

Assessment of Groundwater Quality of Taluka Bulri Shah Karim, District Tando Muhammad Khan, Sindh, Pakistan

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Abstract

This paper deals with groundwater quality of taluka Bulri Shah Karim in district Tando Muhammad Khan of Sindh province, Pakistan. Groundwater samples were collected from 53 borewells during October and November 2018. The groundwater was found very hard and the relative abundance of cations and anions was $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$. The values of Water Quality Index ranged from 40.49 to 636.98 (mean 119.37). Out of 53 samples, 3 were classified as excellent, 23 good, 21 poor, 4 very poor and 2 unsuitable for drinking. Piper scatter plot revealed that 36 samples were sodium chloride type, 14 were mixed type, and 3 were magnesium bicarbonate type. The concentration of arsenic ranged from 0 to 200 $\mu\text{g/L}$ (mean 16.7 $\mu\text{g/L}$). Fluoride values varied from 0.52 to 3.39 mg/L (mean 1.49 mg/L). Sodium adsorption ratio and percent sodium ranged from 1.7 to 30.2 (mean 8.22) and 39.34 to 91.4 (mean 65.40) respectively. Riverside diagram revealed that 17 samples were low in salinity and alkalinity, whereas 11 samples were highly saline. Permeability index varied from 47.74 to 96.26 (mean 71.54). Wilcox's diagram showed that one sample fall in excellent category, whereas 17, 24, and 11 samples fall in good, admissible, and bad categories respectively.

Introduction

Groundwater constitutes approximately 99% of all the freshwater present on the earth in liquid form. Approximately half of the world's population uses groundwater for domestic purposes, whereas about 25% of the groundwater is used in agriculture (United Nations, 2022). Groundwater contributes significantly in maintaining and restoring the earth's ecosystem. However, anthropogenic activities such as excessive use of fertilizers and pesticides, rapid urbanization and industrialization, and increased disposal of waste materials are deteriorating groundwater quality (Zhang et al., 2021). Groundwater recharge process may also come under pressure due to climate change, particularly in dry regions (Brouyere et al., 2004).

In Pakistan, groundwater contributes approximately 70% of drinking water and over 50 to 60% of irrigation water, whereas in rural areas of Pakistan about 90% of domestic water comes from groundwater. In rural areas of Sindh province, groundwater is the main source of domestic water and approximately 20% of irrigation water comes from groundwater (Tahir & Imran, 2010; Lyton et al., 2021).

There have been some studies to investigate groundwater quality from Sindh especially from coastal areas like Karachi and Thatta (Alamgir, et al., 2016; Shahab et al., 2016; Naseem et al., 2018; Bano, 2019). Interior Sindh received less attention and few publications have reported groundwater quality from Nawabshah (Kandhro et al., 2015), Larkana (Kori et al., 2018; Lanjwani et al., 2020a), Qambar Shahdadt (Lanjwani et al. 2020b), and Tando Adam (Naz et al., 2021). However, very little is known about the groundwater quality of Tando Muhammad Khan (TMK), which is also located in interior Sindh. Khan (2014) and Shahab et al. (2019) reported only arsenic pollution in the aquifers of TMK, whereas Merani et al. (2014) studied groundwater quality, for agriculture and drinking purposes of TMK. They examined 14 parameters and reported only percentage of samples beyond permissible limit for each parameter without computing any water quality index. Water quality indices are mathematical tool used to transform large quantity of data into single number that indicates level of water quality for drinking and for irrigation purposes.

Since there has been no detailed investigation of groundwater quality in Taluka Bulri Shah Karim, the present study was initiated. It examines 19 physicochemical parameters of 53 groundwater samples collected from hand-pumps (borewells) in the Taluka. This is the first study from the Taluka that evaluates groundwater quality for drinking and irrigation purposes based on water quality indices.

Materials And Methods

Study area

Taluka Bulri Shah Karim of TMK district is situated in the southern part of Sindh province in Pakistan about 150 Km northeast of the Arabian Sea (Fig. 1). Its area is 770 Km^2 and population, according to 2017 census of Pakistan, was 237,011. The population density is 307.8 Km^2 and the growth rate was 2.2% from 1998 to 2017. Approximately 70% of the population is engaged in agricultural activities. Main crops grown in TMK are: rice, sugarcane, wheat, and cotton. The overall climate of TMK is moderate but April to June is very hot especially during daytime. December and January are the coldest months. Rainfall is mostly restricted to monsoon season (July to September). The average rainfall in the district is approximately 130 mm. Pinyari and Akram canals are the main source of water-reservoir for irrigation in this district, whereas hand-pumps are the main source of domestic water.

Sample collection

Groundwater samples were taken from 53 shallow hand-pumps during October-November, 2018. Water samples were collected directly from the hand-pumps in polystyrene bottles of 0.5 and 1.5 L capacities. Before collecting the samples, bottles were soaked in HNO_3 (10%) and thoroughly rinsed with deionized water. Nitric acid (conc.) and boric Acid (1M) were used as preservatives for trace elements and nitrate-nitrogen determination, respectively. Water samples were collected from the hand-pumps after purging them. Purging was carried out by making one stroke for every foot of depth. Water samples from 1.5 L bottles, without preservative, were used for TDS, hardness, sulphate, chloride, fluoride, carbonates, bicarbonates, sodium, potassium, calcium and magnesium analysis. Water sample from 0.5 L bottle, with boric acid (1M) as preservative, was used for NO_3 -nitrogen. Another bottle of 0.5 L, with HNO_3 (Conc.) was used to analyse arsenic and iron.

Sample analyses

Electrical conductivity (EC), pH, TDS, and turbidity (Turb.) were measured *in situ* using Eu Tech EC/TDS meter (CON11), pH meter (pH 700, HACH), and turbidity meter (2100Q HACH), respectively. Water samples were analysed for aesthetic and physicochemical parameters by using APHA, (1992) standard methods except As for which Merck test-kit (MQuant)1.17927 was used. Ca^{2+} and total hardness (TH) were analysed volumetrically by EDTA (0.01M) method using

murexide and Eriochrome Black T indicators respectively. Mg^{2+} concentration was calculated using formula $Mg^{2+} = [Hardness - 2.5 Ca^{2+}] \times 0.243$. Cl^{-} concentration was determined by titrating against $AgNO_3$ (0.014N) solution (Argentometric method). F^{-} and SO_4^{2-} and total iron concentrations were determined by using HACH colorimeter (DR-2800). A spectrophotometer (UV) method was used to determine concentration of $NO_3^{-}N$ at a wavelength 220–275 nm. Alkalinity was determined by using HCl (0.1N) titration using methyl-orange indicator. Na^{+} and K^{+} were determined by flame photometer (DN7101). Aesthetic parameters like colour, odour and taste were determined by sensory evaluation.

Data analyses

The chemical data obtained were subjected to compute electro-neutrality by the following formula: Electro Neutrality (%) = (total conc. of cations + anions/ total conc. of cations – anions) x 100. The ionic-balance-error values were found to be within the acceptable range of $\pm 5\%$ (Domenico and Schwartz, 1990) (Fig. 2). Piper scatter plot was made on Grapher software, whereas Wilcox's and Riverside diagrams were made using Diagrammes software.

Water Quality Index (WQI) was computed on Microsoft Excel in three steps. First, each parameter was assigned a weight (w_i), on a scale of 1 to 5, depending on their impact on groundwater quality. For instance, the highest weight 5 was given to As and F, whereas lowest weight 2 was given to Na, Ca, and Mg etc. (Table 1) (Lanjwani et al. 2020a). Second, relative weight (W_i) for each parameter was calculated by the formula: $w_i / \sum w_i$. Third, for determining quality rating (Q_i) of each parameter, the concentration (mg/L and $\mu g/L$ in case of As and Fe) of the parameter (C_i) was divided by WHO standard (S_i) for that parameter and then multiplied by 100, that is $Q_i = (C_i / S_i) \times 100$. The sub-index (S_{li}) for a parameter was then computed by multiplying the relative weight (W_i) with the quality rating (Q_i) of the particular parameter ($S_{li} = W_i \times Q_i$). Finally, the WQI value was found by adding all the S_{li} values ($WQI = \sum S_{li}$). The groundwater having WQI values from 0–25 was classified 'Excellent', from 25 to 50 'Good', 50 to 75 'Poor', 75 to 100 'Very poor' and above 100 'Unsuitable for drinking' (Lanjwani et al 2020a).

Table 1
WHO standard, weight (1 to 5) and relative weight of 16 parameters used to compute water quality index (WQI).

Parameters	WHO standards	Weight (w_i)	Relative Weight (W_i)
pH	6.5–8.5	3	0.064
TDS ppm	1000	3	0.064
EC $\mu S/cm$	1500	3	0.067
TH ppm	500	3	0.064
Turbidity NTU	5	3	0.064
Alkalinity m.mol/L	6.5	2	0.042
Ca^{+} ppm	150	2	0.042
K^{+} ppm	12	2	0.042
Na^{+} ppm	200	2	0.042
Mg^{2+} ppm	100	2	0.042
Cl^{-} ppm	250	3	0.064
SO_4^{2-} ppm	10	4	0.086
NO_3^{-} ppm	1.5	5	0.106
F^{-} ppm	0.3	2	0.042
Fe ppm	10	5	0.106
As ppb			
		$\sum = 47$	0.999

The physicochemical data were also subjected to evaluate groundwater quality for irrigation purpose such as SAR (Todd, 1980), permeability index (PI) (Doneen, 1964), residual sodium carbonate (RSC) (Gupta & Gupta, 1987), and %Na (Wilcox, 1995). Following formulae were used to compute these indices. All quantities were in meq/L except %Na which were in mg/L

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

$$PI = \{ [Na^+ + (\sqrt{HCO_3^-})] \times 100 \} / (Ca^{2+} + Mg^{2+} + Na^+)$$

$$RSC = HCO_3^- + CO_3^{2-} - Ca^{2+} - Mg^{2+}$$

$$\%Na = (Na^+ \times 100) / (Ca^{2+} + Mg^{2+} + Na^+ + K^+)$$

Results And Discussion

Physical parameters

The results of the physical parameters are presented in Table 2. The depth of hand-pumps was shallow and it varied from 5 to 27 m (mean 12 ± 5 SD). The pH values ranged from 7.2 to 8.5 (mean 7.9 ± 0.29 SD) indicating that the groundwater was almost neutral to slightly alkaline (Table 2). The pH of water can affect the solubility of chemicals and metals. Groundwater with a very high or low pH can be a sign of heavy metal or chemical pollution. The desirable pH is 6.5 to 8.5 according to WHO standard and all the groundwater samples analysed during present study fall in this range. This also replicates the findings of Merani et al. (2014) and Shahab et al. (2019) who reported that from Taluka Bulri Shah Karim none of the groundwater samples were beyond the range of 6.5 to 8.5. The pH values of groundwater samples from Larkana have been reported to vary from 7.42 to 8.20 (Lanjwani et al., 2020b). The values of TDS varied from 678 to 6163 mg/L (mean 1811.2 ± 97.2 SD) during present investigation (Table 2). WHO standard for TDS in drinking water is $< 1,000$ mg/L. Out of 53 groundwater samples analysed during this study, 40 had TDS $> 1,000$ mg/L revealing that 75.74% of the samples were slightly saline, whereas remaining 13 sample (24.53%) were freshwater on the basis of TDS classification by Freeze and Cherry (1979). According to Davis & De Wiest (1966) classification on TDS basis, groundwaters are of four categories (see Table 3). Most of the groundwater samples (*i.e.*, 40 out of 53) of the present study fell in the third category viz. useful for agriculture (TDS 1,000 to 3,000 ppm). Only four water samples (sample No. 21, 37, 50, and 51) fell in the fourth category 'unsuitable' (TDS $> 3,000$ ppm). Nine samples (sample No. 7, 19, 22, 27, 28, 31, 40, and 43) fell in the second category 'permissible for drinking' (TDS 500 to 1,000 ppm). No water sample was found in the first category 'desirable for drinking' (TDS < 500 ppm). Merani et al. (2014) reported that TDS value of 24 groundwater samples out of 36 (*i.e.*, 66.67%) from Bulri Shah Karim were more than 1,000 mg/L, which is comparable to the results of the present study. Lanjwani et al. (2020b) reported TDS values from 415 to 3085 mg/L for Larkana groundwater that indicates that the groundwater of Bulri Shah Karim is more saline than that of Larkana.

Table 2
Physical parameters of groundwater from Taluka Bulri Shah Karim.

Sample No.	Depth m	pH	TDS ppm	EC $\mu\text{S/cm}$	TH ppm	Turb. NTU	Alkal. m.mol/L
1	9	7.7	1030	1610	370	17.2	8.8
2	11	7.7	1175	1836	480	40.3	9
3	11	7.8	1137	1776	400	7.59	8.6
4	11	8.1	1363	2130	240	2.18	9.4
5	12	8.1	1026	1603	380	1.29	8.8
6	8	7.8	1459	2280	340	1.64	9.2
7	11	8.1	806	1260	350	1.26	6
8	9	8.3	2150	3360	800	2.17	7.2
9	11	8.2	1133	1771	450	0.36	8
10	11	7.9	1594	2490	630	0.84	7.6
11	11	7.7	1241	2220	580	1.39	7.6
12	11	7.8	1208	1887	470	2.44	6.8
13	8	8.5	2144	3350	180	2.94	12.4
14	12	8.0	2035	3180	290	0.32	12
15	12	8.4	2566	4010	220	0.95	13
16	12	8.5	1843	2880	190	0.46	11.2
17	12	8.1	2054	3210	550	0.75	9.2
18	5	7.4	2771	4330	910	0.33	8.4
19	9	7.6	924	1444	480	0.97	6.6
20	11	7.6	1581	2470	580	1.62	9.2
21	18	7.2	6163	9630	2650	12.7	5.6
22	12	7.8	684	1068	360	1.45	6.6
23	12	7.7	1058	1653	440	2.03	8.2
24	12	8.0	869	1358	380	0.90	7
25	15	7.9	1141	1787	410	0.53	9.4
26	11	7.6	2106	3290	680	1.19	10.2
27	14	7.8	736	1150	330	0.58	6.2
28	14	8.0	678	1060	280	0.91	4.6
29	14	8.5	2234	3490	430	3.39	8
30	14	8.0	1734	2710	580	10.3	7
31	14	7.8	942	1472	410	1.26	7.6
32	14	8.1	1747	2730	380	0.94	9
33	14	8.2	1837	2870	370	0.38	8.8
34	15	8.2	1946	3040	300	9.39	8.4
35	9	7.7	1839	2870	440	0.66	9.2
36	9	7.9	2266	3540	650	0.52	7.2
37	8	8.3	4390	6860	380	0.37	12.2
38	8	7.7	2035	3180	490	4.5	11
39	9	7.7	1708	2670	630	1.77	9.8
40	24	8.3	901	1408	440	4.39	7.4

Sample No.	Depth m	pH	TDS ppm	EC μ S/cm	TH ppm	Turb. NTU	Alkal. m.mol/L
41	12	7.7	1215	1899	510	1.32	7
42	11	7.9	1083	1692	490	1.42	7.2
43	12	7.9	977	1527	440	0.49	7.4
44	5	7.6	2323	3630	710	1.85	10.4
45	11	7.5	1990	3110	650	0.84	9.2
46	6	7.6	2272	3550	720	0.62	10.6
47	6	7.8	2144	3350	670	0.82	7.4
48	6	7.7	2003	3130	630	1.16	10.8
49	21	8	1370	2140	340	0.67	8.6
50	27	8.0	3251	5080	560	0.91	9.4
51	24	8.1	3398	5310	620	2.29	9.8
52	24	8.0	2938	4590	470	379	10.4
53	21	7.3	2778	4340	610	0.5	9.8
Min.	5	7.2	678	1060	180	0.32	4.6
Max.	27	8.5	6163	9630	2650	379	13
Mean	12	7.90	1811.2	2835.5	515.8	10.133	8.69
Std. Dev.	5.0	0.29	979.2	1527.3	337.1	52.008	1.79

Table 3
Groundwater classification on the basis of different parameters for irrigation purpose.

Parameters	Reference	Range	Classification	No. of Samples	% Samples
SAR	Richards (1954)	< 10	Excellent	39	73.58
		10–18	Good	11	20.75
		18–26	Doubtful	2	3.77
		> 26	Unsuitable	1	1.89
%Na mg/L	Wilcox (1955)	< 20	Excellent	0	0
		20–40	Good	2	3.77
		40–60	Permissible	19	35.85
		60–80	Doubtful	20	37.74
PI meq/L	Doneen (1962)	≥ 75	Excellent	19	35.85
		25–75	Good	34	64.15
		< 25	Unsuitable	0	0
		> 80	Unsuitable	12	22.64
EC μS/cm	Wilcox (1955)	< 250	Excellent	0	0
		250–750	Good	0	0
		750–2250	Permissible	22	41.51
		2250–5000	Doubtful	27	50.95
RSC meq/L	Eaton (1950)	< 1.25	Suitable	46	86.79
		1.25–2.5	Marginal	2	3.77
		> 2.5	Unsuitable	5	9.43
TH mg/L	Sawyer and McCarty (1967)	0–75	Soft	0	0
		75–150	Moderately hard	0	0
		150–300	Hard	6	11.32
		> 300	Very hard	47	88.68
TDS mg/L	Davis and	< 500	Desirable for drinking	0	0
		500–1000	Permissible for drinking	9	16.98
	De Wiest (1966)	1000–3000	Useful for agriculture	40	75.47
		> 3000	Unsuitable	4	7.55

The mean value of EC was 2835.5 ± 1527.3 μS/cm and it varied from 1060 to 9630 μS/cm (Table 1). According to Wilcox's (1955) classification no water sample was found in the 'excellent' and 'good' categories. However, 22, 27, and 4 groundwater samples fell in categories permissible, doubtful, and unsuitable respectively (Table 3). EC values of 45 water samples were found above the standard level (1,500 μS/cm) for drinking water (WHO, 2008). Shahab et al. (2019) reported EC values from 560 to 4,967 μS/cm for groundwater of Bulri Shah Karim, which does not agree well with the results of the present study. It is well known that in shallow groundwater sometimes high EC values are found due to surface pollution. Shahab et al. (2019) collected groundwater samples at a depth of 20 m or more, whereas in the present study only 4 samples, out of 53, were taken from a depth of more than 20 m. The average depth of borewells in this study was only 12 m and this could be attributed to higher values of EC in the present study from the same Taluka. The relationship between depth and EC for the present study revealed that there is a slight positive correlation ($R^2 = 0.0397$) (Fig. 3) between the two parameters.

Total hardness values were found to vary from 180 to 2,650 mg/L (mean 616.8 ± 337.1 SD) (Table 1). The water hardness is attributed to the presence of calcium and magnesium (Todd, 1980). On the basis of total hardness, groundwater is classified into four categories: soft (< 75 mg/L), moderately hard (75 to 150), hard (150 to 300), and very hard (> 300) (Sawyer & McCarty, 1967; Hem, 1989). Results of this study show that out of 53 groundwater samples, 47 fell in 'very hard' and remaining 6 samples in 'hard' categories (Table 3). The WHO permissible limit of groundwater hardness is 500 mg/L. Total hardness of 17 groundwater samples was found > 500 mg/L during this study. Total hardness of groundwater of Nawabshah has been reported to vary from 84 to 1,695 mg/L by Kandhro et al. (2015) indicating that the level of hardness of TMK groundwater is higher than that of Nawabshah. Turbidity ranged from 0.32 to 379 NTU (mean 10.133 ± 52.01 SD). Only 7 (13.21%) samples were found beyond the WHO standards of 5 NTU, whereas turbidity in 46 (86.79%) samples were found < 5 NTU. Merani et al (2014) from the same locality, that is Bulri Shah Karim, reported that out of 36 groundwater samples 11 (30.55%) were beyond the permissible limit. The difference in turbidity values between the two studies may be attributed to difference in number of water samples analyzed. The alkalinity ranged from 4.6 to 13 m.mol/L (mean 8.69 ± 1.79 SD). The maximum permissible limit of alkalinity in drinking water is 6.5 m.mol/L (= 300 mg/L)

and only 4 samples were found within this range. Merani et al. (2014) did not report alkalinity from Bulri Shah Karim groundwater. However, Lanjwani et al. (2020b) reported alkalinity values for Larkana groundwater that varies from 100 to 320 mg/L (= 2.17 to 6.96 m.mol/L) with a mean value of 200.4 mg/L (= 4.44 m.mol/L). This shows that the groundwater of Bulri Shah Karim is more alkaline than that of Larkana.

Chemical parameters

Table 4 shows the results of chemical parameters analyzed during this study. The mean values of cation show that the Na^+ (69%) was the most abundant cation followed by Ca^{2+} (18%). These two cations constituted 87% of four major cations present in the groundwater (Fig. 4). In case of anions, Cl^- (41%) and HCO_3^- (37%) were the most common and they together accounted for 78% of the major anions present in the groundwater. The least common cation and anion were K^+ (2%) and NO_3^- (0.2%). Results of the present study regarding major cations agree well with the findings of Kandhro et al. (2015) who reported that the groundwater of Nawab Shah city, which is about 150 Km North of TMK, has concentration of major cations in the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$. Similar observations have been reported by Lanjwani et al. (2020b) from Larkana which is about 343 Km North of the present study site. Sodium is one of the dominating cations found in the groundwater and its abundance is related to other anions present in the system. High concentration of Na^+ gives taste to the water and makes it unfit for drinking (Kandhro et al., 2015) and may lead to high blood pressure and cardiac disease (Scheelbeek et al., 2016). Lanjwani et al. (2020b) reported from Larkana that the most abundant anions in the groundwater samples were $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$, whereas during present study the concentration of anions was in the order of $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$.

Table 4
Chemical parameters of groundwater from Taluka Bulri Shah Karim

Sample No.	Ca ²⁺ ppm	K ⁺ ppm	Na ⁺ ppm	Mg ²⁺ ppm	Cl ⁻ ppm	SO ₄ ²⁻ ppm	NO ₃ ⁻ ppm	HCO ₃ ⁻ ppm	F ⁻ ppm	Fe ppm	As ppb
1	72	8.8	196	46	187	88	1.193	440	0.97	0.07	100
2	112	8.8	192	49	247	107	1.601	450	0.69	3.61	70
3	68	8.8	216	56	245	96	1.755	430	1.09	0.04	100
4	36	9.6	370	36	310	136	1.708	470	1.53	0.21	150
5	86	10.6	184	40	193	80	1.503	440	1.54	0.04	150
6	72	11.6	360	39	405	94	1.376	460	1.78	0.06	200
7	68	8.6	121	44	125	144	1.606	300	0.52	0.06	5
8	156	10.5	400	100	690	330	1.240	360	1.16	0.08	0
9	104	9.4	192	46	260	108	1.604	400	1.46	0.04	0
10	128	25.2	264	75	441	225	1.474	380	1.03	0.05	0
11	120	11.5	235	68	405	140	1.265	380	1.03	0.03	10
12	96	7.3	208	56	310	154	1.331	340	0.7	0.05	5
13	20	13.4	672	32	530	265	1.236	620	2.96	0.02	5
14	48	19.5	580	41	515	238	1.463	600	1.88	0.08	5
15	44	11.2	810	27	762	255	1.367	650	1.88	0.11	10
16	28	12.5	558	29	435	240	1.599	560	1.84	0.04	5
17	68	19.3	470	92	575	305	1.302	460	1.45	0.06	0
18	204	16	565	97	922	415	1.474	420	1.44	0.02	0
19	92	7.2	105	61	145	172	1.276	330	1.51	0.14	5
20	104	46.8	270	78	271	340	9.842	460	1.43	0.05	5
21	840	42	940	134	2617	780	3.392	280	1.43	0.04	0
22	52	6.1	74	56	75	88	1.309	330	0.77	0.06	0
23	74	8.4	172	62	185	134	1.244	410	1.18	0.09	5
24	44	6.7	132	66	149	108	1.329	350	1.2	0.05	0
25	60	6.4	214	63	180	150	1.479	470	1.24	0.02	0
26	128	13.0	434	87	496	405	1.452	510	1.68	0.13	0
27	76	6.1	107	34	132	68	1.249	310	1.47	0.04	5
28	54	5.6	105	35	145	84	1.269	230	1.21	0.02	5
29	80	7	604	56	435	690	1.247	400	1.5	0.02	0
30	96	7.8	350	83	510	264	1.231	350	1.7	0.08	0
31	88	7.5	141	46	171	97	1.03	380	1.37	0.03	0
32	44	4.2	445	66	465	360	1.108	450	2.67	0.04	0
33	40	4.2	485	66	435	355	1.476	440	3.39	0.06	5
34	28	7.5	550	56	640	170	1.418	420	2.32	0.04	0
35	44	12.4	445	80	580	142	1.202	460	1.32	0.02	5
36	116	18	495	87	835	226	1.309	360	1.29	0.02	0
37	64	10	1350	53	1454	640	1.452	610	3.16	0.05	0
38	6.0	11	480	83	565	212	1.472	550	0.99	0.07	0
39	128	7.5	310	75	310	370	1.356	490	1.88	0.11	0
40	56	4.8	118	73	170	84	1.162	370	1.42	0.08	0

Sample No.	Ca ²⁺ ppm	K ⁺ ppm	Na ⁺ ppm	Mg ²⁺ ppm	Cl ⁻ ppm	SO ₄ ²⁻ ppm	NO ₃ ⁻ ppm	HCO ₃ ⁻ ppm	F ⁻ ppm	Fe ppm	As ppb
41	116	7.4	196	53	260	210	1.329	350	1.40	0.06	5
42	40	9.1	157	95	225	152	1.392	360	1.41	0.07	0
43	84	6.8	144	56	175	138	1.113	370	2.31	0.04	0
44	88	16.5	490	119	633	350	7.482	520	1.34	0.05	10
45	84	16	405	107	571	260	5.794	460	1.01	0.02	5
46	136	16.5	474	92	644	330	3.307	530	1.38	0.03	0
47	128	15	450	85	545	338	3.305	520	1.35	0.02	0
48	140	16	410	68	500	284	3.151	540	1.40	0.04	5
49	146	6.5	330	12	315	175	1.418	430	1.24	0.06	0
50	144	22.5	890	49	1040	540	5.562	470	1.38	0.04	5
51	152	44.5	910	58	1064	610	6.224	490	1.40	0.04	0
52	136	23	820	32	851	490	3.383	520	1.19	1.49	5
53	128	8.2	705	70	826	474	1.329	490	1.13	0.05	0
Min.	6	4.2	74	12	75	68	1.03	230	0.52	0.02	0
Max.	840	46.8	1350	134	2617	780	9.842	650	3.39	3.61	200
Mean	101.25	12.84	401.89	63.57	493.79	258.68	2.08	437.17	1.49	0.15	16.70
Std. Dev.	11.48	9.25	264.74	24.75	411.50	170.04	1.77	90.01	0.57	0.52	42.93

Iron (Fe) content varied from 0.02 to 3.61 mg/L with an average value of 0.150 ± 0.524 mg/L. Sample 2, which was taken from Qurbam Ali Mallah village exhibited highest value (3.61 mg/L) followed by sample 52 which was taken from village Chodero. The permissible limit of total Fe in drinking water is 0.3 mg/L and 51 samples contained Fe < 0.3 mg/L. Arsenic was found to vary from 0 to 200 µg/L with average value of 16.7 ± 42.9 µg/L. The safe limit of As in drinking water is 10 µg/L. Results of this study revealed that As content of 44 samples was < 10 µg/L and 9 samples was from 10 to 200 µg/L. Sample number 1 to 6 were taken from village Qurban Ali Mallah and their As content varied from 70 to 200 µg/L, which is much higher than the permissible limit. Arsenic is one of the most toxic metalloids found in groundwater due to geological processes and anthropogenic activities (Brahman et. al. 2013). It is widely distributed in the groundwater of Sindh province and it is estimated that approximately 16 to 36% population of Sindh is exposed to high levels of arsenic due to groundwater use (Shahab et al., 2019). Arain et al. (2008) reported that more than 400 people died in 2004 due to consumption of water that contained high levels of arsenic and other heavy metals. Arsenic occurs naturally in sediments and in many rocks as trace element and is released in groundwater from these geological sources. Arsenic is used in wood preservative, animal feed, pesticides and in industry and can be released into groundwater from these sources.

Aesthetic parameters

Aesthetic parameters were: colour, taste, and odour and they were found fit in most cases. However, sample numbers 2, 3, 4 (from village Qurban Ali Mallah) and 52 (from village Chodero) were coloured and unfit for drinking. Objectionable odour was observed in sample number 21 (from village Haji Urs Sathyo), 37 (from village Ali Ghulam Khaskheli), 50 and 51 (from village Chodero).

Correlation coefficient analyses

The Pearson's correlation coefficient values were calculated in order to measure the strength of linear relationship between the two parameters (Table 5). The highest positive correlation ($r = 1.000$) was found between EC and TDS, whereas the second highest positive correlation ($r = 0.977$) was found between EC and Cl⁻ and TDS and Cl⁻. The lowest negative correlation ($r = -0.538$) was observed between pH and TH and turbidity and TH. The second lowest ($r = -0.513$) was found between pH and Mg²⁺. The pH was found negatively correlated with all the parameters studied except HCO₃⁻ and turbidity. HCO₃⁻ was positively correlated with all the parameters except Ca²⁺, Mg²⁺ and TH. There was strong positive correlation between Na⁺ and TDS ($r = 0.901$), Ca²⁺ and TH ($r = 0.955$) and HCO₃⁻ and alkalinity ($r = 0.974$).

Table 5
Pearson's correlation matrix for physical and chemical parameters of groundwater from Taluka Bulri Shah Karim.

	pH	Turb	TDS	Cl ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	TH	NO ₃ ⁻	F ⁻	Fe	As	EC	Alkal.	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	
pH																		
Turb.	0.029																	
TDS	-0.117	0.163																
Cl ⁻	-0.176	0.128	0.977															
SO ₄ ²⁻	-0.040	0.181	0.878	0.789														
Na ⁺	0.163	0.211	0.901	0.824	0.819													
K ⁺	-0.242	0.097	0.594	0.580	0.536	0.445												
TH	-0.538	-0.538	0.672	0.753	0.545	0.286	0.542											
NO ₃ ⁻	-0.260	0.097	0.323	0.261	0.381	0.259	0.729	0.259										
F ⁻	0.432	-0.098	0.266	0.201	0.278	0.432	-0.101	-0.152	-0.120									
Fe	-0.070	0.449	-0.033	-0.043	-0.052	-0.027	-0.009	-0.029	-0.007	-0.208								
As	-0.008	-0.007	-0.207	-0.182	-0.326	-0.166	-0.100	-0.178	-0.090	-0.060	0.166							
EC	-0.120	0.162	1.000	0.977	0.876	0.901	0.595	0.674	0.322	0.264	-0.033	-0.208						
Alakal.	0.215	0.126	0.333	0.190	0.271	0.580	0.153	-0.259	0.186	0.400	0.081	0.075	0.331					
Ca ²⁺	-0.454	0.067	0.666	0.752	0.528	0.305	0.533	0.955	0.199	-0.130	0.022	-0.103	0.668	-0.266				
Mg ²⁺	-0.513	-0.177	0.388	0.424	0.359	0.099	0.330	0.692	0.317	-0.130	-0.151	-0.301	0.389	-0.164	0.453			
HCO ₃ ⁻	0.203	0.119	0.343	0.193	0.285	0.584	0.160	-0.244	0.208	0.391	0.391	0.063	0.341	0.974	-0.257	-0.257	-0.257	-0.257

Groundwater facies

The hydrochemistry of groundwater is a function of aquifer's lithology. The flow pattern of the groundwater through geological formation also influences its hydrochemistry (Ehya & Mosleh, 2018). Hydrogeologists commonly use Piper trilinear diagram (Piper, 1944) to determine groundwater facies and hydrogeological evolution of aquifers (Ehya & Marbouti, 2016). Piper trilinear diagram for the groundwater samples of Bulri Shah Karim is depicted in Fig. 5, which indicates that 36 samples (67.92%) were of sodium-chloride facies, 14 samples (26.42%) were of mixed facies and 3 samples (5.66%) were magnesium bicarbonate facies. The sodium chloride facie indicates dissolution of evaporitic minerals and mixing of domestic wastewater into the groundwater (Ehya & Marbouti, 2016) and it may also be attributed to sea water intrusion (Putranto et al. 2019).

Groundwater quality for drinking purposes

Water quality index is an efficient and simple tool to assess groundwater quality for drinking purposes (Akhter et al., 2016). It is a composite indicator of groundwater quality that put together large amount of water quality data into an aggregate numerical value that can be easily communicated and understood by policymakers and general public. On the basis of WQI, groundwater is classified as: excellent (< 50), good (50 to 100), poor (100 to 200), very poor (200 to 300) and unsuitable for drinking (> 300) (Nazir et al., 2016).

The values of WQI determined for the 53 groundwater samples from Bulri Shah Karim are depicted in Fig. 6. WQI values ranged from 40.49 to 636.98 (mean 119.37 ± 93.02 SD). Only three samples, that is sample No. 22 (N25°04.579: E68°25.284), 24 (N25°03.946: E68°27.568) and 28 (N25°03.946: E68°27.442) all from village Haji Hussain Daal were classified as excellent. From village Haji Hussain Daal 7 samples were analyzed out of which 3 were in excellent, 3 were in good and one was in poor categories. The groundwater of this village was found much better than other 9 villages of Bulri Shah Karim. Altogether the good, poor, and very poor classes were represented by 23 (4.0396%), 21 (39.623%), and 4 (7.547%) samples respectively. There were only two samples, No. 21 (N25°04. 577: E68°25.284) from village Haji Urs Sathyo and No. 52 (N25°04.850: E68°26.838) from village Chodero, which were found unsuitable for drinking (Fig. 6). Previous studies from Bulri Shah Karim (Khan, 2014; Merani et al. 2014; Shahab et al., 2019) have not computed WQI for the groundwater. High values of WQI found during this study were due to high concentrations of turbidity, TDS, and Fe.

Groundwater quality for irrigation purposes

Groundwater quality for irrigation purposes is determined by the presence of dissolved constituents and their concentrations. Irrigation water with high salt content increases soil solution osmotic pressure which adversely affects plant growth (Zaman et al., 2018). Other effects of high salt content in irrigation water include changes in soil structure, aeration, and permeability. The most important parameters used to assess the suitability of groundwater for irrigation are: SAR, %Na, PI and residual sodium bicarbonate (RSBC).

Sodium Adsorption Ratio (SAR)

The sodium adsorption ratio varied from 1.70 to 30.20 (mean 8.22 ± 5.96 SD) (Table 6). According to Richards (1954) classification there are four categories of groundwater based on SAR values: excellent (< 10), good (10–18), doubtful (18–26) and unsuitable (> 26). There were 39, 11, 2, and 1 sample fell in the excellent, good, doubtful and unsuitable categories respectively during this study (Table 3). The only sample (No. 37) which was found unsuitable for irrigation came from village Ghulam Kashkeli (N24°52.019: E68°28.504) The concentration of Na^+ (1,350 ppm), Cl^- (1,454 ppm), SO_4^{2-} (640 ppm) and F^- (3.16) was found high in the water sample and this may be attributed to its unsuitability for irrigation purpose. Previous studies (Merani et al., 2014; Shahab et al., 2019) from Bulri Shah Karim have neither reported SAR values of groundwater nor provided concentration of Na^+ , Ca^{2+} , and Mg^{2+} . However, Kandhro et al. (2015), from Nawabshah, which is about 150 Km North of Bulri Shah Karim, reported that out of 65 groundwater samples, 40 (61.54%) samples have SAR values < 6 and remaining 25 (38.46%) samples have SAR values > 6 . They concluded that 38.46% of the groundwater samples from Nawabshah are not suitable for irrigation purposes. According to Richards (1954) groundwater having SAR value > 26 is not suitable for irrigation (see Table 3).

Table 6
 Computed values of sodium adsorption ratio (SAR), percent of sodium (%N), permeability index (PI) and residual sodium carbonate (RSC) for groundwater of Bulri Shah Karim.

Sample No.	SAR	%Na	PI	RSC
1	4.44	60.72	69.10	-0.17
2	3.81	53.07	60.40	-2.24
3	4.69	61.93	69.63	-0.95
4	10.43	81.93	88.62	2.95
5	4.11	57.39	66.12	-0.37
6	8.49	74.60	80.99	0.74
7	2.81	50.08	59.37	-2.10
8	6.15	60.02	63.87	-10.11
9	3.94	54.64	61.99	-2.42
10	4.58	53.64	60.71	-6.33
11	4.25	54.09	60.16	-5.36
12	4.17	56.63	62.90	-3.83
13	21.68	91.13	96.26	6.53
14	14.85	84.24	90.36	4.07
15	23.70	90.79	94.83	6.24
16	17.64	88.92	94.58	5.40
17	8.73	72.39	78.01	-3.42
18	8.15	64.06	67.61	-11.28
19	2.08	39.59	47.74	-4.20
20	4.87	54.13	64.48	-4.07
21	7.94	48.06	49.99	-48.35
22	1.70	39.34	50.64	-1.79
23	3.57	54.36	62.42	-2.07
24	2.94	53.08	62.28	-1.89
25	4.60	62.32	69.93	-0.47
26	7.25	65.56	70.35	-5.19
27	2.56	47.96	57.42	-1.51
28	2.73	52.61	61.94	-1.80
29	12.66	80.86	84.32	-2.04
30	6.31	65.20	69.70	-5.88
31	3.03	49.91	58.36	-1.95
32	9.91	79.58	84.00	-0.25
33	10.94	81.49	85.61	-0.21
34	13.80	85.74	89.98	0.88
35	9.23	76.54	81.98	-1.24
36	8.46	69.13	73.64	-7.05
37	30.20	91.40	93.71	2.44
38	11.05	82.76	88.48	1.89
39	5.38	59.56	64.74	-4.53

Sample No.	SAR	%Na	PI	RSC
40	2.45	46.86	55.56	-2.74
41	3.78	52.63	58.82	-4.41
42	3.08	52.14	60.26	-3.91
43	2.98	49.52	57.48	-2.74
44	8.00	68.68	73.57	-5.66
45	6.91	66.18	71.55	-5.46
46	7.69	65.97	70.80	-5.67
47	7.56	66.37	71.31	-4.86
48	7.11	64.67	70.10	-3.73
49	7.05	66.73	71.87	-1.22
50	16.34	80.51	84.18	-3.51
51	15.92	78.15	83.23	-4.33
52	16.43	81.11	85.30	-0.90
53	12.44	77.37	80.52	-4.12
Min.	1.70	39.34	47.74	-48.35
Max.	30.20	91.40	96.26	6.53
Mean	8.22	65.40	71.54	-3.12
Std. Dev.	5.96	14.11	12.81	7.25

Sodium Adsorption Ratio (SAR) and Electric Conductivity (EC)

Groundwater is also classified on the basis of SAR and EC (Gupta, 1990) to determine its suitability for domestic and irrigation purposes. There are four categories: good water (SAR < 10 and EC < 2 dS/m), saline water (SAR < 10 and EC > 2), high saline water (SAR > 10 and EC > 4) and alkali water (variable). Results of the present study show that 19 (35.85%), 23 (43.40%), 5 (9.43%) and 6 (11.32%) samples fell in the category of good, saline, highly saline and alkali waters respectively. When the EC and SAR values plotted on Riverside diagram (Fig. 7) it emerged that the better class of water quality is C3S1, average to mediocre, which include 17 (32.08%) groundwater samples and this is the dominant class. The alkalinity and salinity values of the 17 samples were very low and their water quality was good enough to be used on any kind of soil with little or no problem of sodium accumulation. The next dominant classes were C4S3 and C4S4 each containing 10 (18.87%) groundwater samples. The classes C4S4 and C5S4 contained 11 groundwater samples which were highly saline and may cause sodium accumulation related problems.

Percent of Sodium (%Na)

The concentration of Na⁺ in irrigation water is one of the important factors as it decreases the permeability of soil, thereby changing the soil structure (Todd, 1980; Ehya & Mosleh, 2018). Excessive Na⁺ in irrigation water, after long time use, hardens the upper layer of the soils, which prevents proper aeration of plants' roots. The computed values of %Na for groundwater samples varied from 39.34 to 91.40 (mean 65.40 ± 14.11 SD) (Table 3). According to Wilcox (1955) classification, groundwater is grouped into five categories: excellent (< 20%Na), good (20 to 40), permissible (40 to 60), doubtful (60 to 80), and unsuitable (> 80). Results of the present study revealed that no water sample fell in the excellent category. Most of the water samples (37.74%) fell in doubtful category followed by 35.85% samples in permissible category. There were 2 water samples (3.77%) in good category and 12 (22.64%) in unsuitable category (Table 3). The values of %Na from groundwater of Bulri Shah Karim is reported for the first time. When %Na values were plotted against EC values on Wilcox's diagram (Fig. 8) then it was revealed that only one sample (No. 23) fell in excellent category, 11 samples (No. 16, 19, 22, 30, 37, 38, 45, 51 to 54) fell in bad category, and remaining 41 samples fell in good, admissible, and mediocre categories.

Permeability Index (PI)

Irrigation water containing high concentration of Na⁺, Ca²⁺, Mg²⁺ and HCO₃⁻ ions, after long-time use, decreases the soil permeability due to the precipitation of these ions (Ehya & Mosleh, 2018). Hence, PI is used as a tool to evaluate this effect. PI of the groundwater samples analyzed during this study ranged from 47.74 to 96.26 (mean 71.54 ± 12.81 SD) (Table 6). According to Doneen (1962) classification based on PI there are three categories: excellent (≥ 75), good (25 to 75), and unsuitable (< 25). All the groundwater samples fell either in excellent (19 samples) or in good (34) categories (Table 3). This indicates that soil permeability, as it stands, is not an issue at the study site.

Residual Sodium Carbonate (RSC)

The RSC index of groundwater indicates soil's alkalinity hazard. It is used to determine the suitability of groundwater for irrigation purposes. According to Eaton (1950) and Richards (1954) the RSC index is classified into three classes: suitable (< 1.5 meq/L), marginal (1.25 to 2.5), and unsuitable (> 2.5). The results of the present study shows that RSC values of the groundwater varied from - 48.35 to 6.53 (mean - 3.12 ± 7.25 SD) (Table 6). Forty-six samples fell in the suitable category, whereas 2 and 5 samples fell in the marginal and unsuitable categories (Table 3). The unsuitable water samples came from village Qurban Ali Mallah (sample No. 4) and Luqman Khaskheli (No. 13 to 16). There were seven water samples from Qurban Ali Mallah and five from Luqman Khaskheli. This indicates that the groundwater from Luqman Khaskheli was not suitable for irrigation except one sample, that is sample No. 17.

Conclusion

The results of the groundwater analysis reveals that the dominant cations are sodium and calcium while the dominant anions are chloride and bicarbonate. Analyses of the groundwater facies indicate that it is mostly sodium chloride type. The values of all the physical and chemical parameters of the groundwater are highly variable, except pH. The pH values are within the acceptable limits in all the groundwater samples. However, values of some parameters are within or outside the acceptable limits. On average, the groundwater of Bulri Shah Karim is acceptable for drinking purpose based on WQI. Water quality indices such as SAR, %Na, PI, and RSC indicate that the groundwater of the study site is generally suitable for irrigation purposes, although some of them are highly saline and may need some prior treatment. On the basis of WQI, the quality of groundwater from village Haji Hussain Daal is much better than those taken from other 9 villages of Taluka Bulri Shah Karim. On the basis of RSC index, quality of groundwater from village Luqman Khaskheli is much poorer and is hardly acceptable for irrigation purposes.

Declarations

Author's contribution G. M. Arian conceptualized the study, collected groundwater samples and supervised water samples analysis. S. Khatoon analysed the water samples and assisted in data compilation. J. Mustaqim compiled the data, drew diagrams, and wrote original draft. M. Ashraf reviewed and edited the draft.

Competing interest The authors declare no competing interest.

Data availability All the analytical data of this study is available with corresponding author and have been provided in the paper. If raw data are needed, corresponding author should be contacted.

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Figures

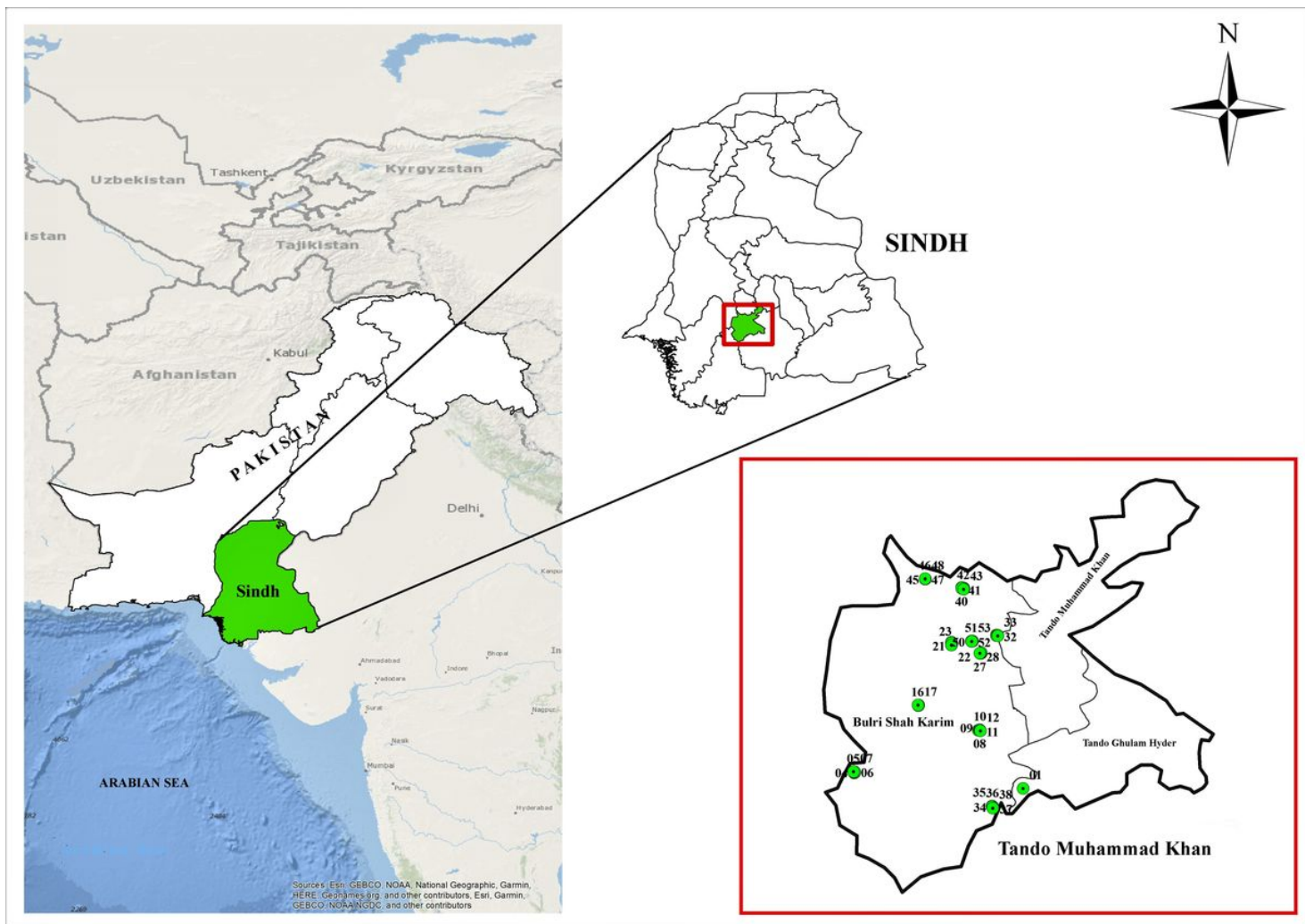


Figure 1

Map showing location of hand-pumps (1 to 53) at Taluka Bulri Shah Karim in Tando Muhammad Khan district of Sindh province, Pakistan.

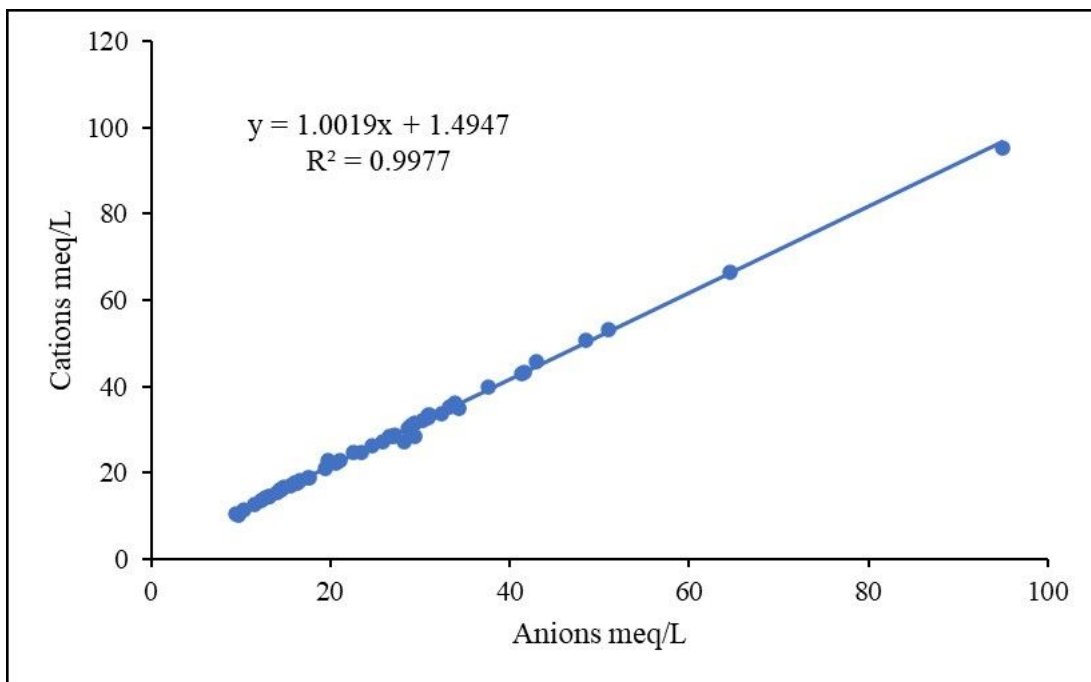


Figure 2

Graph showing ionic balance for the groundwater samples from Taluka Bulri Shah Karim

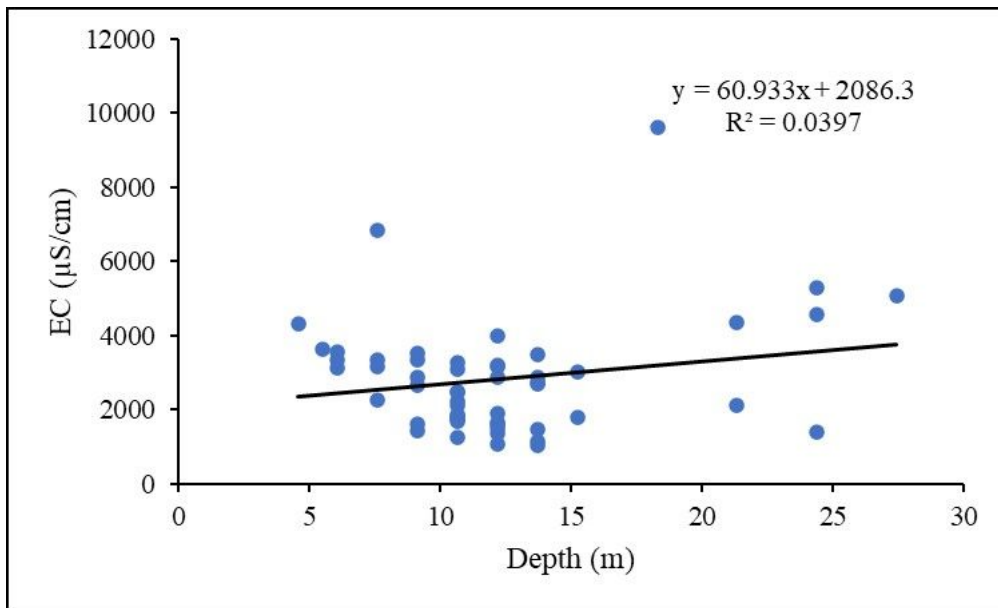


Figure 3

Graph showing relationship between electrical conductivity (EC) and depth of the hand-pumps.

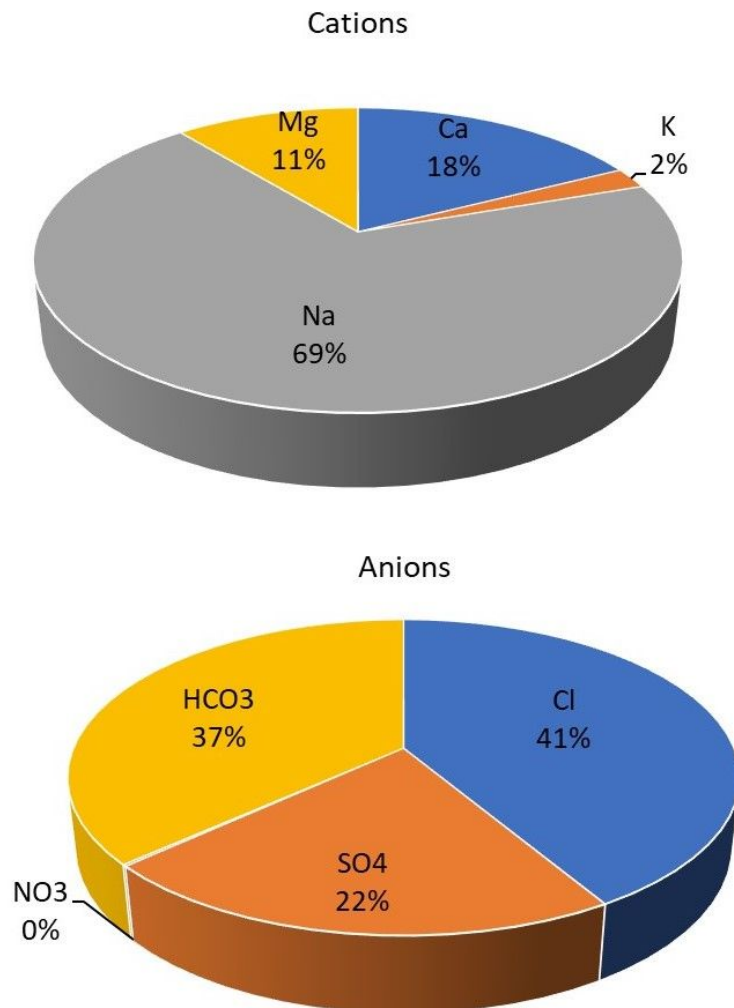


Figure 4

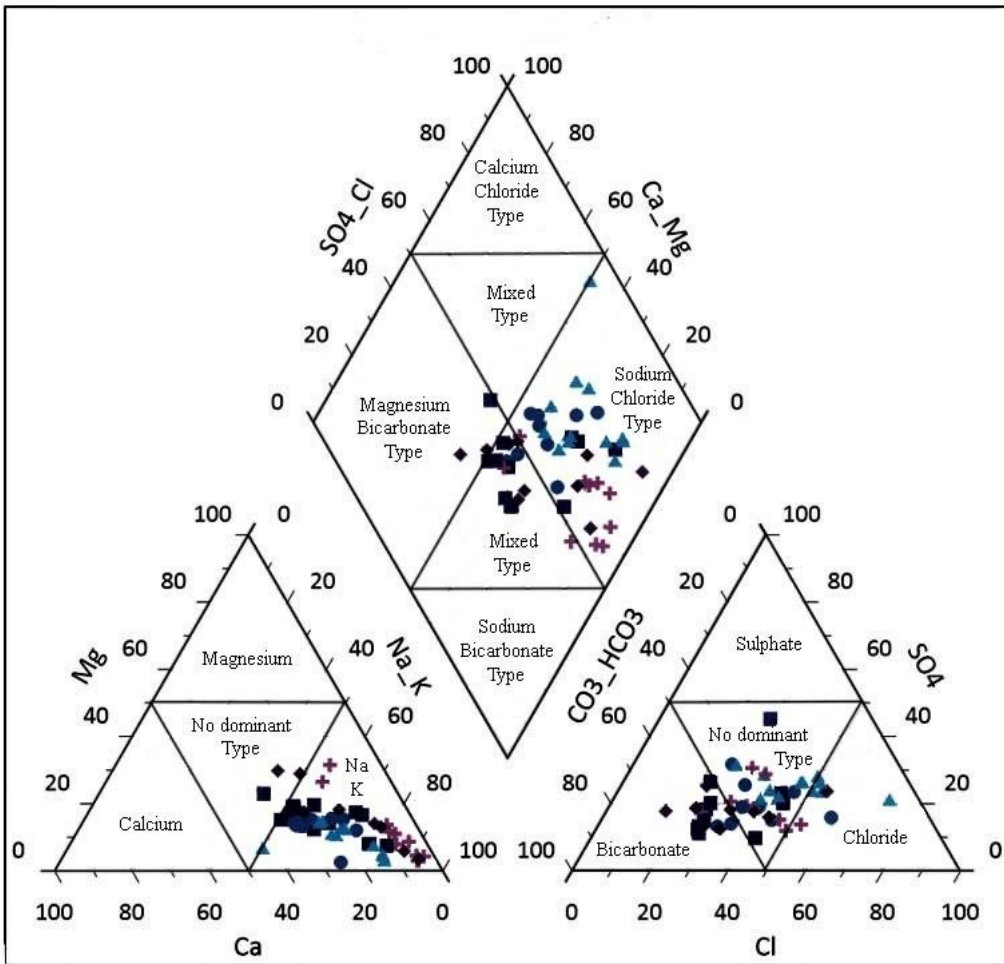


Figure 5

Piper's diagram for the groundwater from Taluka Bulri Shah Karim.

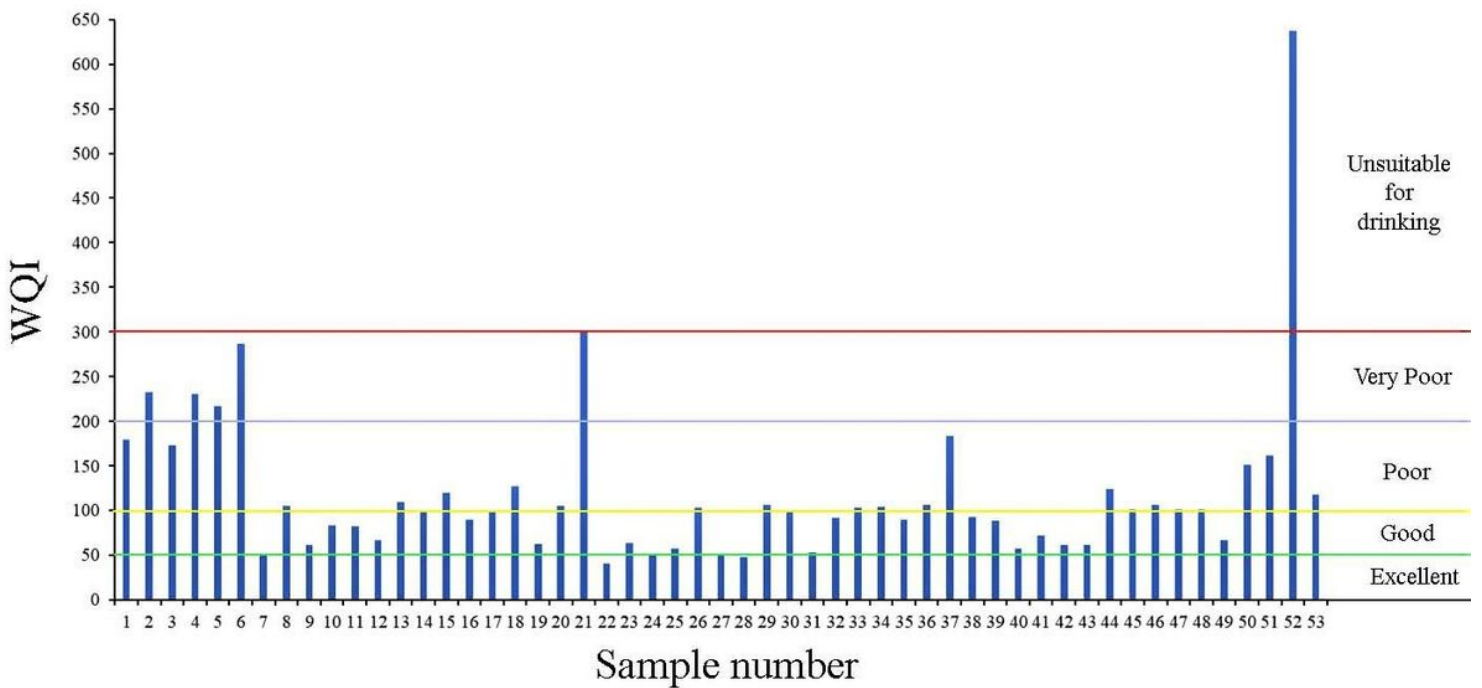


Figure 6

Water quality index (WQI) for the groundwater from Taluka Bulri Shah Karim. Sample number 1 to 7 from village Qurban Ali Mallah, 8 to 11 from Shahmeer Khan Lund, 13 to 17 from Luqman Khaskheli, 18 to 21 from Haji Urs Sathyo, 22 to 28 from Haji Hussain Daal, 29 to 33 from Allah Dino Solangi, 34 to 38 from Ali Ghulam Khaskheli, 39 to 43 from Ghulam Hussain Soomro, 44 to 48 from Suleman Soomro, and 49 to 53 from Chodero

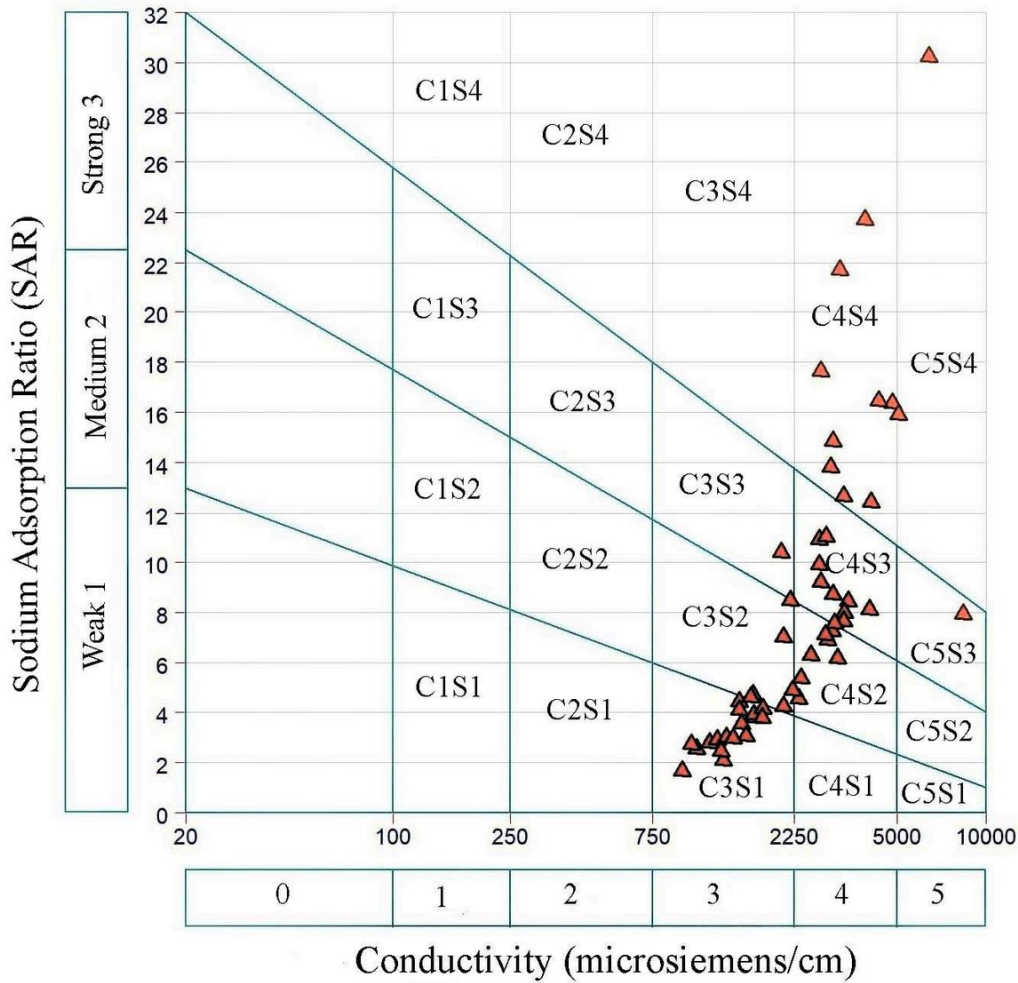


Figure 7

Riverside diagram showing classification on the basis of sodium adsorption ratio (SAR) and electric conductivity (EC) for the groundwater samples from Taluka Bulri Shah Karim

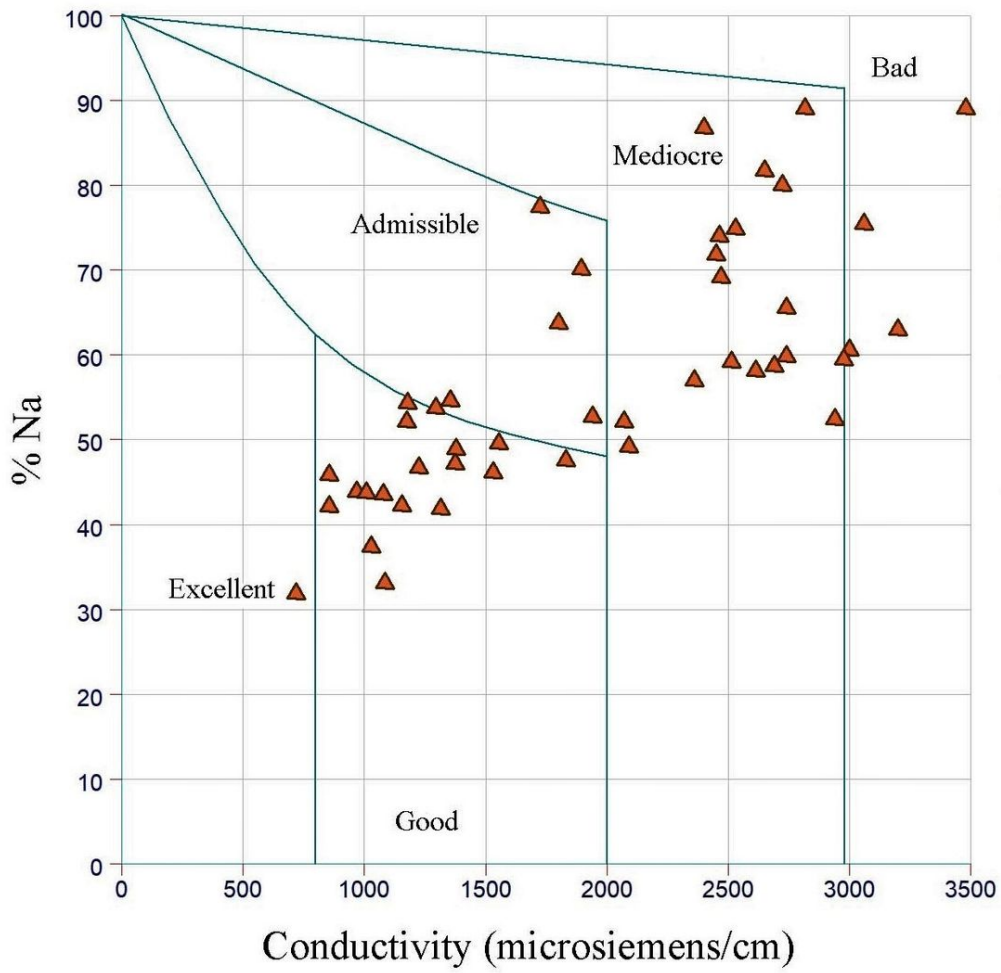


Figure 8

Wilcox's diagram showing classification on the basis of percent of sodium (%Na) and electric conductivity (EC) for the groundwater samples from Taluka Bulri Shah Karim