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Risk assessment of arsenic and heavy metals of drinking water in coastal area: Case for Taluka Keti Bandar, Sindh, Pakistan

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Abstract

The current research work was carried out to examine concentration of Arsenic and heavy metals in the water used by the population of area. From study area, samples were collected from sixteen towns/villages for measurement of heavy metals including arsenic. The DMS coordinates were also measured using GPS device from sampling points. The depth observed for sampling points was in the range of 15-25 feet. Heavy metal levels were determined with the help of Atomic Absorption Spectrophotometer. Arsenic kit method was employed for arsenic analysis from water samples. Concentration of Fe, Cu and Zn were found below WHO limit in all samples. Arsenic was found higher than WHO limit in villages Baghan Town, Manjhi Khan Baloch, Haji Qadir Bux Baloch, Sajjan Wari, M. Hassan Perozani Baloch, Haji Yaqoob Memon, Muhammad Essa Khaskheli, Esso Baloch and Ali Muhammad Utradi. Cadmium was found above permissible limit in all villages except Village Muhammad Essa Khaskheli. Higher Mn concentration was observed in drinking water of Village Pir Usman Shah Jhaloo only. Higher Ni content in villages, Haji Qadir Bux Baloch, M. Hassan Perozani Baloch, Haji Yaqoob Memon, M. Essa Khaskheli and Ranamori was found. HQs were found in the order of As> Cd> Cr> Cu>Mn> Ni> Zn> Fe and the ranges of cancer risks were observed as As (0.00006-0.00031), Cd (0.00004-0.00051), Cr (0.00044-0.00076), Mn (0.00011-0.00072), Ni (0.00020-0.00032), Fe (0.00037-0.00122), Cu (0.00037-0.00392) and Zn (0.00049-0.00355) mgkg-1day-1.

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Introduction

Recent reports show that hundreds of millions of people are affected by arsenic all over the world, mostly arsenic affected people were found in Southeast Asia. Literature reveals that 0.32-2.4 million people living in Cambodia, 3.4 million in Myanmar, 3 million in Nepal, 2-5 million in China, 10 million in Vietnam, 47-60 million in Pakistan, 28-60 million in Bangladesh, and 70 to 80 million in India are affected due to arsenic content greater than water the World Health Organization guideline level of 10 µg/L or higher than 50 µg/L. According to these reports about 150 to 240million people were affected from these areas. High arsenic content in drinking water may cause different diseases like, diabetes, cardiovascular disease, cancers and neurological disorders (DP. Jasudkar *et al.,* 2019; J. S Uppal *et al.,* 2019). Unending research and improvement activities are needed to shield public health from arsenic related diseases (CM. George *et al.,* 2014). Arsenic is broadly circulated in natural atmosphere which may cause mutation, deformities and cancer. It has therefore become a major environmental threat in short period of time. The presence of large amounts of arsenic was found in Southeast China in the form of arsenic ore and coal. Contamination of Surface water, vegetation and soil occurs due to arsenic from mines (L. Zhang *et al.,* 2017). Arsenic is naturally present in sediments, soil and a water source which is extremely toxic for human health with its consumption from contaminated water. Arsenic contaminated drinking water poses serious health hazards including cancer and non-cancer end points. Reports show that higher cancer risks were observed in people having regular exposure to high arsenic concentration in atmosphere (O. Gunduz *et al.,* 2017; Dum *et al.,* 2015; S. Bhowmick *et al.,* 2018). Studies disclose that arsenic is carcinogenic and toxic element and exists in the earth's crust at mean content of 5mg/kg (IARC, 2012; H. Garelick *et al.,* 2008; E. Pellizzari & Clayton, 2008). In the earth's crust, homogeneous distribution of arsenic is not present, though it is related to certain geological sections (SM. Aronson, 1994; National Academy of Sciences, 1977). Geological weathering is the major source of

Arsenic release into groundwater but there are anthropogenic sources of arsenic as well. About 140 million people in at least 70 countries all over the world are suffering due to natural release of arsenic into surface or groundwater (P. Ravenscroft *et al.,* 2009). Arsenic may be entered into our food chain through food preparation, cooking and irrigation with arsenic contaminated water (B. Arslan *et al.,* 2016; S. Bhattacharya *et al.,* 2012; Y. Fu *et al.,* 2012; M. Rahman *et al.,* 2011; Zhao, F *et al.,* 2010; D. Mondal *et al.,* 2010; Zavala *et al.,* 2010). There are numerous activities, through which groundwater resources are going to be contaminated such as, climate, period, aquifer depth, site-specific quality like soil variety and infiltration of pollutants into the soil sub-strata. Probability and Seriousness of a definite impurity as well as severity in water may be affected by these activities (K. Satish Kumar *et al.,* 2015). It is estimated that about two billion people all over the world depend upon the groundwater resources for the drinking purpose due to development of groundwater resources with enormous increase in the last 50 years (K. Murali *et al.,* 2013). Increased amount of water is used for different processes; therefore water quality has focused in numerous areas for the alarm for life of the people (BR. Agarwal *et al.,* 2012). There are many water sources, but groundwater is believed safe for human consumption, since public, industries and agricultural requirements are contaminating to the groundwater sources. Therefore, for huge population accessibility of fresh groundwater is extremely important (R. Abbulu, 2013; Pakistan flood victims flee Thatta, 2010). One of the aims of the paper was to enhance the quality of drinking water. The research described in this paper was carried out to assess the risk assessment of arsenic and heavy metals from drinking water of coastal areas of Keti Bandar collected from sixteen villages/towns to recognize the villagers using unsafe sources.

Materials and methods

Study Area

Keti Bandar is located in Thatta district, Sindh, Pakistan. It is a port on the Arabian Sea. Keti Bandar port was made on the vestiges of the older Debal harbour which was arrival point of Muhammad Bin Qasim along with his army. The driving time of about 3.5-4 hours from Keti Bandar to Karachi was observed with distance of about 150 km. Mirpur Sakro and Gharo are the two major towns on the route from Keti Bandar to Karachi.

The economy of Keti Bandar totally depends upon fishing and about all people of the area are fishermen. The fish caught by fishermen form Arabian Sea, transport their product to Karachi (DP. Jasudkar *et al.*, 2019). The study area has hot desert climate. The average annual rain fall in the study area is 210 mm, while the average annual temperature is about 26.8 °C (Pakistan flood victims flee Thatta, 2010).

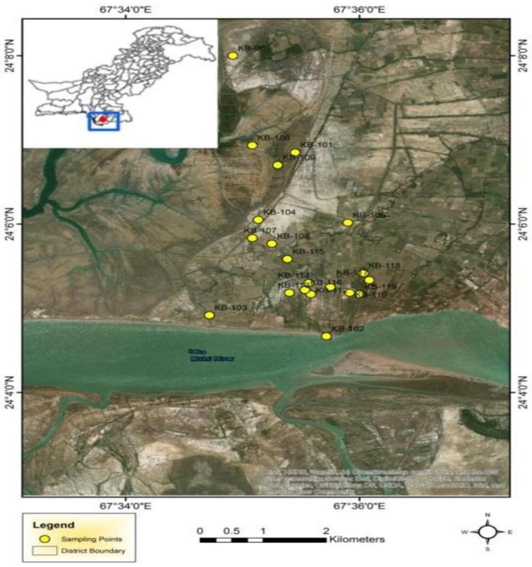


Fig. 1. Sampling location map of the study area.

Samples Collection

All sampling bottles as well as glassware utilized were washed with detergent and then rinsed with double distilled water before sampling. Three replicates of drinking water of each source were collected from each location. Usually hand pumps were fitted by villagers to get groundwater for drinking, cooking and washing purposes. Ground water source was run for 2-5 minutes till fresh water. The depth of water sources was found 15-25 feet in different villages of study area. Some selected villages/areas from water sampling was carried out included Baghan Town, Pir Usman Shah Jhaloo, Ali Hassan Mirgh Baloch, Manjhi Khan Baloch, Manjhi Khan Baloch, Nathoo Khan, Haji Qadir Bux Baloch, Sajjan Wari, M. Hassan Perozani Baloch, Haji Yaqoob Memon, Haji Gul Muhammad Jat, Abdullah Khatri, Abdullah Mallah, M. Essa Khaskheli, Esso Baloch, Ali Muhammad Utradi and Ranamori. GPS was used to record the DMS coordinates of sampling points for authenticity of results (Table 1). From study area, 35 samples were collected in 1500mL capacity of plastic bottles for heavy metals and arsenic determination. For heavy metals analysis, 1 mL of nitric acid was used in sampling bottles to acidify samples.

Sample Preparation

Samples were transported to laboratory of chemistry, Shah Abdul Latif University Khairpur for the process of preparation. Preparation of water samples was carried out to analyse arsenic as well as heavy metal analysis. For analysis of heavy metals 500mL of sample was taken in a beaker, placed in electric hot plate and concentrated 10 times by evaporation at temperature of 80 to 90°C. Solutions were filtered using Whatmann no: 42 filter paper and volume was made up to the mark with double distilled water and placed at lower temperature till analysis (T. Anurag *et al.,* 2010) Prepared samples were transported to the PCRWR laboratory (Pakistan Council of Research in Water Resources) Government of Pakistan ministry of Science & Technology National Water Quality Laboratory, Islamabad. Atomic absorption spectrophotometer (Analytic Jena) was used to analyse heavy metals under study.

Analysis

The concentration of As was analyzed using Arsenic kit in the PCRWR Government of Pakistan ministry of Science & Technology National Water Quality

Laboratory, Nawabshah and samples prepared for heavy metals (Cd, Cr, Mn, Fe, Ni, Co and Zn) were transported to Pakistan Council of Research in Water Resources (PCRWR) Government of Pakistan ministry of Science & Technology National Water Quality Laboratory, Islamabad. Atomic absorption spectrophotometer (Analytic Jena) was used to analyse heavy metals. For the assurance of data quality, samples were run three times and three standards (0.0 mg/L, 2.5 and 5 mg/L) of respective element were also used to check the instrument results after analyzing every ten samples.

The confidence level was found 95% for results reproducibility, while results interpretation average values were used. All glassware's were washed with 2% nitric acid before use and chemicals used were of A.R grade.

Table 1. DMS coordinates and abbreviated names of sampling stations.

Sr. No:	Villages	Abbreviation	Depth (Feet)	Water source	DMS Coordinates
1	Baghan Town	B.T	15	Hand Pump	24° 13' 49" N 67° 36' 36"E
2	Pir Usman Shah Jhaloo	P.U.S.J	15	Hand Pump	24° 10' 43" N 67° 34' 49"E
3	Ali Hassan Mirgh Baloch	A.H.M.B	18	Hand Pump	24° 08' 58" N 67° 34' 49"E
4	Manjhi Khan Baloch	M.K.B	18	Hand Pump	24° 08' 34" N 67° 35' 23"E
5	Nathoo Khan	N.K	20	Hand Pump	24° 06' 51" N 68° 17' 41"E
6	Haji Qadir Bux Baloch	H.Q.B.B	18	Hand Pump	24° 04' 40" N 67° 35' 43"E
7	Sajjan Wari	S.W	18	Hand Pump	24° 04' 55" N 67° 34' 43"E
8	M. Hassan Perozani Baloch	M.H.P.B	20	Hand Pump	24° 06' 03" N 67° 35' 08"E
9	Haji Yaqoob Memon	H.Y.M	25	Hand Pump	24° 06' 01" N 67° 35' 54"E
10	Haji Gul Muhammad Jat	H.G.M.J	20	Hand Pump	24° 09' 43" N 67° 34' 16"E
11	Abdullah Khatri	A.K	18	Hand Pump	------------------------------
12	Abdullah Mallah	A.M	15	Hand Pump	------------------------------
13	M. Essa Khaskheli	M.E.K	15	Hand Pump	------------------------------
14	Esso Baloch	E.B	18	Hand Pump	------------------------------
15	Ali Muhammad Utradi	A.M.U	18	Hand Pump	------------------------------
16	Ranamori	R.M	------	Surface water	24° 08' 39" N 67° 27' 02"E

Results and discussion

Arsenic is naturally occurring metalloid and is found in soil, rocks and water. Water may be contaminated by arsenic because it is present in lots of aquifers. For drinking water the WHO guideline value is recommended as 0.01 mg/L or 10 µg/L. different diseases for instance, loss of movements, pain in hands and feet, skin rashes, vomiting, muscular, stomach weakness, diarrhea may be caused due to short term arsenic exposure. Long term exposure of arsenic in drinking water may cause heart irregularity, reduced formation of blood cells, diarrhea, and nausea, discoloring of membrane and harm blood vessel. Threat of cancer may be increased in lungs, bladder and liver by high arsenic content in drinking water (APHA (American) 2005). Results reveal that arsenic content was found higher than WHO guideline of 0.01 mg/L in drinking water of villages Baghan Town (12.6 µg/L), Manjhi Khan Baloch (25.0 µg/L), Sajjan Wari (17.0 µg/L), Haji Qadir Bux Baloch (22.0µg/L), Haji Yaqoob Memon (18.6 µg/L), M. Essa Khaskheli (11.5µg/L), Esso Baloch (11.0µg/L) and Ali Muhammad Utradi (17.0 µg/L) (Table 2 and Fig. 2).

Use of phosphate fertilizer, industrial waste and deterioration of galvanized plumbing are responsible for cadmium contamination in drinking water.

Cadmium is highly toxic metal and may cause convulsions, sensory disturbances, digestive issues, vomiting and nausea. High Cd content may cause cardiovascular disease, cancer, bone, liver, and kidney damage (Saint-Jacques, N *et al.,* 2018; Qasemi, M *et al.,* 2019). As compared to surface water, cadmium content was observed in higher amounts in groundwater (CH. Huang, & CJ. Chen, 1995). The main source of cadmium contamination in drinking water was reported by plumbing (J. De Zuane, 1997). Ruthless human health hazard may be caused as a result of long term as well as short term exposure of cadmium in drinking water. Long-term contact of Cd can cause Itai-itai disease, bone and kidney disease, whereas short term exposure causes diarrhea, vomiting, and mucous membrane destruction (H. Barton, 2005). Cadmium concentrations in drinking water were found as 0.003 to 0.04 mg/L with maximum value (0.04 mg/L) observed in groundwater at Baghan Town, while the minimum value (0.003 mg/L) in ground water at village M. Essa Khaskheli (Table 3). From study area 93.75% samples drinking water of different villages were found contaminated by cadmium (Table 2 and Fig. 2).

Water supplies may get chromium through the erosion of natural deposits of chromite ores, municipal waste, dyes industry, leather, paper mills and run-off from steel (SO. Lesmana *et al.*, 2010). Liver, lungs and hemorrhage organs may be damaged due to high chromium content in potable water. Concentrations of chromium were observed from 0.040 to 0.06 mg/L in groundwater of Manjhi Khan Baloch village (Table 3). The chromium content of 62.5% was found below them AL set by WHO (2011), (S. Dixit & S. Tiwari, 2008) and Pak EPA (2008) (WHO, 2011). The high level of Cr may also be due to urban waste, domestic water and solid waste dumping. Particular level of chromium is compulsory for lipid metabolism, amino acid utilization as well as metabolism of glucose (Anurag, T *et al.,* 2010). High Cr content may have harmful effects on dermatitis, respiratory organs, liver and kidneys as well as ulceration of skin (Khan S, *et al.,* 2013) (Table 2 and Fig. 2).

The source of manganese in groundwater and surface water is usually rocks and soils. At trace level, manganese is considered as essential element for appropriate performance of animals as well as humans, since its higher concentration may cause lack of vision and memory by damaging nervous system of men. The high level of manganese may also cause lung and bronchitis embolism, as well as Parkinson infection (Achmad, R.T. & Auer Kari, E.I. 2017). The higher and lower Mn content was measured from study area as 0.06 and 0.010 mg/L respectively in villages Pir Usman Shah Jhaloo and Nathoo Khan respectively. The Manganese content except village Pir Usman Shah Jhaloo was found within acceptable limit of 0.05 mg/L given by the WHO (Table: 2 and Fig.: 2).

Manufacturing waste, mining, oxidized metal and mineral from rocks are the main sources of iron in natural water (Seilkop, S. K., & Oller, A. R., 2003).

The highest iron level for drinking water is prescribed by the WHO as 0.3 mg/L, since the iron concentration was observed within allowable level in all samples of the study area. The concentration of iron was ranges from 0.03 mg/L to 0.10 mg/L (Table: 2 and Fig. 2).

Different sources of Ni in water consist of municipal sewage, industrial wastes, fertilizers and soils and rocks weathering however, initial source may be from ultramafic rocks (S. Paul & U. Mishra, 2011; S. Muhammad *et al.,* 2011; S. Muhammad *et. al.,* 2013; T. Shahm *et. al.,* 2012). About 300μg of Ni may be taken through diet on daily basis. Higher Ni content in human my cause nasal cancer, lung cancer, tissue damage, brain, kidney, liver damage, gastro intestinal distress and pulmonary fibrosis (T. Shahm *et al.,* 2014; H. Barton, 2005). Utensils, sinks, kitchen appliances, surgical implants, jewellery, coins, batteries, automobiles, electronic component, fabrication, high grade steel alloy, production of electroplating and ghee mills are considered as the anthropogenic sources of Ni (Pak EPA, 2008) .

Nickel concentration in the study area was found as 0.020-0.03 mg/L with maximum content in the drinking water source of village Haji Yaqoob Memon. Study showed that 50% samples were found contaminated by Ni content greater than WHO maximum level of 0.02 mg/L (S. Dixit & S. Tiwari, 2008; WHO, 2011) (Table 2 and Fig. 2).

Cobalt is very important constituent of vitamin B12 and has found good uses to prevent anaemic condition by creating erythrocytes (KS. Babai *et al.,* 2012). Using cobalt in high amount may spoil skeleton, skeleton muscles, heart, pancreases, kidney and liver (YR. Sharma, 1998).

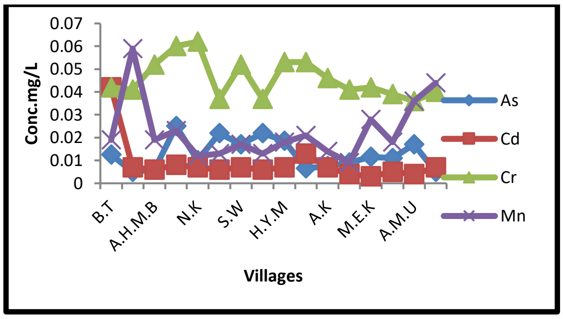
Usually cobalt content greater than 1mg kg-1 of body weight is harmful for human beings; rather it has lower toxicity (CH. Huang *et al.,* 1995). Lower (0.010 mg/L) and higher (0.34 mg/L) cobalt content was determined from potable water of study area, however the highest Co content was determined from village Muhammad Hassan Perozani Baloch (Table 2 and Fig. 2).

Copper is an important source for humans It is essential for human diet to confirm worthy health in less amount. Nevertheless, at higher concentration it may cause vomiting, diarrhea, liver, nausea and kidney damage (L. Simonsen *et al.,* 2012). The WHO guideline of copper in drinking water is suggested as 2.0 mg/L, since all water samples showed copper content within permissible limit. The average range of copper in study area was declared as 0.060 to 0.32 mg/L (Table 2 and Fig. 2). Zinc is considered as one of the most important elements

and is necessary for cofactor of about 80metabolic enzymes, healing of wounds and in production of antioxidants (KJ. Kramer *et al.,* 2004). The highest Zn concentrations (0.29 mg/L) were observed in drinking water at village Ali Hassan Mirgh Baloch, while the lowest concentrations (0.040 mg/L) groundwater at village Ali Muhammad Utradi. The concentration of zinc was found within permissible limit set by the WHO as 3.0mg/L in all the samples collected from different villages of Taluka Keti Bandar (Table 2 and Fig. 2).

Table 2. Arsenic and heavy metals contents (mg/L) in drinking water of Taluka Keti Bandar

	As	Cd	Cr	Mn	Ni	Fe	Co	Cu	Zn
WHO Limit	0.001	0.003	0.05	0.05	0.02	0.3	0.05	2.0	3.0
B .T	0.013	0.042	0.042	0.019	0.018	0.07	0.081	0.10	0.24
P. U. S. J	0.005	0.007	0.041	0.059	0.020	0.06	0.106	0.12	0.23
A. H. M. B	0.006	0.006	0.052	0.019	0.018	0.04	0.059	0.07	0.29
M. K. B	0.025	0.008	0.060	0.023	0.020	0.06	0.024	0.32	0.22
N. K	0.010	0.007	0.062	0.012	0.016	0.05	0.022	0.11	0.08
H. Q. B. B	0.022	0.006	0.037	0.013	0.022	0.06	0.055	0.22	0.08
S. W	0.017	0.007	0.052	0.017	0.017	0.10	0.024	0.06	0.19
M. H. P. B	0.022	0.006	0.037	0.013	0.022	0.06	0.341	0.07	0.04
H. Y. M	0.019	0.007	0.053	0.018	0.026	0.06	0.064	0.11	0.06
H. G. M. J	0.007	0.013	0.053	0.021	0.019	0.07	0.011	0.06	0.12
A. K	0.008	0.007	0.046	0.014	0.019	0.06	0.160	0.06	0.11
A. M	0.009	0.004	0.041	0.009	0.017	0.03	0.211	0.24	0.04
M. E. K	0.012	0.003	0.042	0.028	0.024	0.06	0.038	0.07	0.10
E. B	0.011	0.005	0.039	0.018	0.018	0.10	0.080	0.08	0.05
A. M. U	0.017	0.004	0.036	0.036	0.020	0.06	0.018	0.09	0.04
R. M	0.005	0.007	0.040	0.044	0.023	0.06	0.030	0.06	0.05



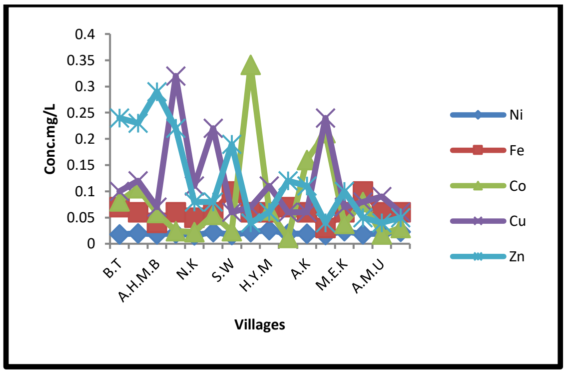


Fig. 2. Variation of arsenic and heavymetals in drinking water of Taluka Keti Bandar.

Risk Assessment

Different pathways are reported for entering heavy metals into human body, as compared to oral ingestion the remainder of all are minor (D. Grafinkel, 1986; Pak EPA, 2008). The average daily intake (ADI), hazard quotient (HQ) and carcinogenic risk (CR) were used to calculate health risk assessment from the study area. The equation to calculate the ADI through drinking water ingestion in the study area was adopted. (ATSDR, 2008) and USEPA (1998) (Muhammad S, 2010) as given below:

$$ADI = \frac{CW \times IR \times EFxED}{BW \times AT} \quad (i)$$

Details are given in references (ATSDR, 2008; Pak EPA, 2008)

Depending on the heavy metal content present in drinking water, carcinogenic risk as well as chronic risk were computed in the Taluka Keti Bandar. Following equation was used to calculate the chronic risk which was adopted from US EPA (1998) (Muhammad S, 2010).

$$HQ = \frac{ADI}{RfD} \quad (ii)$$

Where, HQ = hazard quotient, RfD = reference dose in mg/kg/day.

Following equation was utilized to determine the carcinogenic risk:

CR = x ADI x CSF (iii)

Where, CR = cancer risk, CSF = cancer slope factor in mg/kg/day (ATSDR, 2000)

Interviewed were conducted from the residents of study area regarding economic status, literacy rate, occupation, drinking water, health and age. It was observed during sampling that most of the residents belonged to the low income and could not afford bottled water. Therefore, people from the study area were using mostly groundwater for drinking purpose. It was also observed that women in rural areas were getting water from hand pumps, water supply sources located in neighboring homes, mosques and surroundings for domestic purposes. In the study area, heavy metal contaminations in potable water were calculated for possible chronic and carcinogenic risk assessment. Carcinogenic and chronic risk based on the content and type of metal, rate of ingestion, variety and toxicity in groundwater (US EPA, 1998). The highest ADI value of 3.92E-03mgkg^{-1}day^{-1} was found for copper and the lowest value of 3.67E-05mgkg^{-1}day^{-1} was obtained for cadmium (Table: 3).

Health quotient of cadmium was observed maximum as 2.393 in Baghan Town, while the minimum value of HQ of 0.228 was found in groundwater of village Abdullah Mallah. In the rest of the villages/towns the HQ was measured in between 0.228 and 2.393 (Table: 4).The greater HQ value of Cd is related to low RfD value, high content and toxic nature. The ranges of HQ values of Cr, Mn, Ni, Fe, Cu and Zn were measured as, 0.34-0.59, 0.01-0.08, 0.02-0.04, 0.00-0.00, 0.04- 0.23 and 0.00-0.03mg/L respectively in the study area. Heavy metals such as, Cr, Mn, Fe, Ni, Cu and Zn showed HQ values less than 1 therefore cause no chronic risk through drinking water to the people of the study area as suggested by USEPA.

Table 3. Carcinogenic risk of arsenic and heavy metals through drinking water of coastal area Taluka Keti Bandar (Adults)

Vill:/Town	As	Cd	Cr	Mn	Ni	Fe	Cu	Zn
B. T	0.00015	0.00004	0.00051	0.00023	0.00022	0.00086	0.00122	0.00294
P. U. S. J	0.00006	0.00051	0.00050	0.00072	0.00025	0.00074	0.00147	0.00282
A. H. M. B	0.00007	0.00009	0.00064	0.00023	2.2 E-04	0.00049	0.00086	0.00355
M. K. B	0.00031	0.00007	0.00074	0.00028	0.00025	0.00074	0.00392	0.00269
N. K	0.00012	0.00010	0.00076	0.00015	0.00020	0.00061	0.00135	0.00098
H. Q. B. B	0.00027	0.00009	0.00045	0.00016	0.00027	0.00074	0.00269	0.00098
S. W	0.00021	0.00007	0.00064	0.00021	0.00021	0.00122	0.00074	0.00233
M. H. P. B	0.00027	0.00009	0.00045	0.00016	0.00027	0.00074	0.00086	0.00049
H. Y. M	0.00023	0.00007	0.00065	0.00022	0.00032	0.00074	0.00135	0.00074
H. G. M. J	0.00008	0.00009	0.00065	0.00026	0.00023	0.00086	0.00074	0.00147
A. K	0.00009	0.00016	0.00056	0.00017	0.00023	0.00074	0.00074	0.00135
A. M	0.00011	0.00009	0.00050	0.00011	0.00021	0.00037	0.00294	0.00049
M. E. K	0.00014	0.00005	0.00051	0.00034	0.00029	0.00074	0.00086	0.00122
E. B	0.00014	0.00004	0.00048	0.00022	0.00022	0.00122	0.00098	0.00061
A. M. U	0.00021	0.00006	0.00044	0.00044	0.00025	0.00074	0.00110	0.00049
R. M	0.00006	0.00009	0.00049	0.00054	0.00028	0.00074	0.00037	0.00074

Table 4. Hazard quotient of arsenic and heavy metals (HQ) for adults in water

Vill:/Town	As	Cd	Cr	Mn	Ni	Fe	Cu	Zn
B. T	1.197	2.393	0.399	0.027	0.026	0.003	0.071	0.023
P. U. S. J	0.475	0.399	0.389	0.084	0.028	0.002	0.085	0.022
A. H. M. B	0.570	0.342	0.494	0.027	0.026	0.002	0.050	0.028
M. K. B	2.374	0.456	0.570	0.033	0.028	0.002	0.228	0.021
N. K	0.950	0.399	0.589	0.017	0.023	0.002	0.078	0.008
H. Q. B. B	2.089	0.342	0.351	0.019	0.031	0.002	0.157	0.008
S. W	1.615	0.399	0.494	0.024	0.024	0.004	0.043	0.018
M. H. P. B	2.089	0.342	0.351	0.019	0.031	0.002	0.050	0.004
H. Y. M	1.767	0.399	0.503	0.026	0.037	0.002	0.078	0.006
H. G. M. J	0.617	0.741	0.503	0.030	0.027	0.003	0.043	0.011
A. K	0.712	0.399	0.437	0.020	0.027	0.002	0.043	0.010
A. M	0.855	0.228	0.389	0.013	0.024	0.001	0.171	0.004
M. E. K	1.092	0.171	0.399	0.040	0.034	0.002	0.050	0.009
E. B	1.045	0.285	0.370	0.026	0.026	0.004	0.057	0.005
A.M.U	1.615	0.228	0.342	0.051	0.028	0.002	0.064	0.004
R. M	0.475	0.399	0.380	0.063	0.033	0.002	0.043	0.005

Maximum value of health quotient of 2.374 of arsenic was found in village Manjhi Khan Baloch, whereas the minimum HQ of 0.475 was measured from two villages Pir Usman Shah Jhaloo and Ranamori respectively. Villages in which HQ was found greater than unity were Baghan Town, Haji Qadir Bux Baloch, Sajjan Wari, M. Hassan Perozani Baloch, Haji Yaqoob Memon, M. Essa Khaskheli, Esso Baloch and Ali Muhammad Utradi with HQ values of 1.197, 2.089, 1.615, 2.089, 1.767, 1.092, 1.045 and 1.615 respectively (Table 4). Cancer risk was calculated from drinking water only for adults for arsenic having value of 3.06E-04 mg/kg/day (Table 4).

According to the results amount of As determined in the drinking water of study area causes high cancer risk as compared to USEPA (1999) (Kapaj S, et al., 2006). Literature reveals that these results are lower as reported in drinking water of Vietnam and Northern Pakistan (US EPA, 1999; ATSDR, 2000). The present study as well as reported studies shows that numerous diseases may be caused due consumption of contaminated drinking water (US EPA, 1999). During water sampling from the study area, people complained regarding drinking water contamination and responded about various diseases for instance, cancer, skin lesion, hyperkeratosis, melanosis, heart, liver and kidney problems, hepatitis- A, B and C, abdominal pain, nausea, low blood pressure, hypertension, depression, headache, dehydration, fatigue, vomiting, diarrhea and sleeping disorder. About 80% diseases and 50% beds of hospitals engaged because of contaminated drinking water in developing countries like Pakistan (VA. Nguyen *et al.,* 2008). Therefore special attention is required to the drinking water of the study area for treatments, regular monitoring and provision of pure water to the people.

Table 5. Minimum, maximum, mean and standard deviation of as (mg/L) and heavy metals (mg/L) in drinking water samples of area under study

Parameters	Minimum	Maximum	Mean	Std. Deviation
As	0.005	0.0025	0.0128	0.00658
Cd	0.000	0.04	0.009	0.01
Cr	0.040	0.06	0.046	0.01
Mn	0.010	0.06	0.023	0.01
Ni	0.020	0.03	0.020	0.003
Fe	0.030	0.10	0.063	0.02
Co	0.010	0.34	0.083	0.09
Cu	0.060	0.32	0.115	0.08
Zn	0.040	0.29	0.121	0.08

Table 6. Correlation coefficient among heavy metals in drinking water of different villages under study.

Parameters	As	Cd	Cr	Mn	Ni	Fe	Co	Cu	Zn
As	1.000								
Cd	-.055	1.000							
Cr	-.026	.418*	1.000						
Mn	-.214	.120	-.026	1.000					
Ni	.132	-.104	-.186	.351	1.000				
Fe	.133	.308	-.062	.163	-.052	1.000			
Co	-.034	-.164	-.274	-.237	.052	-.152	1.000		
Cu	.273	-.095	-.027	-.132	-.018	-.316	.149	1.000	
Zn	-.155	.455*	.400*	.224	-.159	.144	-.103	-.062	1.000

*. Correlation is significant at the 0.05 level (2-tailed).

Statistical Analyses

Descriptive statistics and correlation coefficient was calculated with software SPSS version 18 installed in the laptop windows 10. minimum, maximum, mean and standard deviation was measured. Data exposed that each drinking water source contributed in a different way to the average heavy metal contaminations. Consequently, the significant ($p < 0.05$) variation among heavy metals was shown in the drinking water of the study area (Table 6).

Anthropogenic as well as geogenic sources may be responsible for significant variation of heavy metals and metalloids in drinking water. Interesting information on metal sources and pathways may be provided by inter-metal relationships (PCRWR, 2007). Chromium was positively correlated with Cadmium (r= 0.418*), Zn was positively correlated with Cd (r= 0.455*), while Zn and Cr were found positively correlated with each other (r= 0.400*) (Table 6 & 7).

Conclusion

In current study, groundwater samples were determined from Taluka Keti Bandar, district Thatta. Drinking water samples were determined for arsenic and heavy metals and were compared with specified guideline of the WHO for drinking water. In the study area, the concentrations of arsenic was found greater than WHO recommended limit of 0.01 mg/L in villages Baghan Town, manjhi Khan Baloch, Sajjan Wari, Haji Qadir Bux Baloch, Haji Yaqoob Memon, M. Essa Khaskheli, Esso Baloch and Ali Muhammad Utradi. The order of arsenic contamination was found as: Manjhi Khan Baloch> Haji Qadir Bux Baloch> Haji Yaqoob Memon> Sajjan Wari> Ali Muhammad Utradi> Baghan Town> M. Essa Khaskheli> Esso Baloch. Higher Cadmium concentration as compared to the WHO permissible limit of 0.003 mg/L was determined from all the villages except village M. Essa Khaskheli. Chromium content of 0.062mg/L was observed in village Nathoo Khan, although chromium content greater than recommended level was found in villages Ali Hassan Mirgh Baloch, Manjhi Khan Baloch, Sajjan Wari, Haji Yaqoob Memon and Haji Gul Muhammad Jat. The alarming amount of 0.059 mg/L of manganese was found only in one village Pir Usman Shah Jhaloo. Higher nickel content than the WHO suggested level of 0.02 mg/L was determined in villages Pir Usman Shah Jhaloo, Manjhi Khan Baloch, Haji Qadir Bux Baloch, M. Hassan Perozani Baloch, Haji Yaqoob Memon, M. Essa Khaskheli, Ali Muhammad Utradi and Rana Mori. Higher cobalt content greater than 0.05 mg/L was observed in potable water of villages Baghan Town, Pir Usman Shah Jhaloo, Ali Hassan Mirgh Baloch, Haji Qadir Bux Baloch, M. Hassan Perozani Baloch, Haji Yaqoob Memon, Abdullah Khatri, Abdullah Mallah and Esso Baloch. Levels of Fe, Cu and Zn were found with in allowable limit. Carcinogenic effects of arsenic and heavy metals were shown by HQ and CR.

References

Abbulu R. 2013. A study on physico-chemical characteristics of groundwater in the industrial zone of Visakhapatnam, Andhra Pradesh. American Journal of Engineering Research **2(10),** 112-116.

Achmad RT and E.I. Auerkari, 2017. Effects of chromium on human body. Annual Research & Review in Biology, pp.1-8.

Agarwal BR, V. Mundhe, S. Hussain, V. Pradhan, 2012. Assessment of bore well water quality in and around Badnapur Dist. Jalna. Journal of Chemical and Pharmaceutical Research **4,** 4025-4027.

Anurag T, Ashutosh D, Aviral T. 2010. A study on physico-chemical characteristics of groundwater quality. Journal Chemical Pharmacology Research **2(4),** 510-518.

APHA (American) Public Health Association. 2005. Standard methods for the examination of water and wastewater, 21stedition, 382, Washington DC .

Arslan B, MB. Djamgoz, E. Akün, 2016. Arsenic: a review on exposure pathways, accumulation, mobility and transmission into the human food chain. In Reviews of Environmental Contamination and Toxicology Volume **243,** (pp. 27-51). Springer, Cham.

ATSDR (Agency for Toxic Substances and Disease Registry). 2000. Toxicological Profile for Arsenic. US Department of Health and Human Services, Atlanta, Georgia.

Babai KS, Poongothai S, Lakshmi KS, Punniyakotti J, Meenakshisundaram V. 2012. Estimation of indoor radon levels and absorbed dose rates in air for Chennai city, Tamilnadu, India. Journal of Radioanalytical and Nuclear Chemistry **293(2),** 649-654.

Barton H. 2005. Predicted intake of trace elements andminerals via household drinking water by 6-year-old children from Kraków, Poland. Part 2: Cadmium 1997-2001. Food Addit Contam **22,** 816-28.

Bhattacharya S, Gupta K, Debnath S, Ghosh U, Chattopadhyay D, Andmukhopadhyay A. 2012. Arsenic bioaccumulation in rice and edible plants and subsequent transmission through food chain in Bengal basin: a review of the perspectives for environmental health. Toxicological & Environmental Chemistry **94(3),** pp. 429-441.

Bhowmick S, S. Pramanik, P. Singh, P. Mondal, D. Chatterjee, J. Nriagu, 2018. Arsenic in groundwater of West Bengal, India: a review of human health risks and assessment of possible intervention options. Science of the Total Environment **612,** pp.148-169.

De Zuane J. 1997. Hand Book of Drinking Water Quality, 2nd Edition, John Wiley and Sons Inc, New York.

Dixit S, Tiwari S. 2008. Impact assessment of heavy metal pollution of Shahpura Lake, Bhopal, India. International Journal of Environmental Research **2(1),** 37-42.

Dum Wei D, Z. Tan, A. Lin, Y. Du, 2015. The potential risk assessment for different arsenic species in the aquatic environment. J Environ Sci (China)*;* **27,** 1-8.

Fu Y, M Chen, X Bi, Y He, L Ren, W Xiang, S Qiao, S Yan, Z Li, Z. Ma 2011. Occurrence of arsenic in brown rice and its relationship to soil properties from Hainan Island, China. Environmental Pollution **159(7),** pp.1757-1762.

Garelick H, Jones H, Dybowska A, Valsami-Jones E. 2008. Arsenic pollution sources. Rev Environ Contam Toxicol **197,** 17-60.

George CM, L Sima, H Ariasm, J Mihalic, LZ Cabrera, D. Danz. 2014 Arsenic exposure in drinking water: an unrecognized health threat in Peru. Bull World Health Organ **92(8),** 565-72.

Grafinkel D. 1986. Is ageing inevitable? The intracellular zinc deficiency hypothesis of ageing. med Hypotheses **19,** 117-137.

Gunduz O, C Bakar, C Simsek, A Baba, A Elci, H. Gurleyuk, M. Mutlu, A. Cakir. 2017. The health risk associated with chronic diseases in villages with high arsenic levels in drinking water supplies. Exposure and Health **9(4),** pp.261-273.

Huang CH, CJ. Chen. 1995. Incidence of internal cancers and ingested inorganic arsenic: A seven-year follow-up study in Taiwan. Cancer Res **55,** 1296-1300.

International Agency for Research on Cancer. 2012. Arsenic, metals, Fibres and Dusts. Volume 100C. IARC monographs on the Evaluation of Carcinogenic Risks to Humans. Retrieved July **25,** 2015.

Jasudkar DP, AL. Tulankar, S. Satone, R. May. 2019. Arsenic and arsenic health effects. In AIP Conference Proceedings (Vol **1,** p. 020047). AIP Publishing LLC.

Kapaj S, H. Peterson, K. Liber. 2006. Human health effects from chronic arsenic poisoning-a review. J Environ Sci Health Part A **41,** 2399-428.

Khan S, Shahnazm, N. Jehan., 2013. Drinking water quality and human health risk in Charsadda district, Pakistan. J Clean Prod **60,** 93-101.

Kramer KJ, RG. Jak, B. Van Hattum, RN. Hooftman, JJ. Zwolsman 2004. Copper toxicity in relation to surface water dissolved organic matter: Biological effects to Daphniamagna. Environmental Toxicology and Chemistry: An International Journal **23(12),** pp. 2971-2980.

Lesmana SO, Febriana N, Soetaredjo FE. 2009. Studies on potential applications of biomass for the separation of heavy metals from water and wastewater. Biochem Eng J **44,** 19-41.

Mondal D, Banerjee M, Kundu M, Banerjee N, Bhattacharya U, Giri A, Ganguli B, Sen Roy S, Polya D. 2010. Comparison of drinking water, raw rice and cooking of rice as arsenic exposure routes in three contrasting areas of West Bengal, India. Environ Geochem Health **32(6),** pp.463-477.

Muhammad S, Shahm T, Khan S. 2010. Arsenic health risk assessment in drinking water and source apportionment using multivariate statistical techniques in Kohistan region, northern Pakistan. Food Chem Toxicol **48,** 2855-64.

Muhammad S, Shahm T, Khan S. 2011. Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan. Microchem J **98,** 334-343.

Muhammad S, Shahm T, Khan S. 2013. Wild plant assessment for heavy metal phytoremediation potential along the mafic and ultramafic terrain, Northern Pakistan. BioMed Res Int **1,** 1-9.

Murali K, Elangovan R. 2013. Assessment of groundwater vulnerability in Coimbatore South Taluk, Tamilnadu, India using DRASTIC approach. International Journal of Scientific and Research Publications **3(6),** 1.

National Academy of Sciences. 1977. medical and biologic effects of environmental pollutants, arsenic. Washington, DC: National Research Council, National Academy of Sciences.

Nguyen VA, Bang S, Viet PH. 2008. Contamination of groundwater and risk assessment for arsenic exposure in Ha Nam province, Vietnam. Environ Int **35,** 466-72.

Pak EPA (Pakistan Environmental Protection Agency). 2008. National Standards for Drinking Water Quality, (Ministry of Environment) Government of Pakistan.

Paul S, Andmishra U. 2011. Assessment of underground water quality in North Eastern region of India: A case study of Agartala City. International Journal of Environmental Sciences **2(2),** pp. 850-862.

Pellizzari E, Clayton C. 2006. Assessing the measurement Precision of Various Arsenic Forms and Arsenic Exposure in the National Human Exposure Assessment Survey (NHEXAS). Environ Health Perspect **114(2),** pp. 220-227.

Qasemi M, Shams M, Sajjadi SA, Farhang M, Erfanpoor S, Yousefi M, Zarei A, Afsharnia M. 2019. Cadmium in groundwater consumed in the rural areas of Gonabad and Bajestan, Iran: occurrence and health risk assessment. Biological trace element research **192(2),** pp.106-115.

Rahman M, Hasegawa H. 2011. Aquatic arsenic: Phytore mediation using floating macrophytes. Chemosphere **83(5),** pp. 633-646.

Ravenscroft P, Brammer H, Richards KS. 2009. Arsenic Pollution: A Global Synthesis. Wiley Blackwell, U.K, 588p.

Saint-Jacques N, Brown P, Nauta L, Boxall J, Parker L, Dummer TJ. 2018. Estimating the risk of bladder and kidney cancer from exposure to low-levels of arsenic in drinking water, Nova Scotia, Canada. Environment international **110,** pp. 95-104.

Satish Kumar K. 2015. Water availability assessment in Shipra River. International Journal of Research in Engineering and Technology **04(11),** 126-130.

Seilkop SK, Oller AR. 2003. Respiratory cancer risks associated with low-level nickel exposure: An integrated assessment based on animal, epidemiological, and mechanistic data. Regulatory Toxicology and Pharmacology **37(2),** 173-190.

Shahm T, Ara J,muhammad S. 2012. Health Risk Assessment via Surface Water and Sub-Surface Water Consumption in the mafic and Ultramafic Terrain, mohmand Agency, Northern Pakistan. J. Geochem Explor **118,** 60-7.

Shahm T, Ara J,muhammad S. 2014. Potential heavy metal accumulation of indigenous plant species along the mafic and ultramafic terrain in the mohmand agency, Pakistan. CLEAN-Soil, Air, Water **42,** 339-46.

Simonsen LO, Harbak H, Bennekou P. 2012. Cobalt metabolism and toxicology-A brief update. The Science of the Total Environment **432,** 210-215.

Uppal JS, Zheng Q, Le XC. 2019. Arsenic in drinking water–Recent examples and updates from Southeast Asia. Current Opinion in Environmental Science & Health).

US EPA (US Environmental Protection Agency). 1998. Arsenic, Inorganic. United States Environmental Protection Agency, Integrated Risk Information System (IRIS), (CASRN 7440-38-2). http://www.epa.gov/iris/subst/0278.htm

US EPA (US Environmental Protection Agency). 1999. A Risk Assessment-Multiway Exposure Spreadsheet Calculation Tool. United States Environmental Protection Agency, Washington, DC.

WHO (World Health Organization). 2011. World Health Organization Guidelines for Drinking Water Quality, 4th edit. Recommendations, vol 1. Geneva, Switzerland.

Zavala Y, Duxbury J. 2008. **Arsenic in Rice I.** 2008. Estimating Normal Levels of Total Arsenic in Rice Grain. Environmental Science & Technology **42(10),** pp. 3856-3860.

Zhang L, Qin X, Tang J, Liu W, Yang H. 2017. Review of arsenic geochemical characteristics and its significance on arsenic pollution studies in karst groundwater, Southwest China. Applied Geoch Emistry **77,** pp. 80-88.

Zhao F, mc Grath S, meharg A. 2010. Arsenic as a Food Chain Contaminant: mechanisms 1395 of Plant Uptake and metabolism and mitigation Strategies. Annual Review of Plant Biology **61(1),** 1396 pp. 535-559.