ORIGINAL ARTICLE

Assessment of Arsenic and Essential Metal Ions in the Quality of Groundwater Sources of Taluka Daur, District Shaheed Benazeer Abad, Sindh, Pakistan.

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ABSTRACT

Objective: To analyze the quality of groundwater, before it is used for drinking purpose.
Study Design: Comparative descriptive study.
Place & Duration: Water Testing & Surveillance of Drinking Water Laboratory, Department of Community Medicine, PUMHSW during September & October 2014.
Material and Methods: 68 groundwater samples were collected from Daur and its catchment areas (Bandhi, 60th Mile, Jam Sahib and Villages). Different physical and chemical characteristics of water samples were estimated in the field and at the laboratory. The analysis of different chemical characteristics of water samples were measured with conductivity meter HANNA H1 8733 at the field. pH was measured by HANNA H1 2211 pH/ORP pH meter. Alkalinity, Hardness and chloride were estimated by titration method with standard solutions of disodium ethylene diamine tetra-acetate dihydrate, hydrochloric acid & silver nitrate. Arsenic was estimated by using (Merck Arsenic field testing Kit (0.01-0.5 mg/l) Darmstadt, Germany) respectively. Sulfate was determined by turbidimetry as $BaSO_4$ using 721 Vis-Spectrophotometer Ltd., China. Essential metals were determined by (Na, K, Ca, Mg and Cl-ISE) ion selective electrode by H1 2216 pH/ORP/ISE Multi-parameter water quality meter HANNA Instruments Ltd., USA.
Results: The present work was carried out for the estimation of arsenic and essential metal ions in the groundwater samples from taluka Daur. 68 groundwater samples of the study area were examined. The physical and chemical characteristics of the groundwater samples were obtained within following ranges. pH 6.67-8.81, total dissolved salts (TDS) 158-20527 mg/L, HCO_3 47-4901 mg/L, total hardness (TH) 72-12207 mg/L, chloride 31-12857 mg/L, SO_4 28-4625 mg/L. The amount of essential metal ions such as (Na, Ca, Mg and K) was varied within the ranges of 28-4504 mg/L, 20-3517 mg/L, 9-1331 mg/L and 6-578 mg/L respectively. Seven samples indicated arsenic concentrations in the range was (10-200 µg/L) respectively.
Conclusion: The analysis of ground water samples of taluka Daur revealed that (72 %) of the greater part of parameters of the study area were elevated the maximum permissible limits prescribed by WHO. The majority of the locations of (groundwater) samples were exceedingly impure with toxic metals. The higher concentrations of metals in ground water may cause several health problems to consumers of taluka Daur.
Key Words: Physical & Chemical Parameters, Groundwater Quality, Domestic Use, Arsenic Contamination, Essential Metals, Irrigation, Sodium Absorption Ratio.

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INTRODUCTION:

The health that causes effects of environmental exposure to arsenic has amazingly increased in last few years. The water that is used for drinking constitutes for one of the principle pathways of environmental arsenic exposure in humans. Arsenic is one of the major contaminants in the groundwater. A number of countries face pollution they get from water and its effects on groundwater samples were collected from Daur,

Bandhi, 60thMile, Jam Sahib and Villages. Different physical and chemical characteristics of water samples were measured in the field and at the laboratory. The homogenized sample was transferred to a clean 500ml plastic bottle. For sampling, clean polyethylene containers of volume 500ml were used and the samples received were immediately processed for analysis. The temperature of the air at meter above the surface of the water was recorded with a mercury thermometer. The analysis of different chemical characteristics of water samples was done with conductivity meter HANNA H1 8733 at the field. pH was measured by HANNA H1 2211 pH/ORP pH meter. Alkalinity, hardness and chloride were estimated by titration method with standard solutions of disodium ethylene diamine tetra-acetate dehydrate, hydrochloric acid and silver nitrate using following standard procedures recommended by the (American Public Health Association APHA).[13] Arsenic was estimated by using (Merck Arsenic field testing Kit (0.01-0.5 mg/l) Darmstadt, Germany) respectively. Sulfate was determined by turbidimetry as $BaSO_4$ using 721 Vis-Spectrophotometer.[14] The chloride and essential metal ions (K, Na, Mg and Ca) were determined by pH/ORP/ISE Multi-parameter H1 2216 HANNA Instruments Ltd, USA. The metal standard solutions were prepared by dilution from 1000ppm stock solution of each standard. All further dilutions required for preparation of working standards were carried out using this blank solution. The calibration standard solutions were divided into three sets, for K, Na, Mg, Ca with 0.5 ppm, 1 ppm, 5 ppm 10 ppm 20 ppm, 30 ppm and Chloride, 50mg/l, 100mg/l, 200mg/l, 250 mg/l, 300mg/l.The SAR values were calculated using the formula:

$$SAR = Na/(Ca+Mg)^{1/2}/2.$$

RESULTS:

The average results of physical and chemical parameters of the groundwater samples are summarized in table1. The work reports the analysis of groundwater samples from Taluka Daur, located at the center of Sindh province.

The physical &chemical parameters of the groundwater samples were varied within the ranges. pH 6.64-8.81, total dissolved solids (TDS) 158-20527 mg/L, HCO_3 47-4901 mg/L, total hardness (TH) 72-12207 mg/L, chloride 31-12857 mg/L, SO_4 28-4625 mg/L, orthophosphate (P) 0.07-0.135 mg/L, total phosphate (P) 0.085-0.823 mg/L, NO_2-N 0.13-0.645 mg/L, NO_3-N 0.018-1.836 mg/L and dissolved oxygen 1.2-9.0 mg/L. The quantity of essential metal ions (Na, Ca, Mg and K) were varied in between 28-4504 mg/L, 20-3517 mg/L, 9-1331 mg/L and 6-578 mg/L. Seven samples indicated arsenic concentrations in the range were (10-200 µg/L) correspondingly Table 1 & 2.

DISCUSSION:

In all the natural ecosystems, water acts as the primary transport medium for dissolved particulate and determines. The rate at which these fluids are added or removed from the system. A complete identification of hydrological characteristics is hence essential for understanding biological, chemical and physical processes that operate within the ecosystem.

The results of physical & chemical parameters of water samples reveal the varying nature of the underground water of the taluka Daur. The difference in the quality of groundwater possibly the geography of top soil; diverse earth layers and consequence of recharge sources (canals etc.) on underground water. The samples were examined to find out the levels of both physical and chemical limitation of groundwater. The deviation was obtained in the concentration of different physical and chemical characteristics of the era, which show different nature of the soil.

According to the laws of Hydrology, the water quality alongside a canal or river is good because of the natural filtration process. The recharge from canals has produced good quality water at selected sites, where downward infiltration occurs. Infiltration of founded rain water and effluent water in low-lying depressions appear to be causing get higher in the water level in parts of Taluka Daur. In Taluka Daur, people fill large cans of drinking water from the taps fixed alongside the canal.

human health. The sources of arsenic in groundwater are geochemical. There are certain resources of arsenic pollution like treated wood & smelting, pesticide, and fossil fuel combustion and removal waters. Weather conditions of rocks change arsenic sulfide to oxides of arsenic, which penetrate into the arsenic cycle on suspension in groundwater. The arsenic is present in the hard layer of earth and sediments as a component of the minerals, containing ores of sulfides along with copper, nickel, lead, cobalt and iron. However, others such as As, Cd, and Pb are non-essentials or toxic metals and causing numerous human health risks after ingestion. Among metals such as Na, K, Mg & Ca are essential & required at certain concentrations for normal body function and growth but present in excess, have an adverse effect on human body, toxic effects of these metals include abdomen pain, headache, blood pressure and kidney damage.[1] The water in the Indus basin is of erratic quality. It is not saline in the vicinity of sources of recharge, i.e. Rivers and major canals, but slowly becomes saline with deepness as the distance from the recharge source increases. Indus is the only river running along the western side of the district. Taluka Daur formerly a part of district Nawabshah is located at the northern edge. The soil of the taluka is saline; however, some of its parts are fertile and well cultivated. The climate is mostly dry, hot in summer and cold in winter. About 80 % of the peoples reside in villages and use groundwater for drinking and other domestic purposes. No any water supply schemes are working in the Daur, Bandhi, Jam Sahib and 60th Mile towns, but the rest of taluka rely on ground water.[2] According to World Health Organization (WHO) declaration, access to potable water is a basic right for all. However, in developing and also developed countries, so many masses rely on groundwater and surface water for drinking purposes, being unaware of its quality. The water contains organic as well as inorganic pollutants if present in the above concentration, and then some fixed levels, cause health problems to users. It is necessary to check the quality of water, especially the concentration of arsenic and essential metals before it is used for drinking purpose.[3]

The contamination of groundwater consequences from all the course of action and response which the water countenance from the instant. It is reduced in the atmosphere at the time it is released by a well or hand pump and varies from consigning to transfer with depth. The most important constituent of the rural inhabitants depends on the groundwater due to unavailability of water treatment and supply of potable water. 40% of the deaths in Pakistan are the route by water-borne diseases directly or ultimately.[4] Polluted water is the main source of human diseases misery and fatality. There are so many sources of water toxic waste between them. Inappropriately planned rural sanitary services also supply to the contagion of underground water.[5] The quality of groundwater in Pakistan is deteriorating day by day. A serious problem appears due to the stagnant management of effluent water, which becomes penetrating into the soil with the passage of time and can become a part of nature and groundwater. The compilation of work has been conceded on the quality of groundwater of different parts of Pakistan,[6-12] but no any reasonable work reports on the quality of underground water of Taluka Daur. The quality of water that people use for survival needs to be analyzed in the laboratory to learn the quantity of its pollution and its suitability for the people in their routine life. Above highlighted problems must be analyzed in an ecological structure in which the quality and quantity of water resources are burning issues. This motive of this research is to analyze the quality of water that is used for people. This study was conducted at the Department of Community Medicine, Peoples University of Medical & Health Sciences for Women Nawabshah.

MATERIAL & METHODS:

Physical and Chemical Parameters

All the reagents used were of analytical grade and all the glassware used was washed properly with double distilled water before use.The study aimed to analyze the groundwater samples of the taluka Daur. 68 groundwater samples were collected from different towns and union councils of taluka Daur. Greater numbers of

pH of the Groundwater

The pH and temperature take part in major role in the population and growth of bacteria. The normal, acceptable pH limits for water supply lies between 6.5-8.5 pH units. The acceptable alkalinity of public utility water is generally between 30 to 500mg $CaCO_3$ equivalent/L.Some water sources may have an extended range between pH 5.0 -10.0units. This has a significance of being a direct indicator of solubility of various alkali and alkaline earth species in water. Hence, the overall quality of water is greatly influenced by the pH value, as is well established[11] that water with high pH tends to be scale forming and that of low pH normally corrosive to certain metals, asbestos, cement and lined pipes. The pH of water samples varied between within the ranges 6.64-8.81. Sixty-two samples confirm pH within the safe guidelines of 6.5-8.5 prescribed by WHO for drinking water, while only 6 samples were above the limits of WHO. Higher values of pH may be due to human activity (domestic and industrial waste) and water logging respectively. The waters with pH below 7.0 are termed as acidic and acidity in water is due to the presence of dissolved carbonic acid. It increases the solubility of different materials including metal ions like Na, K, Ca and Mg. Twenty samples indicated pH below 7.0 but indicated within the permissible limit of 6.5.

Total Dissolve Solids (TDS)

The total dissolved solid in the sequence is used to find out the effect of ions on a water resource. Elevated salt substances in water have physiological on plants and animals. It is noticed that dissolved salts cause mineral taste in water.

The values of TDS varied between within the ranges 158-20527mg/L. Results on TDS of water samples of 72.06 % has highest in comparison to other samples and this area is mostly residential. Arrange of variation was observed in TDS of water samples. The divergence in TDS may be unsettled to diverse earth beds and drain sources. Generally, the water samples have high values of TDS making them unsuitable for drinking purpose. The water samples with elevated values of TDS may cause several health problems to living organisms and adversely affect the fertility of soil if used for irrigation purpose (Figure 1).

Salinity

Salinity is the suspended salt contented of a corpse of water. In the saline underground water, the dominant ions are likely to be chloride and sodiumalthough potassium, magnesium, and sulfate are also most important constituents present in concentrations above WHO guideline values for drinking water. The salinity of groundwater samples varied between 0.1-6 g/L.

Bicarbonates and Hardness

Water hardness is the capability of water to precipitate soap. Soap is precipitated mostly by the calcium and magnesium ions present. The contents of bicarbonate and hardness fluctuated varied between within the range 47-4901 mg/L and 72-12207 mg/L respectively. A parallel behavior of bicarbonate with hardness was noted. One possible explanation for this could be linked with soil conditionsand underground hydrology.The hardness of 33 samples was within the safe limits prescribed by WHO for drinking water and six samples indicated their hardness above 700 mg/L may be due to geological reasons. The water with elevated hardness than the WHO guidelines may cause gastric problems, dehydration, gas trouble, kidney stone and heart problems.[15] (Figure 2)

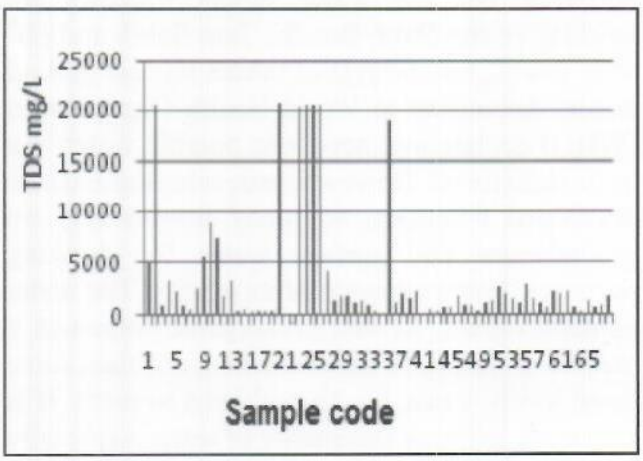

Figure 1: Graphical representation of Total dissolved solids of water samples

Table 1. Critical Parameter Exceeding the Permissible Limit

S.No	Parameters	WHO Permissible limit	No. of sample exceeding permissible limit	Percentage of sample exceeding permissible limit
1	pH	6.5-8.5	5	3.4%
2	Conductivity	1000 µs/cm	53	77.94%
3	TDS	800 mg/L	49	72.06%
4	Total hardness	500 mg/L	25	36.76%
5	Alkalinity	500 mg/L	12	17.65%
6	Chloride	250 mg/L	37	54.41%
7	Ca	200 mg/L	18	26.47%
8	Mg	100 mg/L	18	26.47%
9	Na	200 mg/L	40	58.82%
10	K	12 mg/L	29	42.64%
11	SO_4	500 mg/L	25	36.66%
12	As	10	7	10.29 %

Table-2 Physical & chemical analysis of groundwater samples in the study area

S.No	Parameters	Unit	Maximum	Minimum	Average
1	pH		8.81	6.64	7.72
2	Conductivity	µS/cm	40500	304	20402
3	TDS	mg/L	20527	158	10342
4	Total hardness	mg/L	12207	72	6139
5	Alkalinity	mg/L	4901	47	2474
6	Chloride	mg/L	12857	31	6444
7	Ca	mg/L	3517	20	1768
8	Mg	mg/L	1331	9	670
9	Na	mg/L	4504	28	2266
10	K	mg/L	578	6	292
11	SO_4	mg/L	4625	28	2326
12	As	µg/L	200	5	102.5

Chloride and Sulfate

The concentration of total chloride of groundwater indicated the variation within 31-12857mg/L. Nearly half of the (30 samples) showed their chloride concentration above, the regulations (250 mg/L) set by WHO. The chloride in water is present in a mixture with sodium, calcium, and magnesium. Sources of chloride are mostly the human waste, mineral rocks, irrigation discharge and industrial effluents like dying and bleaching materials. The water samples with a higher concentration of chloride may have toxic effects on health.

The sources of sulfate in surface and subsurface water are mainly calcium sulfate and sodium sulfate. The sulfates entering in water bodies come from the dissolution of minerals containing sulfides and thiosulfates. Sulfate contributes to the permanent hardness to the water. The elevated level of sulfate in water causes bad taste of water and also shows corrosive action.[13] The concentration of sulfate was varied within 30-4625 mg/L. Some of the water samples (28 samples) indicated their sulfate contents above the limits of WHO. A parallel trend was found in the concentrations of chloride and sulfate in water samples.

The concentration of essential metal ions (Na, Ca, Mg and K) was varied between the ranges of 28-4504 mg/L, 20-3517 mg/L, 9-1331 mg/L and 3-578 mg/L respectively. It was observed that the concentration of major metal contents higher in groundwater of the study area (Table 3& 4).

Table-3 Classification of water on the basis of total hardness

Total hardness mg/L	Type of water	No. samples
0-60	Soft	Nil
61-120	Moderate hard	7
121-180	Hard	7
>180	Very hard	54

Chemistry of Metal Elements

Although sodium and potassium are not strictly considered as trace metals present in drinking water, yet they do constitute an important indicator of water quality. It is well known that certain metals such as Na are concentrated in body fluids, and are circulated throughout the human body. These elements are known to participate in life-sustaining processes operating throughout the complicated nervous system controlled by the brain.

Table-4 Classification of water on the basis of total dissolved solids

TDS mg/L	Classification of Groundwater	No. of Samples
<1000	None saline	15
1000-3000	Slightly saline	29
3000-10000	Moderately saline	13
>10000	Very saline	11

Results of sodium in most areas of taluka Daur were relatively high concentration. Higher sodium concentration may create a problem of hypertension and affect the public health. As the reported values are higher than the maximum permissible limits there may exist serious threats of underground water pollution.

The concentration of major metal ions Na, K, Ca, and Mg varied with the high concentration of ground samples. The concentration of major metal ions follows following decreasing order:

Na > Ca > Mg > K

Sodium is present in all natural waters. The presence of sodium in water depends on the anions present in that system and the temperature. The high concentration of sodium imparts tastes to the water and make it unfit for everyday use and leads to cardiovascular diseases and high blood pressure.[14] The concentration of Na in water samples of the study area varied as 28-4504 mg/L. The Na ion concentration of the 25 samples was found within the safe guidelines of 200 mg/L set by WHO for drinking water. All the rest of the samples indicated high values of Na ion concentration than WHO limits (Figure 3).

Potassium plays a key role in the metabolism process of animals and it is the main micro nutrient for living organisms (plants and animals). The WHO threshold of potassium in drinking water is 12 mg/L. The potassium concentration of

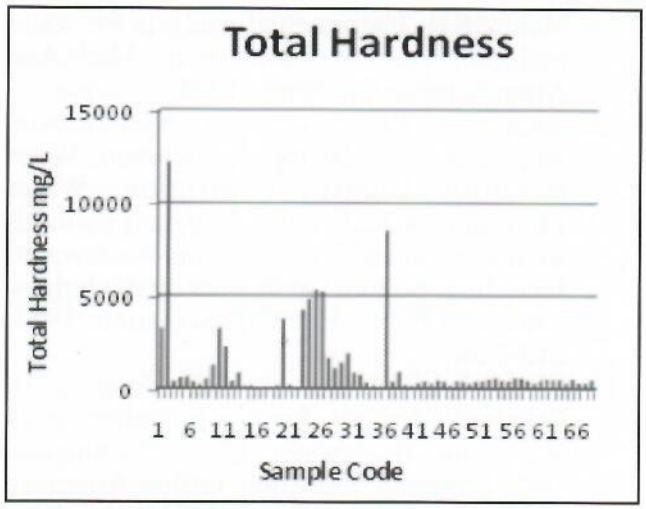

Figure 2: Graphical representation of Total hardness of water samples

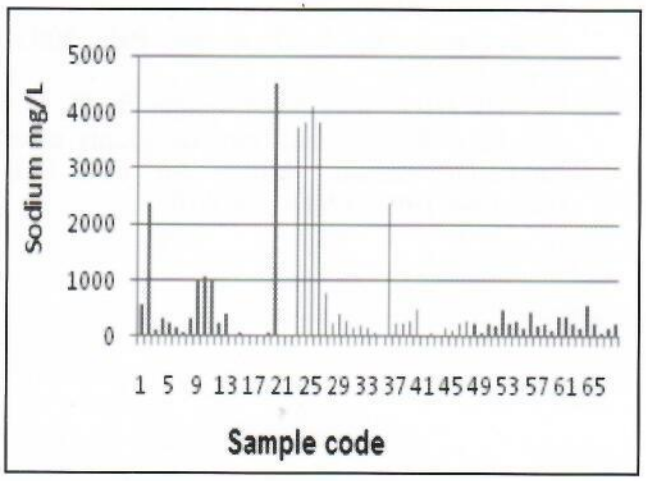

Figure 3: Graphical representation of Sodium of groundwater samples

the water samples studied was varied between 3-578 mg/L, including 32 samples with K ion concentration within the permissible limits.

Calcium and magnesium are rich in rocks and soil, mainly limestones and dolomites. They are comparatively soluble and dissolve in surface water and then enter into ground water. There are no health concerns associated with calcium and magnesium, but the water containing these metals may contribute towards human dietary needs; however, their high concentration may cause scaling of pipes. The concentrations of Ca and Mg ions in the water samples of the area were found in the ranges of 20-3517mg/L and 9-1331mg/L respectively. Ca in 40 samples and Mg in 42 samples were found to be within the permissible limits of WHO. The rest of the water samples were observed very hard with high concentrations of Ca and Mg.

Sodium Adsorption Ratio (SAR)

Salt contents of the irrigation water, put adverse effects on crop production via osmotic pressure of a solution, whereas the elevated proportion of Na to other metals damage the soil structure.[16] Sodium adsorption ratio (SAR) was calculated to check the suitability of the waters to be used for irrigation purpose. The results revealed that determined 68 samples, only (45 out of 68 underground water samples) were suitable for irrigation with SAR value below 6 and remaining 24 samples were unsuitable for irrigation with SAR value above 6, all these 24 samples were underground water samples (Table 5).

Table-5 Classification of groundwater on the basis of Sodium absorption ratio

Parameter	Range	Water class	Samples	% age
SAR	<6	Excellent	44	63.23
	>6	Unsuitable	24	36.76

CONCLUSION:

The analysis revealed that a number of ground water samples (72%) showed their majority of parameters above the maximum permissible limits prescribed by WHO. The greater part of the sites of (groundwater) samples was highly impure with toxic metals. The higher concentrations of metals in ground water may be a concern for the human health of taluka Daur. The high salt concentration in the drinking water of taluka Daur suggests a further research work and some action plans must be implemented to resolve this problem. Many metals present in drinking water at major, minor, and trace levels are essential for human health. However, their drinking in excessive amounts may possibly cause severe health problems. Therefore, the groundwater of taluka Daur may not be considered as safe to be used for drinking purposes.

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