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Assessment of Groundwater Quality and Hydrochemistry using Water Quality Index in District Mirpur Khas, Sindh, Pakistan

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Groundwater is a major source of drinking water in the rural areas of Sindh province, including District Mirpur Khas of Pakistan. This study was undertaken to evaluate the suitability of groundwater in Mirpur Khas for drinking purposes. In October and November 2018, the groundwater samples were collected from 50 bore wells and analyzed 17 physico-chemical parameters. The pH ranged from 7.8 to 8.8, indicating the slightly alkaline nature of the water. The mean abundance of major cations is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and for major anions, it is $SO_4^{2-} > Cl^- > HCO_3^- > NO_3^- > F^-$. The hydrochemical facies of groundwater samples show that 29 have a mixed composition, Na^+-K^+-Cl^- characterized by 17 and the remaining 4 fall into the Ca^{2+}-Mg^{2+}-HCO_3^- category. The water quality index (WQI) was calculated based on WHO standards for drinking water using 16 physico-chemical parameters. The computed WQI values range from 20.4 to 503.1. Out of the 50 samples, 9 are classified as 'excellent,' 21 as 'good,' 13 as 'poor,' 4 as 'very poor,' and 3 as 'unsuitable for drinking.' The average WQI value is 118.7 for 50 samples, which falls under the 'good' category. Turbidity and EC exhibited the highest mean effective weight values, indicating their significant influence on the WQI values.

Keywords: Groundwater, Mirpur Khas, Pakistan, Physico-chemical properties, Water quality index.

INTRODUCTION

Pakistan's groundwater resources are in a crisis, grappling with the effects of population growth, industrialization, urbanization and climate change. The alarming decline in per capita water availability from 5,237 m^3 in 1962 to 1,188 m^3 in 2017 [1] underscores the gravity of the situation. Rural areas, heavily reliant on groundwater for domestic use, are particularly at risk from over-abstraction and contamination due to excessive fertilizer use in agriculture. With an annual groundwater extraction of 60 bm^3, Pakistan is the third-largest groundwater user globally [2]. The continuous and excessive extraction, especially with low recharge rates, threatens to deplete and degrade the quality of our groundwater [3].

Groundwater depletion and deterioration are complex issues that require careful monitoring. Groundwater quality is usually assessed by comparing the concentration value of each parameter with its corresponding water quality guideline value. This is done using monitoring data on a parameter-by-parameter basis. If any parameter concentration value exceeds its limit, the water sample is expected to have potential health implications [4]. However, it is important to note that assessing water quality based on individual parameters provides only partial information on the overall quality and fails to indicate any spatial and temporal trends. Additionally, interpreting results from this approach can be challenging, especially when some parameters meet guideline limits while others do not, leading to ambiguity in the overall quality of water. In light of these challenges, modern approaches, such as water quality indices (WQIs), offer a promising solution, providing a comprehensive assessment of water quality and aiding in effective monitoring.

Horton [5] proposed the first WQI for assessing drinking water supply. Later, Brown and his colleagues developed a general WQI to compare the water quality of different water bodies [6]. Since then, various researchers and organizations have developed several methods to calculate the WQI and evaluate the quality of surface water and groundwater for different purposes. These indices differ in how their sub-indices are formulated and in the aggregation process of these sub-indices to compute the final index value [7-9].

In Pakistan's Sindh province, several researchers [10-15] have analyzed the groundwater quality in different cities of Pakistan. However, a thorough examination of the water quality in district Mirpur Khas, the sixth largest district in Sindh province, has not been performed yet. This study mainly aimed to assess groundwater suitability in the Mirpur Khas district for drinking purposes using the WQI approach. The focus was on evaluating the physico-chemical properties of groundwater and identifying the key parameters that affect groundwater quality in the area. By understanding the impact of each water quality parameter on the WQI values, this research will enable water managers and policymakers to make informed decisions about managing the quality of groundwater.

EXPERIMENTAL

Study area: District Mirpur Khas is situated in the south-eastern part of Sindh at coordinates 25º28′46′′N: 69º04′03′′E (Fig. 1). Its total area is 140,914 Km^2 and according to the 2017 census, it had a population of 1.504 million. About 71% of the population lives in rural areas, while 29% lives in urban areas. The climate is subtropical desert, with May being the warmest month with an average temperature of 39.2 ºC and January being the coldest with an average temperature of 20.8 ºC. The average rainfall is 230 mm, which falls during the monsoon season (July to September). The district is known for its fertile land, which produces various crops such as wheat, bananas, mangoes, sugarcane, cotton, onion, chilies, *etc*. It is connected to the Indus River *via* the Let Wah Canal. The district also has sugar and edible oil mills, cotton and fertilizer factories and a donkey-breeding farm.

Sample collection: We collected groundwater samples during October and November 2018 from 50 shallow bore wells in 10 villages. Five samples were taken from each village. These bore wells, ranging in depth from 3 to 12 m (Table-1), were installed at the household level. Water samples were collected directly from the pumps (after removing standing water) in polystyrene bottles that had been soaked in a 10% HNO_3 solution and rinsed with deionized water. Preservatives such as H_3BO_3 (1 M) and HNO_3 (conc.) were used for NO_3-nitrogen and arsenic and iron determination, respectively.

Sample analyses: Electrical conductivity (EC) and total dissolved solids (TDS) were determined using the Eutech meter, while turbidity and pH were measured using HACH meters. For arsenic, a Merck test kit (MQuant 1.17929) was used. All other parameters were analyzed according to the standard methods outlined in APHA (1998) [16]. Ca^{2+} and total hardness (TH) were analyzed volumetrically using the EDTA (0.01M) method. Mg^{2+} concentration was calculated using the formula $Mg^{2+} = (TH - 2.5\ Ca^{2+}) \times 0.243$. Using the argentometric

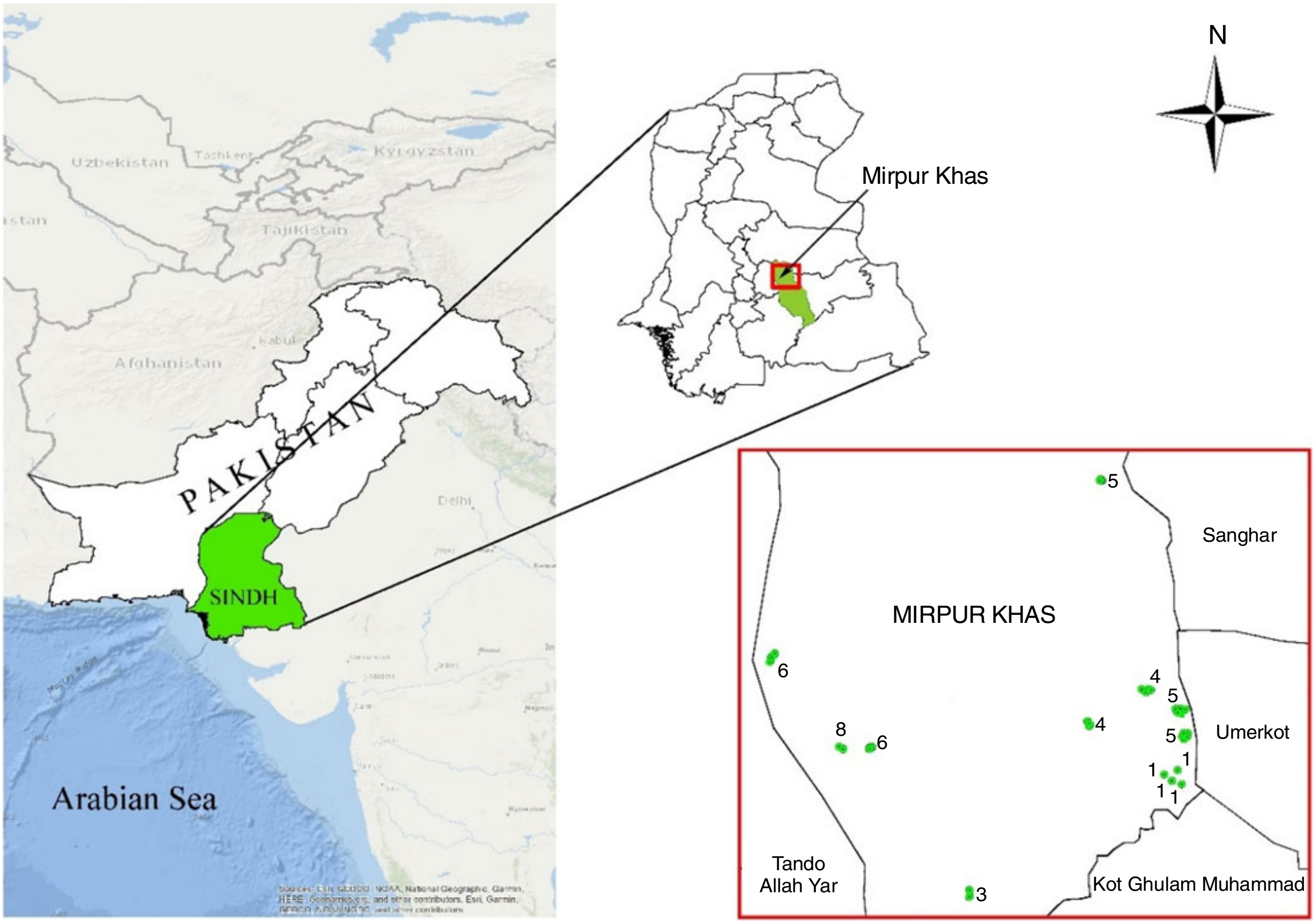

Fig. 1. Map of the studied area: District Mirpur Khas in Sindh province, Pakistan

TABLE-1
NAME OF VILLAGES IN DISTRICT MIRPUR KHAS FROM WHERE GROUNDWATER SAMPLES WERE COLLECTED WITH DEPTH AND COORDINATES OF THE BORE WELLS

Village	Sample ID No.	D.m	Coordinates N:E	Village	Sample ID No.	D.m	Coordinates N:E
Haji Fareed Khan	1	5	25°29.316:69°10.249	Wali Muhammad Rind	26	7	25°28.871:68°57.960
	2	5	25°29.299:69°10.256		27	6	25°28.893:68°57.946
	3	5	25°29.332:69°10.274		28	7	25°28.893:68°57.854
	4	5	25°29.641:69°10.228		29	7	25°28.806:68°57.838
	5	5	25°29.358:69°10.305		30	7	25°28.801:68°57.861
Abdullah Abad	6	11	25°30.931:69°10.939	Hussain Bux Mari	31	5	25°32.494:68°53.908
	7	8	25°30.921:69°10.930		32	12	25°32.422:68°53.904
	8	9	25°30.898:69°10.970		33	8	25°32.275:68°53.847
	9	9	25°30.918:69°11.010		34	6	25°32.594:68°54.047
	10	5	25°30.908:69°11.014		35	6	25°32.646:68°54.048
Rehmat Ali	11	8	25°29.275:69°11.776	Ameer Bux	36	6	25°39.570:69°07.212
	12	5	25°29.071:69°11.475		37	6	25°39.572:69°07.180
	13	8	25°28.811:69°11.336		38	7	25°39.604:69°07.154
	14	8	25°28.983:69°11.459		39	8	25°39.630:69°07.144
	15	5	25°29.104:69°11.577		40	9	25°39.586:69°07.119
Suleman Rajar	16	5	25°31.110:69°08.985	Chaudhry Nizam	41	9	25°22.897:69°01.878
	17	5	25°31.316:69°09.063		42	9	25°22.866:69°01.868
	18	6	25°31.182:69°09.172		43	9	25°22.868:69°01.868
	19	6	25°31.206:69°08.784		44	3	25°23.141:69°01.875
	20	8	25°31.080:69°08.962		45	6	25°23.142:69°01.885
Dost Muhammad Mahar	21	5	25°29.764:69°06.733	Gul Muhammad Rind	46	5	25°28.814:68°56.796
	22	9	25°29.764:69°06.733		47	5	25°28.820:68°56.795
	23	5	25°29.764:69°06.733		48	8	25°28.802:68°56.794
	24	5	25°29.764:69°06.733		49	8	25°28.792:68°56.802
	25	5	25°29.764:69°06.733		50	8	25°28.894:68°56.633

method, Cl^- concentration was determined by titrating against silver nitrate solution (0.014 N). Whereas F^-, SO_4^{2-} and total Fe concentrations were determined using a HACH colorimeter. NO_3^- nitrogen concentration was measured using a UV spectrophotometer at 220-275 nm. Alkalinity was determined by titration with HCl (0.02 N), while Na^+ and K^+ were determined using a flame photometer.

Data analyses: The chemical data was analyzed to calculate the electro-neutrality percentage. The formula for this calculation was (concentration of cations + concentration of anions)/(concentration of cations – concentration of anions) × 100. The ionic balance error value was within the acceptable range of ± 5%, which complies with the standards set by Domenico & Schwartz [17].

To calculate the WQI, we first assigned a weight (wi) from 1 to 5 to each parameter based on its impact on water quality [13]. Each parameter's relative weight (Wi) was calculated using the formula wi/Σwi. Then, the quality rating (Qi) of each parameter was determined by dividing the concentration of the parameter (Ci) by the WHO standard (Si) for that parameter and multiplying the result by 100. 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 × Qi). Finally, we calculated the WQI by adding all the SIi values (WQI = ΣSIi).

The impact of each water quality parameter on the WQI values was also calculated by determining its effective weight. We determined each parameter's effective weight (EWi) by dividing its sub-index value (SIi) by the WQI value of sample. The resulting value was multiplied by 100 [18,19].

RESULTS AND DISCUSSION

Physical parameters: Table-2 displays the physical properties of the groundwater samples that were considered in this investigation. The pH values ranged from 7.8 to 8.8, with a mean of 8.32 ± 0.23, indicating the slightly alkaline nature of the groundwater. The pH of water is a crucial parameter to monitor as it can influence the solubility and toxicity of heavy metals and chemicals. Any significant change in pH value within a relatively short period can indicate the presence of pollutants in water. According to the WHO standards, the desirable pH range is 6.5 to 8.5. Of the 50 water samples analyzed in the study, 42 were within this range, while eight had a pH above 8.5. Several factors, both natural and anthropogenic, can affect the pH levels of groundwater. Natural changes in pH occur mainly due to interactions with surrounding rocks, particularly carbonate forms and other materials. The groundwater flowing through limestone usually has a pH value as high as 8.5, whereas water flowing through sandstone has a pH value between 6.5 and 7.5 [19]. Previous studies conducted in various districts of Sindh province have reported that the pH of groundwater falls within the desirable range of 6.5 to 8.5 [11,13,20,21].

Water turbidity measures light-emitting qualities and waste discharge quality in relation to colloidal particles by measuring the suspended solid matter. Tururbidity levels during this study ranged from 0 to 364 NTU, with an average value of 28.86 ± 66.08. The study revealed that out of 50 samples, 24 samples were above the permissible limit set by the WHO of 5 NTU, while the remaining 26 samples were within the permissible limit. These findings are more or less similar to those of previous

TABLE-2
PHYSICAL PARAMETERS OF GROUNDWATER FROM THE MIRPUR KHAS DISTRICT

Sample ID No.	pH	Turbidity (NTU)	TDS (mg/L)	TH (mg/L)	Alkalinity (mmol/L)	EC (µS/cm)
1	8.5	9.31	740	350	4.2	1157
2	8.4	6.01	397	230	3.2	620
3	8.4	7.80	712	310	4.4	1112
4	8.6	83.8	1212	380	4.6	1894
5	8.6	19.6	433	230	3.6	676
6	8.4	0.32	1196	430	8.0	1868
7	8.3	6.87	1121	450	8.4	1752
8	8.6	1.97	1164	460	6.6	1818
9	8.5	21.1	1103	450	7.2	1724
10	8.7	0.77	1059	480	7.4	1654
11	8.7	34.4	1395	270	8.8	2180
12	8.3	0.76	1907	880	8.0	2980
13	8.5	0.39	1158	350	7.6	1810
14	8.8	3.16	1208	340	8.0	1887
15	8.4	18.1	3526	850	7.6	5510
16	8.8	27.4	262	120	2.0	410
17	8.2	0.47	599	300	5.2	936
18	8.2	0.51	739	330	6.2	1155
19	8.2	11.4	1562	650	6.6	2440
20	8.1	0.69	282	130	2.4	441
21	8.2	9.96	1555	680	6.8	2430
22	8.3	143	1933	650	8.6	3020
23	8.2	238	1843	610	7.8	2880
24	8.3	364	637	270	4.8	996
25	8.3	0.74	490	220	4.0	765
26	8.2	5.50	2054	710	8.2	3210
27	8.1	1.31	1370	570	6.0	2140
28	8.7	111	441	200	3.6	689
29	8.5	0.63	1990	680	8.8	3110
30	8.4	0.92	1453	670	8.2	2270
31	8.2	1.64	1510	660	8.6	2360
32	8.1	ND	7424	2650	5.4	11600
33	8.4	0.37	1683	740	6.6	2630
34	8.3	0.98	650	350	5.2	1015
35	8.3	1.10	719	380	5.4	1123
36	8.1	4.91	1894	780	9.6	2960
37	8.2	1.73	2170	840	7.4	3390
38	8.1	19.9	2822	1070	8.4	4410
39	8.2	0.83	1128	550	6.8	1762
40	7.8	56.6	4013	1360	9.2	6270
41	8.1	18.7	1069	450	6.0	1670
42	8.0	3.26	3053	1080	8.4	4770
43	8.4	0.37	688	310	5.2	1075
44	8.5	0.69	979	370	6.8	1530
45	8.3	0.90	1246	400	6.6	1947
46	8.0	50.5	1754	710	7.6	2740
47	8.3	1.30	1562	680	7.0	2440
48	8.5	14.6	3187	1350	8.2	4980
49	8.2	77.0	1709	930	7.6	2670
50	7.8	ND	4902	1080	8.0	7660
Min.	7.8	0.32	262	120	2.0	410
Max.	8.8	364	7424	2650	9.6	11600
Mean	8.32	28.86	1594.06	599.8	6.62	2490.72
Std. Dev.	0.23	66.08	1277.28	418.88	1.86	1995.81

studies conducted by Merani *et al*. [20] and Arain *et al*. [13] in district BSK in Sindh, where 11 out of 36 and 7 out of 53 groundwater samples, respectively, were found beyond the acceptable limit. The high turbidity levels detected in the groundwater samples may be ascribed to multiple reasons, which can vary considerably between locations. Generally, shallow bore wells exhibit elevated turbidity levels compared to deeper wells; however, this study did not reveal such pattern. The combined effect of surface water and natural geological processes can also result in the turbidity of groundwater.

The TDS values were variable during the present investigation, ranging from 262 to 7,424 mg/L, with a mean value of 1,594.06 ± 1,277.28 (Table-2). According to the WHO, the standard for TDS in drinking water should be less than 1,000 mg/L. However, out of the 50 groundwater samples collected, 35 were found to have TDS values greater than 1,000 mg/L. This indicates that 70% of the samples were saline, while the remaining 30% were classified as freshwater based on the TDS classification by Freeze & Cherry [22]. Comparable results were observed in previous studies conducted by Merani *et al.* [20] and Arain *et al*. [13], who reported that TDS values of 66.7% and 75.7% of groundwater samples from BSK were more than 1,000 mg/L, respectively. Furthermore, Lanjwani *et al*. [11] reported TDS values ranging from 415 to 3,085 mg/L for Larkana groundwater, indicating that the groundwater of Mirpur Khas has a broader range of TDS than Larkana's. It is important to observed that the high TDS values observed in the groundwater samples may affect human health. Therefore, further studies are required to investigate the sources of TDS in the groundwater of Mirpur Khas and to develop appropriate measures to mitigate its harmful effects.

The total hardness of groundwater in Mirpur Khas exhibited a wide range of variability, ranging from 120 to 2,650 mg/L, with a mean value of 599.8 ± 418.88 mg/L (Table-2). According to the WHO standards, the desirable limit of total hardness in drinking water is 500 mg/L. However, the results of present study reveal that nearly half of the water samples, *i.e.* 24 out of 50, had total hardness values exceeding this limit. The groundwater in the study area was classified into four categories based on total hardness, namely soft (< 75 mg/L), moderately hard (75-150 mg/L), hard (150-300 mg/L) and very hard (> 300 mg/L) [23,24]). Of the 50 groundwater samples tested, 41, 7 and 2 were very hard, hard and moderately hard, respectively. Notably, no water sample was found to be in the soft category.

According to Kandhro *et al*. [10], the total hardness groundwater in Nawabshah district, Sindh, ranged from 84 to 1,695 mg/L. Similarly, a study by Arain *et al*. [13] reported that the TH of groundwater in BSK ranged from 180 to 2,650 mg/L. These findings suggest that the groundwater in Mirpur Khas exhibits a higher degree of hardness than that of Nawabshah and BSK. The hardness of water is mainly due to the presence of Mg^{2+} and Ca^{2+}, which are present in sedimentary rocks such as limestone and chalk. While Mg^{2+} and Ca^{2+} are essential for human health, excessive intake may lead to hypermagnesemia and hypercalcemia. The hardness of water also leads to an increase in scale deposition in plumbing and elevated soap consumption during washing.

The alkaline levels in the groundwater samples varied from 2.0 to 9.6 mmol/L, with a mean of 6.62 ± 1.86 (Table-2). The maximum desirable alkaline limit in drinking water is 6.5 mmol/L and 18 of the 50 samples analyzed had alkaline levels below this limit. Previous studies conducted in Sindh province by Lanjwani *et al*. [11] reported the alkaline levels ranging from 100 to 320 ppm (= 2.17 to 6.96 mmol/L) in groundwater from Larkana, with an average value of 200.4 ppm (= 4.44 mmol/L). Arain *et al.* [13] reported alkaline levels ranging from 4.6 to 13 mmol/L in groundwater from BSK. It is widely acknowledged that high alkaline levels in water, often associated with elevated hardness, pH and TDS values, can result in an unpleasant taste. However, it is crucial to understand that high alkaline levels in drinking water, while not harmful to human health, as per a previous study [25], can still pose challenges regarding the taste and acceptability.

The present study reports significant variations in the EC of groundwater samples, with a range of 410 to 11,600 µS/cm and an average value of 2,490.73 ± 1,995.81 µS/cm (Table-2). The desirable limit of EC in drinking water, as per WHO, is 1,500 µS/cm. However, 36 out of 50 samples exceeded this limit during this study. A previous study conducted in BSK [13] reported EC values ranging from 1,060 to 9,630 µS/cm, with an average value of 2,835.5 ± 1527.3 µS/cm. It is established that higher EC values indicate higher concentrations of salts in water, which may depend on factors such as temperature and the type of ions present [26]. The high EC of groundwater may be attributed to anthropogenic activities and geological weathering conditions, which can result in high concentrations of dissolved minerals [27].

Chemical parameters: Table-3 displays the results of the chemical parameters analyzed during the present study. The findings revealed that Na^+ was the most abundant (57.8%) followed by Ca^{2+} (24.8%). These two cations constituted 82.6% of the four major cations present in the groundwater. In terms of anions, SO_4^{2-} (36.3%) and Cl^- (32.5%) were the most common, accounting for 68.8% of the major anions in groundwater. The least common cation and anion were K^+ (2.8%) and F^- (0.1%) (Fig. 2). The major cations and anions concentrations were in the order of $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $SO_4^{2-} > Cl^- > HCO_3^- > NO_3^- > F^-$. The results on the major cations and anions are in agreement with the findings of Lanjwani *et al.* [11] from Larkana, which is about 343 km north of the study site. Kandhro *et al*. [10] also reported the same order of concentrations of cations in the groundwater of Nawab Shah city, located approximately 150 km north of the study area.

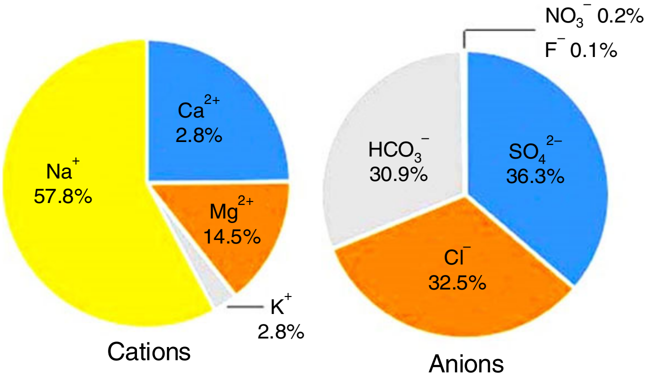

Fig. 2. Percentage composition of cations and anions in the groundwater of District Mirpur Khas

The Na^+ concentration in the groundwater ranged from 34 to 1,420 mg/L with an average of 284.5 ± 273.9. According to WHO standards, the concentration of Na^+ in drinking water should be < 200 mg/L. During this study, 29 samples had > 200 mg/L Na^+, while 21 had Na^+ < 200 mg/L. The presence of

TABLE-3
CHEMICAL PARAMETERS OF GROUNDWATER FROM THE MIRPUR KHAS DISTRICT
ALL QUANTITIES ARE IN mg/L EXCEPT ARSENIC (µg/L). Fe REFERS TO TOTAL IRON

S. No.	Ca^{2+}	K^+	Na^+	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-	HCO_3^-	F^-	Fe	As
1	80	6.4	102	36	95	215	1.23	210	1.34	0.07	0
2	44	3.2	34	29	60	56	1.20	160	0.35	0.04	0
3	68	5.9	107	34	75	216	1.19	220	0.64	0.03	0
4	64	5.5	256	54	160	455	1.56	230	0.73	1.41	0
5	48	4.0	46	27	45	78	1.40	180	1.13	0.09	0
6	60	10	224	68	185	255	1.73	400	0.76	0.02	0
7	64	10.4	188	71	155	216	1.53	420	1.71	0.06	0
8	68	6.4	202	70	195	282	2.01	330	1.66	0.11	5
9	56	7.1	184	75	190	208	3.47	360	1.71	2.62	5
10	64	4.6	152	78	191	167	3.06	370	2.13	0.08	0
11	58	6.4	370	30	255	260	1.23	440	0.44	2.21	0
12	104	38.4	254	151	361	540	3.54	400	0.37	0.06	0
13	56	5.5	248	51	195	234	1.20	380	0.87	0.08	0
14	60	5.6	271	46	215	218	1.21	400	0.76	0.07	0
15	176	210	740	100	910	1020	1.47	380	2.00	0.03	5
16	24	4.2	36	15	45	32	1.45	100	0.66	0.09	0
17	54	6.6	71	40	88	68	2.40	260	0.47	0.04	0
18	60	7.3	108	44	85	116	6.68	310	0.48	0.06	0
19	112	6.2	256	90	190	580	1.31	330	0.90	0.13	0
20	28	3.9	38	15	41	34	1.33	120	0.19	0.02	0
21	128	13.4	234	88	355	345	1.41	340	1.22	0.05	0
22	124	6.3	390	83	335	570	1.84	430	1.32	0.04	0
23	128	6.5	370	70	271	630	1.38	390	1.55	1.97	0
24	40	3.1	102	41	118	78	1.22	240	1.15	1.71	0
25	38	3.1	72	30	85	52	1.31	200	1.95	0.06	0
26	132	8.2	403	92	570	370	1.27	410	0.76	0.03	10
27	108	8.4	224	73	345	265	1.42	300	0.99	0.04	0
28	28	6.5	61	32	68	58	1.11	180	1.45	0.49	0
29	124	9.5	390	90	460	435	1.29	440	1.70	0.05	5
30	36	9.2	206	141	310	260	1.22	410	1.41	0.04	0
31	184	30	220	49	315	274	1.16	430	0.88	0.03	10
32	760	24	1420	182	2630	1680	2.98	270	2.06	5.41	0
33	180	6.8	248	71	230	610	1.08	330	1.02	0.04	5
34	64	5.6	68	46	115	74	1.50	260	1.11	0.07	0
35	78	6.9	74	45	105	122	1.21	270	1.87	0.06	0
36	144	24.2	302	102	385	410	3.62	480	0.97	0.13	5
37	152	10.5	380	112	545	480	6.42	370	0.98	0.09	10
38	220	15.4	510	126	925	440	3.17	420	1.11	0.10	5
39	92	8.2	142	78	221	210	1.54	340	0.69	0.07	0
40	268	33.8	790	168	1277	780	5.60	460	1.37	3.69	0
41	80	8.2	168	61	241	174	2.20	300	1.12	0.37	0
42	172	19.0	570	158	1039	430	1.84	420	1.31	0.05	5
43	68	6.4	98	34	127	84	1.26	260	1.19	0.07	5
44	64	6.2	176	51	210	118	1.37	340	1.16	0.03	0
45	68	5.0	258	56	195	340	1.67	330	1.63	0.04	10
46	160	9.5	296	75	184	680	1.29	380	1.54	0.06	5
47	172	8.5	240	61	304	410	1.42	350	1.38	0.07	0
48	508	17	510	19	319	1540	1.31	410	2.09	0.09	0
49	180	9.2	178	117	370	405	1.35	380	1.50	0.81	5
50	264	13.4	1240	102	1028	1860	1.48	400	1.99	0.51	5
Min.	24	3.1	34	15	41	32	1.08	100	0.19	0.02	0
Max.	760	210	1420	182	2630	1860	6.68	480	2.13	5.41	10
Mean	122.2	11.0	284.5	71.5	348.4	388.7	1.94	330.8	1.19	0.47	2
Std. Dev.	124.0	29.3	273.9	40.4	431.6	396.6	1.29	9.8	0.51	1.04	3.2

Na^+ in groundwater can stem from diverse origins, including the weathering of minerals in the soil, salt-bearing geological formations, salt spray deposition and, in coastal regions, the intrusion of saline ocean water into freshwater aquifers. The present study site is approximately 212 km away from the sea; hence, seawater intrusion is highly unlikely. A high concentration of Na^+ is known to impart an unpleasant taste to the water and make it unfit for drinking [10].

The Ca^{2+} concentration in the groundwater exhibited a range of 24 to 760 mg/L, with an average of 122.2 ± 124 mg/L.

Among the samples, 37 contained Ca^{2+} levels below the WHO standards of 150 mg/L, while 13 exceeded this limit. The Mg^{2+} content varied from 15 to 182 mg/L, averaging 71.5 ± 40.4. 38 samples displayed Mg^{2+} levels lower than the maximum permissible limit of 100 mg/L for drinking water. The primary source of Ca^{2+} and Mg^{2+} in groundwater is the weathering of rocks such as limestone and dolomite, as well as minerals like calcite and magnesite. Groundwater near calcite and magnesite tends to have high mineral content, contributing significantly to water hardness. The presence of hard water can result in adverse effects on skin, hair, household appliances and plumbing systems. However, it is important to note that hard water also contains essential minerals that are advantageous for the human health.

The concentration of K^+ in the groundwater ranged from 3.1 to 210 mg/L, with an average concentration of 11 ± 29.3 mg/L. The WHO has established a maximum permissible limit of 12 mg/L for K^+ in drinking water. Out of the 50 samples analyzed, only 9 surpassed this limit. K^+ can come from human activities such as using K-rich fertilizers, or it can be extracted from rocks that contain K-bearing minerals. Additionally, regions with ancient geological formations that have trapped brine or saline water may also serve as a source of K^+ in groundwater. These potential sources are relevant for the non-coastal environments, like the one in the present study site.

Among the anions, the SO_4^{2-} concentration in the samples ranged from 32 to 1,860 mg/L, with an average of 388.7 ± 396.6. Twenty-eight samples exceeded the maximum permissible limit of 250 mg/L set by WHO. Groundwater can contain SO_4^{2-} from various sources, such as mineral dissolution, atmospheric deposition and human activities like mining and fertilizer use. Gypsum also contributes to high SO_4^{2-} levels in many aquifers worldwide. While SO_4^{2-} is not highly toxic, it can cause diarrhea and dehydration when ingested in large amounts. It can also impact the levels of methemoglobin and sulfhemoglobin in the bodies of humans and animals [28].

The Cl^- levels found in the samples varied from 41 to 2,630 mg/L, with an average value of 348.4 ± 431.6 mg/L. The WHO recommends a maximum permissible limit of 250 mg/L for Cl^- in drinking water. Of the water samples tested, 29 did not exceed this limit. Cl^-in groundwater is sourced from the dissolution of salts, like NaCl, $CaCl_2$ and $MgCl_2$, commonly found in the earth's crust. Groundwater from rainwater usually contains Cl^- levels below 10 mg/L. When Cl^- from chemical fertilizers used in farming or from wastewater discharged onto the land seeps into the groundwater, the Cl^- levels can rise to 20 or 30 mg/L or even higher. While these concentrations are typically too low to affect the taste of the water, they can be detected in groundwater samples and used to identify contamination and provide insights into the potential sources. Common sources of contamination include animal waste, fertilizers and septic systems. For instance, groundwater deterioration due to excessive effluent application or intensive land use will almost always increase Cl^- concentration.

The concentration of NO_3^- in the samples ranged from 1.08 to 6.68 mg/L, with an average of 1.94 ± 1.29 mg/L, indicating that all samples were below the recommended concentration of 10 mg/L. The sources of NO_3^- in groundwater are varied and complex, including septic tanks, animal and human waste and commercial fertilizers. Identifying specific sources can be challenging, but highly contaminated groundwater often has local sources that can be managed. Waters containing more than 50 mg/L of NO_3^- can cause health problems for humans and animals [29].

The HCO_3^- concentration in the samples ranged from 100 to 480 mg/L, averaging 330.8 ± 9.8 mg/L. No specific guideline value has been set for HCO_3^- in drinking water. HCO_3^- could originate from the organic matter in the aquifer, which is oxidized to generate CO_2, which in turn promotes the dissolution of minerals. The fossil carbon of the calcite and dolomite in the aquifer could contribute half of the HCO_3^-. This weathering process enriches the groundwater in Ca^{2+}, Mg^{2+} and HCO_3^-, moreover, HCO_3^- may result from the weathering of silicate minerals [30,31].

The total Fe content ranged from 0.02 to 5.41 mg/L, with an average value of 0.47 ± 1.04 mg/L. Although the permissible limit of total Fe in drinking water is 0.3 mg/L, concentrations as high as 3 mg/L are acceptable [32]. The primary source of iron in groundwater is the weathering of iron-bearing minerals and rocks. The iron levels can also increase due to the ferrous boreholes and hand pump components. A higher concentration of iron in groundwater makes it coloured and taste bad. High iron in drinking water can cause health issues such as diabetes, hemochromatosis, stomach problems and nausea. It can also damage the liver, pancreas and heart [33]. A previous study carried out in BSK, reported iron concentrations in groundwater as high as 3.61 mg/L [13].

Arsenic (As) content was also varied in concentration from 0 to 10 µg/L, with an average value of 2 ± 3.19 µg/L. The safe limit for arsenic in drinking water is < 10 µg/L, indicating that most of the samples studied were within safe limits. However, four samples contained arsenic at the maximum permissible level of 10 µg/L. Arsenic in groundwater has been a growing concern due to its potential toxicity and health risks. Arsenic is considered one of the most toxic metalloids in groundwater due to geological processes and anthropogenic activities [34]. Studies have reported a wide distribution of arsenic in the groundwater of Sindh province and it is estimated that approximately 16 to 36% of the population is exposed to high levels of arsenic due to groundwater use [21]. A previous study has also reported high mortality rates due to the consumption of water that contained high levels of arsenic and other heavy metals [35]. As occurs naturally in sediments and many rocks as a trace element and is released into groundwater from these geological sources. Additionally, arsenic is used in various industrial processes and can be released into groundwater through these activities.

Pearson's correlation coefficient: Pearson's correlation coefficient (r) is the predominant method for quantifying linear correlation. This numerical measure, ranging from -1 to 1, elucidates the strength and direction of the relationship between two variables**.** A correlation coefficient (r) close to +1 or -1 signifies a robust relationship between two variables, while r = 0 denotes no relationship. A correlation with r > 0.7 indicates a strong relationship, r between 0.5 and 0.7 is moderate and r < 0.5 is weak [36,37].

The correlation matrices for physico-chemical parameters of the groundwater of Mirpur Khas were calculated and are presented in Table-4. The pH shows a weak negative correlation with the other 16 parameters. A previous study by Saha *et al.* [38] found similar results for groundwater pH, negatively correlated with Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe, Cl^-, HCO_3^- and SO_4^{2-}. Turbidity also shows a weak negative correlation with all parameters except F^- and Fe. The correlation between Fe and As was also negative, while other parameters were positively correlated.

The strongest correlation (r = 1) was observed between EC - TDS and HCO_3^- - Alkaline. The EC was also strongly correlated (r > 0.7) with Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and total hardness. The Cl^- exhibited a strong positive correlation with cations like Na^+, Ca^{2+} and Mg^{2+}. Similarly, SO_4^{2-} also exhibited a strong positive correlation with Na^+ and Ca^{2+}, whereas strong to moderate correlation was observed among Ca^{2+}, Mg^{2+}, Na^+, Cl^- and SO_4^{2-}, indicating their involvement in various physico-chemical reactions such as oxidation-reduction and ion exchange in the aquifer system [39].

The salinity, expressed as EC, exhibited a moderate to strong positive correlation with salt ions (Cl^-, SO_4^{2-}, Na^+, K^+) and carbonate ions (Ca^{2+}, Mg^{2+}, HCO_3^-), indicating a close relationship between salinity, saliferous and carbonate ions. The molar ratio of carbonates to evaporite components with EC to explore this relationship further. The resulting plot (Fig. 3) revealed that the impact of carbonates and evaporites can be observed in two distinct groups, demonstrating that EC increases with evaporites (Group 2) while maintaining stability with carbonates (Group 1). This observation agrees with a previous study on Algerian groundwater [37].

Groundwater facies: The lithology of aquifers significantly impacts the hydrochemistry of groundwater. Moreover, the groundwater flow behaviour within geological formations is crucial in determining its hydrochemistry [40]. Hydrogeologists commonly employ the Piper trilinear diagram [41] to delineate the groundwater facies and gain insights into the hydrogeological evolution of aquifers [42].

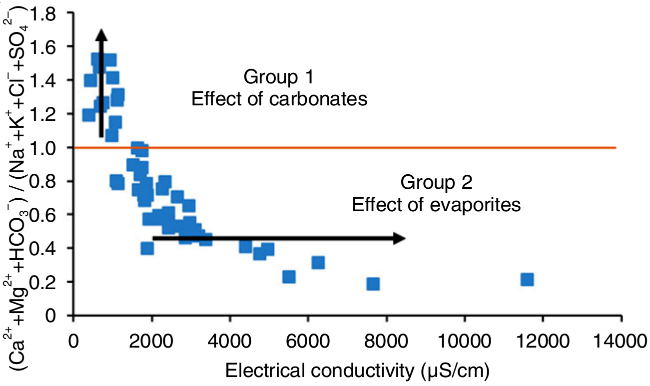

Fig. 3. Plot of $(Ca^{2+} + Mg^{2+} + HCO_3^-)/(Na^+ + K^+ + Cl^- + SO_4^{2-})$ *versus* electrical conductivity (EC)

The analysis position on a Piper diagram provides valuable insights into the composition and origin of water samples. The diagram categorizes water into four main types based on its positioning relative to the four corners of the diamonds. Water samples at the top of the diamond exhibit high levels of Ca^{2+} + Mg^{2+} and Cl^- + SO_4^{2-}, indicating the permanent hardness. Those near the left corner are characterized by elevated Ca^{2+} + Mg^{2+} and HCO_3^- levels, representing water with temporary hardness. Water samples positioned at the lower corner primarily consist of alkali carbonates (Na^+ + K^+ and HCO_3^- + CO_3^{2-}), while samples near the right-hand side may be identified as saline (Na^+ + K^+ and Cl^- + SO_4^{2-}).

The Piper diagram visually represents the hydrogeological characteristics and changes in groundwater composition in the studied area (Fig. 4). The distribution of cations depicted in the diagram indicates no clear dominance in 34 samples. The following combination was Na^+ and K^+, found in 14 samples. In terms of anions, 35 samples showed no dominance, followed by SO_4^{2-} in 6 samples, Cl^- in 5 samples and HCO_3^- in 4 samples. 29 groundwater samples exhibited a mixed composition. 17 samples were characterized by Na^+-K^+-Cl^-, while the remaining

TABLE-4
PEARSON'S CORRELATION MATRIX OF THE ANALYZED GROUNDWATER QUALITY PARAMETERS FROM THE MIRPUR KHAS DISTRICT

	pH	TD	TDS	TH	AK	EC	Ca^{2+}	K^+	Na^+	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-	HCO_3^-	F^-	Fe
TD	-0.04															
TDS	-0.47	-0.07														
TH	-0.48	-0.09	**0.94**													
AK	-0.28	-0.06	0.44	0.43												
EC	-0.47	-0.07	**1.00**	**0.94**	0.44											
Ca^{2+}	-0.36	-0.08	0.89	**0.94**	0.27	0.89										
K^+	-0.07	-0.06	0.36	0.25	0.20	0.36	0.20									
Na^+	-0.44	-0.05	**0.98**	0.86	0.42	**0.98**	0.80	0.36								
Mg^{2+}	-0.52	-0.08	0.73	0.77	0.57	0.73	0.50	0.27	0.65							
Cl^-	-0.46	-0.08	**0.94**	0.91	0.31	**0.94**	0.83	0.33	0.91	0.76						
SO_4^{2-}	-0.38	-0.02	0.89	0.82	0.38	0.89	0.83	0.34	0.89	0.49	0.71					
NO_3^-	-0.30	-0.11	0.24	0.29	0.23	0.24	0.17	0.06	0.20	0.41	0.29	0.09				
HCO_3^-	-0.28	-0.06	0.44	0.43	**1.00**	0.54	0.27	0.20	0.43	0.57	0.31	0.38	0.23			
F^-	-0.06	0.07	0.44	0.42	0.23	0.44	0.42	0.23	0.42	0.25	0.35	0.48	0.08	0.23		
Fe	-0.17	0.31	0.57	0.56	0.06	0.57	0.55	0.02	0.56	0.39	0.65	0.40	0.27	0.06	0.22	
As	-0.24	-0.16	0.21	0.18	0.36	0.21	0.11	0.18	0.21	0.24	0.17	0.16	0.14	0.36	0.14	-0.14

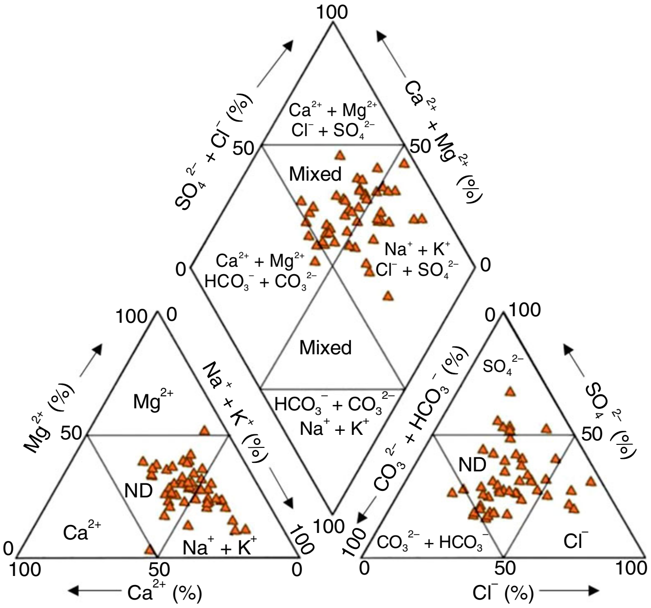

Fig. 4. Piper trilinear diagram showing groundwater types of District Mirpur Khas

4 samples fell into the Ca^{2+}-Mg^{2+}-HCO_3^- category. The presence of the Na^+-K^+-Cl^- facies indicates potential influences such as the dissolution of evaporitic minerals, infiltration of domestic wastewater and possible seawater intrusion, as reported in prior research [42,43]. The Ca^{2+}-Mg^{2+}-HCO_3^-type water is likely attributed to rainfall recharge processes, often associated with low EC values. The presence of Ca^{2+} and Mg^{2+} suggests the potential dissolution of calcium and magnesium carbonate deposits during recharge [44].

Water quality index (WQI): The WQI is a practical and uncomplicated means of evaluating groundwater quality for potable use [25]. As a comprehensive indicator, the WQI amalgamates extensive water quality data into a unified numerical value, enabling straightforward comprehension and communication for policymakers and the general public. Groundwater quality is categorized based on the WQI as follows: excellent (< 50), good (50 to 100), poor (100 to 200), very poor (200 to 300) and unsuitable for drinking (> 300) [13,45]. The WQI values for the 50 groundwater samples from Mirpur Khas are plotted in Fig. 5.

These values range from 20.4 to 503.1, with a mean value of 118.7 ± 97.8, indicating varying water quality levels. Only nine samples were in the excellent category. Out of these, three samples (#17, 18, 20) were from Suleman Rajar village, two each from Haji Fareed Khan (#2, 3) and Hussain Bux Mari (#34, 35) villages, while one sample each was from Dost Muhammad Mahar (#25) and Chaudhry Nizam (#43) villages. Around 21 samples represented good and 13 poor water quality categories. The very poor category contained 4 water samples, whereas 3 samples (2 from Dost Muhammad Mahar village and one from Hussain Bux Mari village) were found unsuitable for drinking. Based on the average WQI values, the water quality of Suleman Rajar village was excellent, while that of Dost Muhammad Mahar village was very poor. Overall, the average water quality of Mirpur Khas district may be classified as good (Table-5).

Table-6 presents the effective weight values for each water quality parameter. Among the parameters considered, turb., EC and F^- exhibited the highest mean effective weight values at 18.13%, 9.98% and 9.87%, respectively, indicating their significant influence on the WQI values of Mirpur Khas's groundwater. Conversely, iron, alkalinity and arsenic had lower mean effective weight values and exerted minimal influence on the WQI.

Conclusion

The study reveals that the mean concentration of major cations in the groundwater samples was $Na^+ > Ca^{2+} > Mg^{2+} > K^+$, whereas the major anions $SO_4^{2-} > Cl^- > HCO_3^- > NO_3^- > F^-$. Among the cations, Na^+ was the dominant and K^+ was the lowest constituent, whereas SO_4^{2-} was the most abundant and F^- was the minor constituent in anions. The salinity, as measured by EC, was positively correlated with salt ions (Na^+, K^+, Cl^- and SO_4^{2-}) and carbonate ions (Ca^{2+}, Mg^{2+} and HCO_3^-), indicating that salinity is closely associated with saliferous and carbonate species. The molar ratio of carbonates to evaporite components with EC revealed that EC increases with evaporites while maintaining stability with carbonates. The WQI values ranged from 20.4 to 503.1, indicating varying water quality

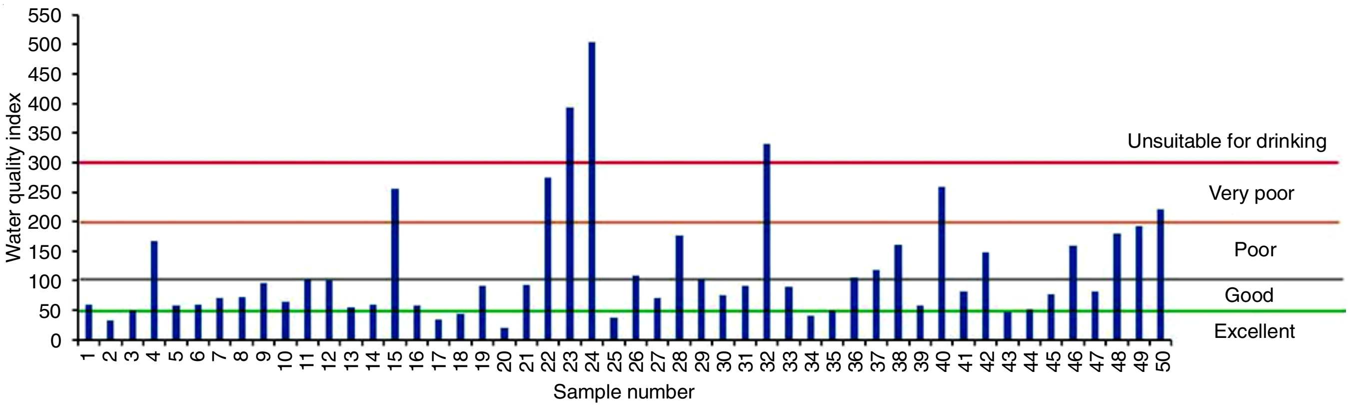

Fig. 5. Water quality indices of 50 groundwater samples collected from Mirpur Khas. Samples number 1 to 5 were collected from the village Haji Fareed Khan Lashari, 6 to 10 from Abdullah Abad, 11 to 15 from Rehmat Ali, 16 to 20 from Suleman Rajar, 21 to 25 from Dost Muhammad Mahar, 26 to 30 from Wali Muhammad Rind, 31 to 35 from Hussain Bux Mari, 36 to 40 from Ameer Bux, 41 to 45 from Chaudhry Nizam and 46 to 50 from Gul Muhammad Rind

TABLE-5
DISTRIBUTION OF WATER QUALITY CATEGORIES IN TEN VILLAGES OF THE MIRPUR KHAS DISTRICT AND THE MEAN WQI FOR EACH VILLAGE

Village	Sample number	Excellent	Good	Poor	Very poor	Unsuitable for drinking	Mean WQI	Category
Haji Fareed Khan	1-5	2	2	1	0	0	73.4	Good
Abdullah Abad	6-10	0	5	0	0	0	72.4	Good
Rehmat Ali	10-15	0	2	2	1	0	114.9	Poor
Suleman Rajar	16-20	3	2	0	0	0	49.4	Excellent
Dost Muhammad Mahar	21-25	1	1	0	1	2	260.2	Very Poor
Wali Muhammad Rind	26-30	0	2	3	0	0	106.9	Poor
Hussain Bux Mari	31-35	2	2	0	0	1	120.9	Poor
Ameer Bux	36-40	0	1	3	1	0	140.2	Poor
Chaudhry Nizam	41-45	1	3	1	0	0	81.5	Good
Gul Muhammad Rind	46-50	0	1	3	1	0	166.9	Poor
Total	1-50	9	21	13	4	3	118.7	Good

TABLE-6
EFFECTIVE WEIGHT (%) VALUES OF EACH WATER QUALITY PARAMETERS FOR THE GROUNDWATER OF THE MIRPUR KHAS DISTRICT

Parameters	Effective weight (%)			
	Min.	Max.	Mean	S.D.
Turbidity (Turb.)	0.000	92.363	18.133	24.580
Electrical conductivity (EC)	0.842	14.867	9.977	3.391
Fluoride (F^-)	1.621	34.700	9.873	6.455
Total dissolved solids (TDS)	0.808	14.272	9.578	3.256
Sulphate (SO_4^{2-})	0.396	21.916	8.421	4.516
pH	1.239	29.886	8.329	5.360
Total hardness (TH)	0.685	12.085	7.693	2.769
Chloride (Cl^-)	0.599	20.224	7.497	4.152
Sodium (Na^+)	0.431	11.936	5.333	2.413
Potassium (K^+)	0.218	29.110	4.383	4.309
Magnesium (Mg^{2+})	0.347	7.963	3.263	1.534
Calcium (Ca^{2+})	0.226	8.033	3.261	1.520
Nitrate (NO_3^-)	0.206	13.091	2.105	2.014
Arsenic (As)	0.000	13.696	2.035	3.615
Alkalinity (Alk.)	0.014	0.211	0.112	0.053
Total iron (Fe)	0.000	0.039	0.004	0.007

levels. Only 18% of the samples were in the excellent category. Most samples represented good (42%) and poor (26%) water quality categories. The very poor category contained 8%, while the unsuitable for drinking category contained 6%. On average, the water quality of Mirpur Khas district was classified as good. Among the parameters considered, turbidity, EC and F^- showed the highest mean effective weight values, indicating their significant influence on the WQI. Piper plot revealed that 58% of water samples were of mixed composition, Na^+-K^+-Cl^- characterized 34%, while 8% were of Ca^{2+}-Mg^{2+}-HCO_3^- type. In conclusion, this research emphasizes the necessity of regularly monitoring groundwater quality to ensure adherence to the WHO standards for potable water. This ongoing surveillance would facilitate the identification of contributors to heightened turb. levels in groundwater, enabling the implementation of targeted mitigation strategies.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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