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

Ghulam Murtaza Arain[1]*, Nazia Sattar[1], Sumaira Khatoon[2], Javed Mustaquim[2]

[1]Pakistan Council of Research in Water Resources, University Road, Karachi, Pakistan
[2]Centre of Excellence in Marine Biology, University of Karachi, Karachi, Pakistan

* Email: drmurtaza1977@gmail.com

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Abstract: Groundwater in Pakistan is the main drinking water source, highlighting the significance of regularly monitoring its quality. There have been several examples of high concentrations of elements like arsenic and nitrate in groundwater that harm human health and the environment. Our aim with this study was to assess the groundwater quality of the sub-district Bhulri Shah Karim for drinking and irrigation purposes. We collected groundwater samples from 53 shallow bore well hand pumps in October and November 2018. We determined the concentration of four cations, five anions and other parameters like pH, turbidity, TDS, total hardness, EC, alkalinity, total iron, and arsenic. The groundwater was found to be very hard, and the relative abundance of cations and anions was $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $Cl^- > HCO_3^- > SO4^{2-} > NO_3^- > F^-$. The concentrations of arsenic and iron varied from 0 to 0.2 mg/L and 0.02 to 3.6 mg/L, respectively. We discussed groundwater quality for drinking and irrigation purposes by calculating the water quality index, sodium adsorption ratio, percent of sodium, permeability index, and residual sodium carbonate. In conclusion, the groundwater of the studied area is suitable for drinking on average and irrigation. However, some water samples were high in arsenic content, and some were highly saline and may need some prior treatment.

Keywords; Groundwater quality, Bhulri Shah Karim, Sindh, Pakistan.

Introduction

Pakistan is a water-stressed country. With the increasingly variable surface water supply, Pakistan depends heavily on groundwater. In rural Pakistan, groundwater is the main source of domestic water, and a considerable amount of groundwater is also used for irrigation. Despite this, the status of groundwater quality is poorly understood, especially in Sindh province. Although there have been some studies to investigate groundwater quality from Sindh coastal areas (Alamgir et al., 2016; Shahab et al., 2016; Naseem et al., 2018; Bano, 2019), little attention has been given to the rural areas of Sindh (Kandhro et al., 2015; Kori et al., 2018; Lanjwani et al., 2020a, b; Naz et al., 2021). Taluka Bulri Shah Karim (BSK), in rural Sindh, has received even less attention, and the only study that assesses the groundwater quality of BSK is by Meerani et al. (2014), which shows that most of the groundwater samples were unsafe to drink. Their conclusion is based on the number of samples with physicochemical properties beyond the permissible limit of WHO. Shahab et al. (2019), who studied arsenic contamination in groundwater in Sindh, observed a high concentration of arsenic (mean = 46.8 µg/L; range = 0 to 125 µg/L), which exceeds the WHO permissible limit of 10 µg/L.

This study aims to assess the groundwater quality of Taluka BSK for drinking and irrigation purposes based on the Water Quality Index (WQI), Sodium Adsorption Ratio (SR), Percent of Sodium (% Na), Permeability Index (PI), and Residual Sodium Carbonate (RSC).

Materials and Methods

Study Area

Taluka BSK is situated in the southern part of Sindh province in Pakistan (Fig. 1), about 150 Km northeast of the Arabian Sea. Its area is 770 Km^2, and its population, according to the 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. The main crops grown in BSK are rice, sugarcane, wheat, and cotton. The overall climate is moderate, but April to June is very hot, especially during the daytime. December and January are the coldest months. Rainfall is mostly restricted to the monsoon season (July to September). The average rainfall is approximately 130 mm. Pinyari and Akram canals are the main water sources for irrigation, whereas hand pumps are the main source of domestic water.

Sample Collection

Groundwater samples were collected from 53 shallow bore well hand pumps located in 10 villages of BSK in October and November 2018. Before collecting the water sample, the standing water in the hand pump was pumped out to ensure that the sample was representative of the groundwater. Water samples were collected in polystyrene bottles; presoaked in HNO_3 (10%), and thoroughly rinsed with deionized water. HNO_3 (conc.) and H_3BO_3 (1M) were used as preservatives for trace elements (arsenic and total iron) and NO_3-N determination, respectively.

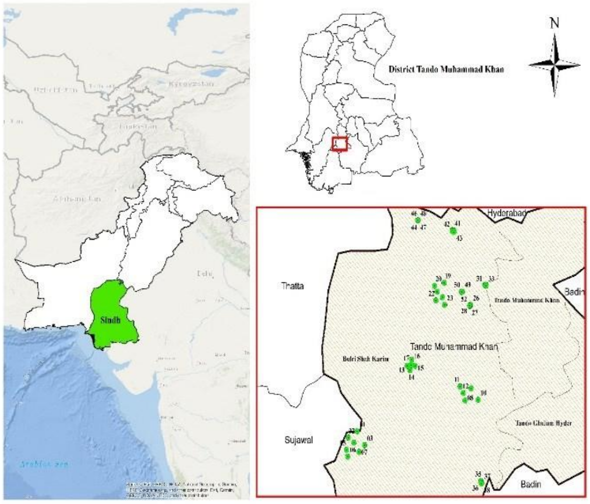

Fig. 1 Map showing locations of handpump (1 to 53) at Taluka Bulri Shah Karim in Tando Muhammad Khan district of Sind province, Pakistan.

Sample Analyses

Electrical conductivity (EC), pH, TDS, and turbidity were measured in situ using an Eu Tech EC/TDS meter (CON11), pH meter (pH 700, HACH), and turbidity meter (2100Q HACH), respectively. Water samples were analyzed according to APHA (1998) standard methods for the examination of water and wastewater except for As, which was determined by Merck test-kit (M Quant). $Ca^{2+}$and total hardness (TH) as $CaCO_3$ were analyzed volumetrically by the EDTA (0.01M) titrimetric method using murexide and Eriochrome Black T indicators, respectively. Mg^{2+} concentration was calculated using formula Mg^{2+} = [Hardness - 2.5 Ca^{2+}] x 0.243. Cl^- concentration was determined by titrating against $AgNO_3$ (0.014N) solution (argentometric method). F^-, SO_4^{2-}, and total iron (Fe) concentrations were determined by using a HACH colorimeter (DR-2800). A spectrophotometer (UV) was used to determine the concentration of NO_3-N at a wavelength of 220-275 nm. Alkalinity as $CaCO_3$was determined by titration with HCl 0.02N using a methyl-orange indicator. Na^+ and K^+ were determined by a flame photometer (DN7101).

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 within the acceptable range of ± 5% (Domenico & Schwartz, 1990). The Piper scatter plot was made using Grapher software, whereas Wilcox's and Riverside's diagrams were made using Diagrammes software.

Microsoft Excel computed the Water Quality Index (WQI) in three steps. First, each parameter was assigned a weight (wi), on a scale of 1 to 5, depending on their impact on groundwater quality. For instance, the highest weight of 5 was given to arsenic and fluoride, whereas the lowest weight of 2 was given to Na, Ca, Mg, etc. (Table 1) (Lanjwani et al., 2020a). Second, each parameter's relative weight (Wi) was calculated by the formula: wi ∑wi. Third, for determining the quality rating (Qi) of each parameter, the concentration of the parameter (Ci) was divided by the WHO standard (Si) for that parameter and then multiplied by 100, that is, Qi = (Ci / Si) x 100.

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

Parameters	WHO standard	Weight (wi)	Relative Weight (Wi)
pH	6.5 - 8.5	3	0.064
TDS ppm	1000	3	0.064
EC µS/cm	1500	3	0.067
Hardness 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	250	3	0.064
NO_3^- ppm	10	4	0.086
F^- ppm	1.5	5	0.106
Fe ppm	0.3	2	0.042
As ppb	10	5	0.106
		∑ = 47	0.999

The sub-index (SIi) for a parameter was then computed by multiplying the relative weight (Wi) with the quality rating (Qi) of the particular parameter (SIi = Wi x Qi). Finally, the WQI value was found by adding all the SIi values (WQI = ∑SIi). The groundwater having WQI values from 0 – 25 was classified as 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).

The physicochemical data were also subjected to evaluate groundwater quality for irrigation purposes such as SAR (Todd, 1980), permeability index (PI) (Doneen, 1964), residual sodium carbonate (RSC) (Gupta & Gupta, 1987), and %Na (Wilcox, 1995). The following formulae were used to compute these indices. All quantities were in mEq/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 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. 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 standards, and all the groundwater samples analyzed during the present study were in this range. This also replicates the findings of Merani et al. (2014) and Shahab et al. (2019), who reported that none of the

Table 2. Physical & chemical parameters of groundwater fromTaluka Bulri Shah Karim.

Sample No.	Depth m	pH	TDS ppm	EC µS/cm	Hardness ppm	Turbidity NTU	Alkalinity 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
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. Classification of groundwater based on differentparameters for irrigation purposes.

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
		>80	Unsuitable	12	22.64
PI mEq/L	Doneen (1962)	≥75	Excellent	19	35.85
		25 – 75	Good	34	64.15
		<25	Unsuitable	0	0
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
		>5000	Unsuitable	4	7.54
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 De Wiest (1966)	<500	Desirable for drinking	0	0
		500-1000	Permissible for drinking	9	16.98
		1000-3000	Useful for agriculture	40	75.47
		>3000	Unsuitable	4	7.55

Groundwater samples from Taluka BSK were beyond 6.5 to 8.5. Similar values (7.42 to 8.20) were also reported by Lanjwani et al. (2020b) for district Larkana in Sindh. The values of TDS varied from 678 to 6163 mg/L (mean1811.2 ± 97.2 SD) during the present investigation. WHO standard for TDS in drinking water is <1,000 mg/L. Out of 53 groundwater samples analyzed during this study, 40 had TDS >1,000 mg/L, revealing that 75.74% of the samples were slightly saline, whereas the remaining 13 samples (24.53%) were freshwater on the basis of TDS classification by Freeze &Cherry (1979).

According to Davis & De Wiest's (1966) classification on a TDS basis, groundwater is of four categories (Table 3). Most groundwater samples (*i.e*., 40 out of 53) of the present study were in the third category, *viz*. useful for agriculture (TDS 1,000 to 3,000 ppm). Only four water samples (# 21, 37, 50, and 51) were in the fourth category 'unsuitable' (TDS >3,000 ppm). Nine samples (# 7, 19, 22, 24, 27, 28, 31, 40, and 43) were 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 the TDS values of 24 groundwater samples out of 36 (*i.e*., 66.67%) from BSK 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 district Larkana groundwater, which indicates that the groundwater of BSK is more saline than that of Larkana.

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
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

The mean value of EC was 2835.5 ± 1527.3 µS/cm and varied from 1060 to 9630 µS/cm (Table 2). According to Wilcox's (1955) classification of water for irrigation purposes, no water sample was found in the 'excellent' and 'good' categories. Twenty-two and 27 groundwater samples were in permissible and doubtful categories, whereas four were in unsuitable categories (Table 2). 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 the groundwater of BSK, which does not agree well with the results of the present study. It is well known that high EC values are sometimes found in shallow groundwater 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 bore wells in this study was only 12 m, which could be attributed to higher EC values in the present study from the same Taluka. The relationship between depth and EC for the present study

Table 5. Pearson's correlation matrix for physical and chemical parameters of groundwater from taluka Bulri ShahKarim.

	pH	Turb.	TDS	Cl^-	SO_4^{2-}	Na^+	K^+	Hard.	NO_3^-	F^+	Fe	As	EC	Alkal.	Ca^{2+}	Mg^{2+}
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										
Hard.	-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	-.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	-0.136

revealed a slight positive correlation (R^2 = 0.0397) (Fig. 2) between the two parameters.

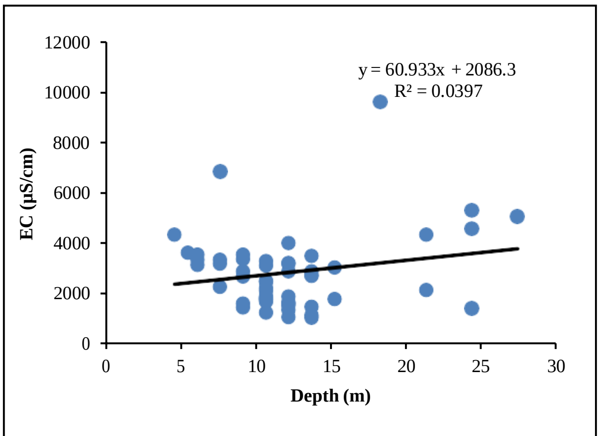

Fig. 2 Graph showing the relationship between electrical conductivity (EC) and depth of the hand pumps.

Total hardness values were found to vary from 180 to 2,650 mg/L (mean 616.8 ± 337.1 SD) (Table 2). The water hardness is attributed to calcium and magnesium (Todd, 1980). Based on 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 were in the very hard category, and the remaining six were in the hard category (Table 2). The WHO permissible limit of groundwater hardness for drinking water is 500 mg/L. The total hardness of 17 groundwater samples was > 500 mg/L during this study.

The total hardness of the groundwater of district 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 BSK groundwater is higher than that of Nawabshah. Turbidity ranged from 0.32 to 379 NTU (mean10.133 ± 52.01 SD). Only seven (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 BSK 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 the difference in the 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); only four samples were found within this range. Merani et al. (2014) did not report alkalinity from BSK groundwater. However, Lanjwani et al. (2020b) reported alkalinity values for district 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 BSK is more alkaline than Larkana's.

Chemical Parameters

Table 4 shows the results of chemical parameters analyzed during this study. The mean cation values show that Na+ was the most abundant cation, followed by Ca2+, Mg2+, and K+. In the case of anions, Cl^- was the most common, followed by HCO_3^-. SO_4^{2-}, NO_3^-, and F^-.

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

Results of the present study agree well with the findings of Kandhro et al. (2015), who reported that the groundwater of Nawabshah City, which is about 150 Km North of BSK, has concentrations of major cations in the order of Na^{+}> Ca^{2+}> Mg^{2+}> 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. A 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 (Scheel beek et al., 2016). Lanjwani et al. (2020b) reported from Larkana that the most abundant anions in the groundwater samples were Cl^{-}> SO_4^{2-}> $HCO3^{-}$, whereas, in the present study, the concentration of anions was in the order of Cl^{-}> HCO_3^{-}> SO_4^{2-}> NO_3^{-}>F^{-}.

Total 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, taken from the Qurban Ali Mallah village, exhibited the highest value (3.61 mg/L), followed by sample # 52, taken from the Chodero village. The maximum permissible limit of total iron in drinking water is 0.3 mg/L, and 51 samples contained less than that. Arsenic was found to vary from 0 to 200 µg/L with an average value of 16.7 ± 42.9 µg/L. The safe limit of Asin drinking water is 10µg/L (WHO). Results of this study revealed that As content of 44 samples was < 10 µg/L, and 9 samples were from 10 to 200 µg/L. Samples # 1 to 6 were taken from village Qurban Ali Mallah, and the As content varied from 70 to 200 µg/L, 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% of the population of Sindh is exposed to high levels of As due to groundwater use (Shahab et al., 2019). Arain et al. (2008) reported that more than 400 people died in 2004 due to the consumption of water that contained high levels of As and other heavy metals. Arsenic occurs naturally in sediments and many rocks as a trace element and is released in groundwater from these geological sources. Arsenic is used in wood preservatives, animal feed, pesticides, and industry and can leach into groundwater.

Aesthetic Parameters

Aesthetic parameters were color, taste, and odor, and they were found fit for drinking in most cases. However; samples # 2, 3, and 4 (from village Qurban Ali Mallah) and 52 (from village Chodero) were colored and unfit for drinking. The objectionable odor was observed in samples # 21 (from village Haji Urs Sathyo), 37 (from village Ali Ghulam Khaskheli), 50, and 51 (from village Chodero).

Correlation Coefficient Analyses

Pearson's correlation coefficient values were calculated to measure the strength of the 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 hardness and turbidity and hardness. The second lowest (r = -0.513) was found between pH and Mg^{2+}. The pH negatively correlated with all the parameters studied except HCO_3^- and turbidity. HCO_3^- was positively correlated with all the parameters except Ca^{2+}, Mg^{2+}, and hardness. There was a strong positive correlation between Na+ and TDS (r = 0.901), Ca^{2+} and hardness (r = 0.955), and HCO_3^- and alkalinity (r = 0.974).

Groundwater Facies

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

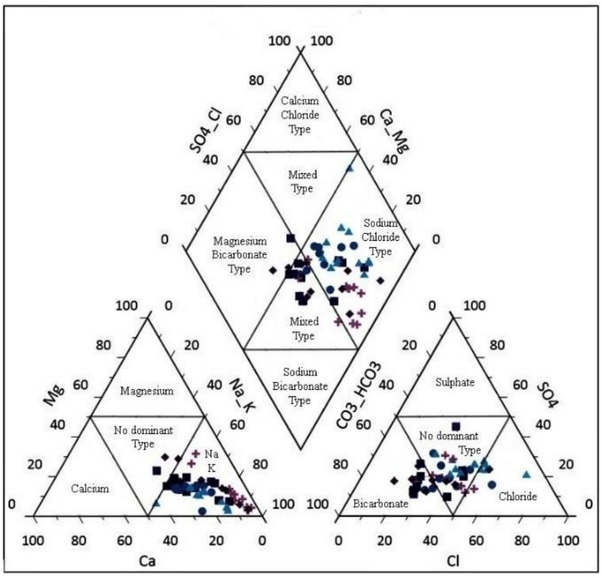

Fig. 3. Piper's diagram for the groundwater from Taluka Bulri Shah Karim.

Groundwater Quality for Drinking Purposes

The 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 puts much water quality data into an aggregate numerical value that can be easily communicated and understood by policymakers and the general public. Based on 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 BSK are depicted in Fig. 4.WQI values ranged from 40.49 to 636.98 (mean 119.37 ± 93.02 SD). Only three samples, that is, samples # 22, 24, and 28, all from village Haji Hussain Dall were classified as excellent. Seven samples from this village were analyzed, of which three were in excellent, three were in good, and one was in poor categories. The groundwater of this village was found to be much better than the other nine villages of BSK. Altogether, the good, poor, and very poor classes were represented by 23 (4.0396%), 21 (39.623%), and four (7.547%) samples, respectively. There were only two samples, #21 from village Haji Urs Sathyo and #52 from village Chodero, which were found unsuitable for drinking. Previous studies from BSK (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 total iron.

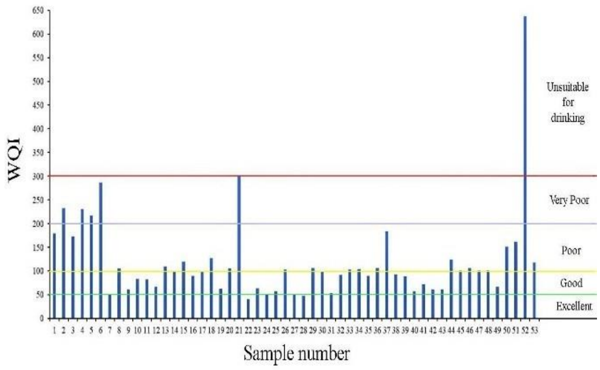

Fig.4. Water quality index (WQI) for the Taluka Bulri Shah Karim groundwater. Samples # 1 to 7 from village Qurban Ali Mallah, 8 to 11 from Shahmeer Khan Lund, 13 to 17 from Luqman Khaskheli, 18 to 21 from Haji Urs Sathyo, 22 to 28 from Haji Hussain Dall, 29 to 33 from Allah Dino Solangi, 34 to 38 from Ali Ghulam Khaskheli, 39 to 43 from Ghulam Hussain Soomro, 44 to 48 from Suleman Soomro, and 49 to 53 from Chodero

Groundwater Quality for Irrigation Purposes

The presence and concentrations of dissolved constituents determine groundwater quality for irrigation purposes. Irrigation water with high salt content increases soil solution osmotic pressure, adversely affecting 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 ranged from 1.70 to 30.20 (mean 8.22 ± 5.96 SD) (Table 6). According to Richards's (1954) classification, there are four categories of groundwater based on SAR values: excellent (<10), good (10 – 18), doubtful (18–26), and unsuitable (>26). Thirty-nine samples of the present study were in the excellent category, whereas 11 were in the good category. The doubtful and unsuitable categories had two and one sample, respectively (Table 3). The only sample (# 37) found unsuitable for irrigation came from the village of Ghulam Khaskheli. High concentrations of Na^+ (1,350 ppm), Cl^- (1,454 ppm), SO_4^{2-}(640 ppm), and F^- (3.16) were found in the sample, and this may be attributed to their unsuitability for irrigation purposes. Previous studies (Merani et al., 2014; Shahab et al., 2019) from BSK have neither reported SAR values of groundwater nor provided concentrations of Na^+, Ca^{2+}, and Mg^{2+}. However, Kandhro et al. (2015), from Nawabshah, which is about 150 Km North of BSK, reported that out of 65 groundwater samples, 40 (61.54%) samples have SAR values < 6, and the remaining 25 (38.46%) samples have SAR values > 6. They concluded that 38.46% of the groundwater samples from Nawabshah are unsuitable for irrigation purposes. However, according to Richards (1954), groundwater having a SAR value >26 (not >6 as mentioned above by Kandhro et al. (2015) is unsuitable for irrigation (see Table 3).

Riverside Method: When the EC and SAR values were plotted on the Riverside diagram (Fig. 5), it emerged that the better class of water quality was C3S1 (average to mediocre), which includes 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 soil with little or no problem of sodium accumulation. The next dominant classes were C4S3 and C4S4, each containing 10 (18.87%) groundwater samples. Class C4S4 and C5S4 contained 11 highly saline groundwater samples that may cause sodium accumulation-related problems.

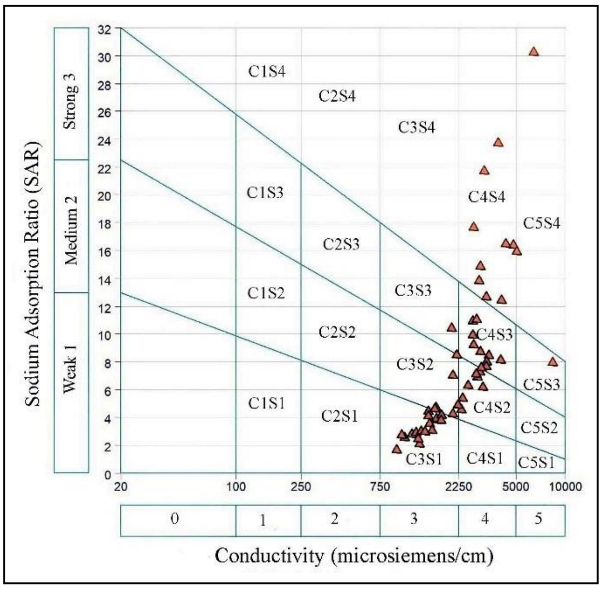

Fig. 5. Riverside diagram showing classification on the basis of sodium adsorption ratio (SAR) and electric conductivity (EC) for the groundwater samples from Taluka Bulri Shah Karim.

Percent of Sodium (%Na): The concentration of Na^+ in irrigation water is one of the important factors as it decreases the permeability of the soil, which changes the soil structure (Todd, 1980; Ehya & Mosleh, 2018). After long-time use, excessive Na^+ in irrigation water hardens the soil's upper layer, preventing 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 5). According to Wilcox's (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 was in the excellent category. Most water samples (37.74%) were in the doubtful category, followed by 35.85% in the permissible category. There were two water samples (3.77%) in the good category and 12 (22.64%) in the unsuitable category. The values of %Na from the groundwater of BSK are reported for the first time. When %Na values were plotted against EC values on Wilcox's diagram (Fig. 6) then, it was revealed that only one sample (# 23) was in the excellent category, 11 samples (# 16, 19, 22, 30, 37, 38, 45, 51 to 54) were in the bad category. The remaining 41 samples were in good, admissible, and mediocre categories.

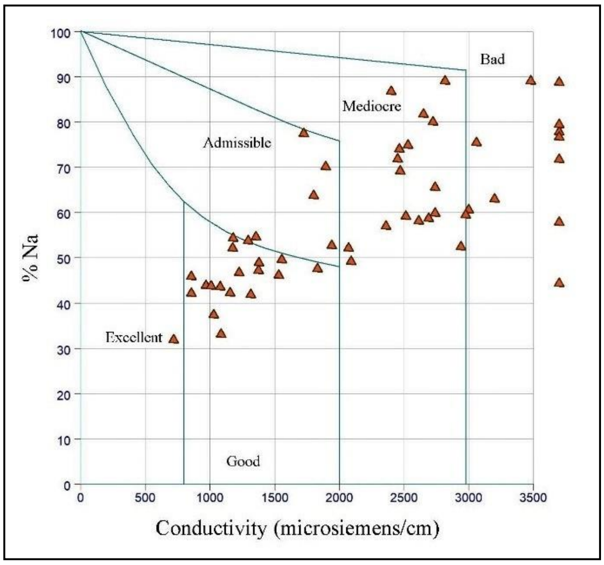

Fig. 6. Wilcox's diagram shows the classification of the groundwater samples from Taluka Bulri Shah Karim based on the percent of sodium (%Na) and electric conductivity (EC).

Permeability Index (PI): After long use, water containing high concentrations of Na^+, Ca^{2+}, Mg^{2+}, and HCO_3^- ions 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's (1962) classification based on PI, there are three categories: excellent (≥ 75), good (25 to 75), and unsuitable (< 25). All the groundwater samples were either in the excellent (19 samples) or 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 the soil's alkalinity hazard. It is used to determine the suitability of groundwater for irrigation purposes. According to Eaton (1950) and Richards1954), the RSC index is classified into three classes: suitable (<1.5 meq/L), marginal (1.25 to 2.5), and unsuitable (>2.5). The present study's results show that the groundwater's RSC values vary from -48.35 to 6.53 (mean -3.12 ± 7.25 SD) (Table 6). Forty-six samples were in the suitable category, whereas two and five were in the marginal and unsuitable categories (Table 3). The unsuitable water samples came from the village Qurban Ali Mallah (sample #4) and Luqman Khaskheli (# 13 to 16).

Conclusion

The results of the groundwater analysis reveal that the dominant cations are Na^+ and Ca^{2+}, while the dominant anions are Cl^- and HCO_3^-. Analyses of the groundwater facies indicate that they are mostly of the 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 acceptable limits in all the groundwater samples. However, the values of some parameters are within or outside the acceptable limits. On average, the groundwater of BSK is acceptable for drinking purposes 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. However, some are highly saline and may need prior treatment. Based on WQI, the quality of groundwater from village Haji Hussain Dall is much better than those taken from the other nine villages of Taluka BSK. Based on the RSC index, the quality of groundwater from the village of Luqman Khaskheli is much poorer and is hardly acceptable for irrigation purposes.

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