (2011). To the best of our knowledge no report has been published regarding the quality of water of Larkana city, Sindh, Pakistan. The purpose of this research was to evaluate the potential hazards of As in groundwater of different union councils of Larkana using flame atomic absorption spectrometer (FAAS) and to measure the health risks associated with As contamination.

2. Material and method

2.1. Description of study area

Larkana city has situated on right bank of River Indus. Larkana is a district of Sindh province, Pakistan. In Larkana, there are 4 subdivisions and 48 union councils (UCs). Larkana is a subtropical area, so hot weather is prevalent in summer and cold in winter. Larkana temperature has average from 2 to 48 °C with a mean rainfall >240 mm. There are 1.4 million people living in the district Larkana, out of which 28.70% are living in city. Study area is located north of the River Indus and positioned between North (6.41 km) and East (3.43Km) with an area of 18.08 km squares and its coordinates are 27°33′30″ N 68°12′40″E. All UCs of Larkana are situated in urban area of the city as shown in Figure 1.

2.2. Sampling

It is always advised to get groundwater sampling by hand pumps 5 min in order to remove sand and insoluble impurities as well as depth water must be obtained to contain desired elemental quantities (Shar, Shar, Jatoi, Shar, & Ghouri, 2014). Water was obtained from hand pumps having depth 80–100 feet. After running water, samples were attained. Plastic bottles were used to collect 1000 mL water. Ten UCs of Larkana city were selected to acquire water samples of hand pumps and small motors used in houses to draw water from the ground with depth 80 to 120 feet as shown in Figure 2(A) and (B). Method of collection of water samples from different points of Larkana was done with the help of global positioning system (GPS) in 2014. A total of 110 samples were obtained from all UCs of Larkana city. Samples were shifted to laboratory to protect them from atmosphere and kept at room temperature to avoid their pH and temperature. Experimental work was carried out for checking of their chemical parameters in the laboratory.
2.3. Chemicals and reagents

Standard solution was prepared from reagents purchased from Merck (Darmstadt, Germany) and diluted with de-ionized water for required concentration of ppm solution for detection of As.

2.4. Instrumentation

This study was conducted using latest techniques of analysis such as Modern Atomic absorption spectroscopic (Perklin A 700) coupled with Mercury Hydride System (MHS-15) to measure the contamination of As in water. This technique provides a simple and precise measurement of quantitative and qualitative analysis of metals present in different samples of water (Fisher, Tu, & Baldocchi, 2008).

2.5. Microwave digestion method

500 mL of water samples were put in PTFE flask, then flasks were closed and subjected to microwave irradiation in closed vessel microwave digestion system using Milestone Ethos D model (Sorisole-Bg, Italy). Digestion programme of microwave oven was applied 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) HNO₃. Similarly reagent blanks were also made by same procedure. Microwave digestion method has superiority to conventional digestion method because it takes less time to digest water sample as well as it has less chance of evaporation of elements so more accurate extraction of elements from samples than in conventional method. It also uses less acid for digestion (Guven & Akinci, 2011).

3. Results and discussion

In Pakistan, more than 40% population bear the As contamination in water. Hence, nation of Pakistan has more risk exposure of As. More than 20% people living in Punjab are suffering from higher pollution of As in either ground or surface water sources but tolerate higher quantity of As in industrial areas (Azizullah et al., 2011). Part of East Punjab has been most affected by As contamination in groundwater up to 1900 μg/L (Farooqi, Masuda, & Firdous, 2007). As also causes hazardous effect for population in northern areas of Pakistan, where 25% people face perilous effect of As (Azizullah et al., 2011). In Sindh, people are suffering from 16–36%, exposing high level of As up to 315 μg/L in some areas of groundwater (Jakhri et al., 2011).

According to results obtained in current study, maximum concentration of As was found 17.0 μg/L from UC-6 and minimum was 0.1 μg/L from UC-10. However in UC-1, UC-2, and UC-10 the concentration of As was found within the safe limit recommended by WHO (10 μg/L). Out of 110 groundwater samples of Larkana city, 13 samples found above the permissible limit, which was 11.8% (~12%) of total samples as shown in Table 1. Comparative mean values of As level in ground water of all UCs showed As within safe limit of WHO recommended value, while UC-5 had maximum mean 6.79 μg/L and UC-1 had minimum mean 3.58 μg/L.

Water is being deteriorated and not safe for drinking purpose in populous areas of Pakistan like Karachi, Lahore, Peshawar and various other cities due to various anthropogenic activities. In comparison to the quality of ground water of Larkana city is much better and safe than other cities of Pakistan specially in Punjab province, where ground water is contaminated more and unsafe for people due to high concentration of As. Many studies have reported high concentration of As in different cities such as Dera Gazi Khan (1–29 μg/L), Rahim Yar Khan (20–500 μg/L), Bahawalpur (0.5–59 μg/L), Muzzafargarh (0.01–900 μg/L), Multan (0–50 μg/L), Lahore (0–50 μg/L) Faisalabad (1.0–23 μg/L) and Sheikhupura (5–76 μg/L) as shown in Table 2.

In comparison to the ground water quality of Larkana city with the cities of Khyber Pakhtunkhwa province is almost identical with the results of present study. The level of As in ground water of Peshawar city was reported in the range of 5–20 μg/L. In another study the level of As in the ground water of Nowshera city was reported in the range of 0.01–17.58 μg/L as shown in Table 2. The As contamination of ground water quality of various cities of Sindh province with Larkana city was found comparatively higher and levels are shown

| UCs | UC-1 | UC-2 | UC-3 | UC-4 | UC-5 | UC-6 | UC-7 | UC-8 | UC-9 | UC-10 |
|-----|------|------|------|------|------|------|------|------|------|-------|
| 1   | 4.43 | 4.83 | 1.73 | 5.30 | 2.23 | 1.63 | 2.97 | 5.57 | 1.40 | 2.63  |
| 2   | 4.17 | 4.38 | 3.08 | 8.43 | 3.63 | 3.87 | 4.10 | 12.0 | 3.77 | 3.40  |
| 3   | 5.30 | 3.93 | 4.17 | 5.23 | 7.0 | 16.5 | 4.10 | 12.0 | 5.23 | 4.87  |
| 4   | 6.0 | 3.48 | 5.50 | 14.6 | 5.43 | 17.0 | 4.90 | 6.0 | 5.63 | 5.23  |
| 5   | 3.50 | 3.19 | 7.07 | 9.07 | 8.23 | 6.0 | 3.27 | 4.80 | 6.0 | 4.13  |
| 6   | 2.20 | 12.0 | 6.07 | 2.67 | 15.6 | 3.10 | 2.73 | 6.77 | 7.33 | 4.17  |
| 7   | 3.03 | 3.70 | 13.8 | 3.83 | 12.3 | 4.20 | 2.17 | 2.97 | 1.30 | 3.50  |
| 8   | 2.27 | 1.50 | 2.67 | 5.57 | 4.70 | 3.90 | 3.03 | 3.30 | 4.47 | 2.67  |
| 9   | 4.33 | 2.80 | 2.73 | 0.39 | 2.63 | 2.60 | 0.61 | 2.63 | 13.0 | 3.33  |
| 10  | 2.30 | 0.20 | 8.03 | 0.67 | 1.90 | 6.53 | 11.7 | 0.28 | 7.63 | 4.27  |
| 11  | 1.90 | 0.10 | 0.55 | 0.50 | 11.0 | 3.27 | 1.10 | 0.54 | 13.0 | 2.83  |
| Mean | 3.59 | 3.65 | 5.04 | 5.13 | 6.79 | 6.24 | 3.63 | 5.17 | 6.25 | 3.75  |
| Standard deviation | 1.37 | 3.19 | 3.71 | 4.33 | 4.54 | 5.38 | 2.93 | 3.96 | 3.91 | 0.88  |
When comparing concentration of As in ground water of Larkana city with other countries, it has been found to be much lower level (10 to 17 μg/L) in some UCs. But it can be deteriorated with passage of time as neighbouring countries of Pakistan such as India and Bangladesh where people are suffering from too much contamination of As (2000 μg/L and 4 × 10^4 μg/L, respectively) in ground water. In East Asian countries, high level of As in ground water of Inner Mongolia, Thailand, Burma, Vietnam and Cambodia have been reported. The As contamination in ground water of Asian countries are shown in Table 3.

3.1. Pearson correlation coefficient

Table 4 shows Pearson correlation among studied UCs of Larkana city. It was observed that UC-1 showed strong relation with UC-4, 6 and 8, less strong relation with UC-10 and weak relation with UC-2, while negative relation was detected with UC-3, 5, 7 and 9. UC-2 indicated strong relation with UC-5 and significant relation with UC-3, 4, 8 and 10. It showed negative relation with UC-6, 7 and 9. In UC-3, it was noticed less strong relation with UC-5 and 10 while weak significant relation with UC-4, 6, 7 and negative relation was observed with UC-9. It was noted that UC-4 had strong relation with UC-6 and weak relation with UC-7 and 10, while negative relation

### Table 2. Concentration of Arsenic in different cities of Pakistan.

| Province       | City          | As (μg/L) | References                  |
|----------------|---------------|-----------|------------------------------|
| Punjab         | Dera Gazi Khan| 1–29      | Malana & Khosa, 2011         |
|                | Rahim Yar Khan| 20–500    | Mahar, Khuhawar, Jahangic, & Baloch, 2015 |
|                | Muzaffargarh  | 0.01–900  | Nickson, McArthur, Shrestha, Kyaw-Myint, & Lowry, 2005 |
|                | Bhawalpur     | 0.3–59    | Artiz, 2001                  |
|                | Multan        | 0–50      |                             |
|                | Lahore        | 0–50      |                             |
|                | Faisalabad    | 1.2–23    |                             |
| Khyber Pakhtunkhwa | Peshawar     | 5–20      | Abbas & Cheema, 2015         |
| Sindh          | Khairpur      | 0.24–315.6| Jakhrani, Chaudhry, Malik, Mazari, & Jakhrani, 2009 |
|                | Gambat        | 0.01–126  | Jakhrani et al., 2011        |
|                | Nawab Shah    | 10–200    | Kandhrro, Samoon, Laghari, Chandio, & Yousfani, 2016 |
|                | Dadu          | 8–67      | Memon et al., 2016          |
|                | Tando Allahyar| 0.04–300  | Majidano, Arain, Bajaj, Iqbal, & Khuhawar, 2010 |
|                | Matiari       | 0.05–50   | Uqaili et al., 2012         |
|                | Jamshoro      | 13–106    | Baig et al., 2009           |
|                | Thatta        | 10–200    | Rubab, Naseem, Khan, Husain, & Arain, 2014 |
|                | Karachi       | 1–80      | Rahman, Lee, & Khan, 1997    |
|                | Larkana       | 0.01–17   | Current study               |

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|                | Bhawalpur     | 0.3–59    | Artiz, 2001                  |
|                | Multan        | 0–50      |                             |
|                | Lahore        | 0–50      |                             |
|                | Faisalabad    | 1.2–23    |                             |
| Khyber Pakhtunkhwa | Peshawar     | 5–20      | Abbas & Cheema, 2015         |
| Sindh          | Khairpur      | 0.24–315.6| Jakhrani, Chaudhry, Malik, Mazari, & Jakhrani, 2009 |
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The ground water quality of Jamshoro was also reported with the contamination of As level with 13.0–106 μg/L. Research also conducted on the ground water assessment of Tando Allahyar, Thatta and Karachi, where higher concentration of As was reported 0.04–300 μg/L, 10–200 μg/L and 1–80 μg/L, respectively. However, one research study was also reported on the quality of ground water of Larkana villages where As had found from 0.40–20.0 μg/L (Akhan, Siddqui, & Usmani, 2006). The study concluded that 10% of ground water samples were exceeded the limit of WHO permissible level and found unsafe for drinking purpose. This study also confirms that results of our findings are almost identical with the data previously published on the water of Larkana. Furthermore, these results confirm the worsen situation of ground water quality of Punjab and other cities of Sindh province, where higher level of As found in ground water and people has been suffering from various diseases caused by As contamination. However, ground water of Larkana city and few cities of Khyber Pakhtunkhwa are comparatively safe and showed lower concentration of As.

### Table 3. Arsenic concentration in ground water of different parts of world.

| Country       | Concentration μg/L | Reference                  |
|---------------|--------------------|----------------------------|
| India         | 2000               | Kumar & Shah, 2006         |
| Bangladesh    | 4 × 10^4           | Guo et al., 2001          |
| Inner Mongolia, China | 4000 | Guo et al., 2001 |
| Vietnam       | 3100               | Berg et al., 2001         |
| Taiwan        | 1800               | Lin et al., 2013          |
| Thailand      | 114                | Kim, Charpiwat, Hanh, Phan, & Sthiannop-kao, 2011 |
| Burma         | 350                |                            |
| Cambodia      | 350                |                            |

Note: WHO permissible level for As 10 μg/L.

When comparing concentration of As in ground water of Larkana city with other countries, it has been found to be much lower level 10 to 17 μg/L in some UCs. But it can be deteriorated with passage of time as neighbouring countries of Pakistan such as India and Bangladesh where people are suffering from too much contamination of As 2000 μg/L and 4 × 10^4 μg/L, respectively, in ground water. In East Asian countries, high level of As in ground water of Inner Mongolia, Thailand, Burma, Vietnam and Cambodia have been reported. The As contamination in ground water of Asian countries are shown in Table 3.

3.1. Pearson correlation coefficient

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Table 4. Pearson correlation of Arsenic concentration of different UCs of Larkana city.

| S. No | UC-1 | UC-2 | UC-3 | UC-4 | UC-5 | UC-6 | UC-7 | UC-8 | UC-9 | UC-10 |
|-------|------|------|------|------|------|------|------|------|------|-------|
| UC-1  | 1    |      |      |      |      |      |      |      |      |       |
| UC-2  | .06  | 1    |      |      |      |      |      |      |      |       |
| UC-3  | −.12 | .128 | 1    |      |      |      |      |      |      |       |
| UC-4  | .647*| .100 | .050 | 1    |      |      |      |      |      |       |
| UC-5  | −.404| .522*| .368 | −.137| 1    |      |      |      |      |       |
| UC-6  | .661*| −.085| .113 | .563*| −.070| 1    |      |      |      |       |
| UC-7  | −.056| −.250| .296 | .029 | −.380| .318 | 1    |      |      |       |
| UC-8  | .584*| .476 | −.151| .485 | −.016| .406 | −.125| 1    |      |       |
| UC-9  | −.248| −.236| −.405| −.492| .054 | −.105| −.343| −.422| 1    |       |
| UC-10 | .488 | .213 | .380 | .442 | .123 | .837**| .448 | .344 | −.017| 1     |

Notes: *Correlation is significant at the .05 level.; **Correlation is significant at the .01 level.

Table 5. Arsenic daily intake from drinking water of different UCs of Larkana city

| S.No | UC-1 | UC-2 | UC-3 | UC-4 | UC-5 | UC-6 | UC-7 | UC-8 | UC-9 | UC-10 |
|------|------|------|------|------|------|------|------|------|------|-------|
| As   | 3.59 | 3.65 | 5.04 | 5.13 | 6.79 | 6.24 | 5.17 | 6.25 | 3.73 |
| ADI  | 0.21 | 0.21 | 0.29 | 0.30 | 0.40 | 0.36 | 0.21 | 0.30 | 0.36 | 0.22 |

Notes: Safe As daily intake in water 0.66 μg/day. As (μg/L).

was spotted with UC-5 and 9. UC-5 had showed weak relation with UC-9 and 10, while negative relation was observed with UC-6, 7 and 8. It was observed that UC-6 had very strong relation with UC-10 and significant relation with UC-7 and 8. UC-7 had shown less strong relation with UC-10 and observed negative relation with UC-8 and 9. It was observed that UC-8 has less strong relation with UC-10 and less negative with UC-9. UC-9 had indicated negative relation with UC-10. Matrix of correlation result showed contamination of ground water with As was man-made activities, erosion of bed rocks, homes, industrial effluent, agricultural runoff activities and solid waste dumping (Srinivasamoorthy, Vasanthavigar, Chidambaram, Anandhan, & Sarma, 2011).

3.2 Human health risk assessment

3.2.1. Arsenic daily intake (ADI)

Total As intake was estimated using following formula as reported by Baig et al. (2009). ADI = mean concentration of As in ground water × daily water intake/mean weight of body. The daily water intake and body weight of common people were assumed average 3.0 to 3.5 litres and 65 kg, respectively. The results of the ADI are reported in Table 5. It was observed that As accumulation in body was found within safe limit in all UCs of Larkana city and values varied from 0.209 to 0.396 μg/day. Hence, people of Larkana city are much safer than the other parts of the country, where higher levels of ADI reported (Abbas & Cheema, 2015; Khan, Rauf, Muhammad, Qasim, & Din, 2016; Khan, Shah, Muhammad, Malik, & Shah, 2015). Comparatively UC-5 and UC-6 showed higher ADI values than rest of the studied UCs. The higher ADI values may cause health problems in future, such as keratosis, black foot disease, hypertension, cardiovascular, diabetes, and also some typical skin lesion disease, lungs and bladder cancers in local people consuming As contaminated water (Memon et al., 2016; Uqaili, Mughal, & Maheshwari, 2012).

4. Conclusion

Keeping in view of the results obtained in this study, it can be concluded that groundwater of Larkana city is safe for drinking purpose than other cities of Pakistan and particularly other cities of the province of Sindh, where As contamination reported higher. Except UC-5 and UC-6, where high concentration of As found which showed that 27% sample were contaminated than safe limit recommended by WHO. Therefore, it may cause health problems for local inhabitants and pose future complication of Larkana community, if they continue drinking unsafe water. Hence, it is recommended to Pakistan state and particularly Sindh government to pay special attention and protect people from contaminated water and improve solid waste management in order to keep groundwater of Larkana city safe for future as well as increase awareness among farmers to use chemicals (pesticides) sparingly to keep water safe.

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No potential conflict of interest was reported by the authors.

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