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Impact of Mineral Processing and other Industries on Groundwater Quality: A Case Study of Baldia Town, Karachi, Pakistan

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Abstract: The aim of the present study is to assess the groundwater quality of western parts of Baldia Town, Karachi, for drinking purpose. For this purpose, groundwater samples (n = 25) were collected from boring wells at various depths (55–250 feet) for physiochemical analysis. Quantitative assessment was carried out including physical (temperature, pH, Eh, TDS, hardness) and chemical parameters (Na+, K+, Ca2+, Mg,2+ Fe2+, Pb2+, Cr5+, Cu2+, Mn2+, Co,2+ Cl-, NO_3-, $SO_4$2-, HCO_3-). Major cations varied in the order of Na+ > Ca2+ > Mg2+ > K+ while anions in the order of Cl- > $SO_4$2- > HCO_3- > NO_3-. The concentration of trace elements declined in the order of Ni2+ > Fe2+ > Cr5+ > Cu2+ > Mn2+ > Pb2+ > Co2+. The analytical results revealed the occurrence of extremely high TDS (Range: 2070 to 6650 mg/l; Mean: 3768 mg/l) and hardness content (Range: 1000 to 3200 mg/l; mean: 1900 mg/l). The pH varied between 6.49 and 7.31 (mean: 6.86), while Eh span between +199 to +473 mV (mean +267 mV). Temperature of the collected groundwater samples was 27±1°C indicating alluvial aquifers. About 52% wells are found to be microbially contaminated. Furthermore, all major ions exceeded the permissible limits set by WHO for drinking water. The mean concentrations of all minor/trace elements were within the permissible limits set by the WHO. The calculated Water Quality Index (WQI = 109) indicated that the groundwater in the study area is unfit for drinking, irrigation, or industrial purposes.

Keywords: Physicochemical parameters, Groundwater quality, Water quality index, Karachi.

Introduction

Water is a fundamental component of the ecosystem and serves as a renewable natural resource vital for the socio-economic development of any nation (Chima et al., 2007). It exists on Earth in the forms of surface water and groundwater (Sarada and Bhushanavathi, 2015). The availability and quality of water have become significant global challenges in recent times, impacting numerous countries worldwide. The quality of water used for domestic and agricultural purposes directly affects human health and livestock. The rapid population growth, urbanization, industrialization, and increased use of chemicals have led to escalating water pollution (Knudsen and Slooff, 1992). Groundwater is commonly utilized globally for domestic consumption, industrial processes, and irrigation (Ramakrishnaiah et al., 2009). Various factors, such as the geological characteristics of an area, geochemical processes, and land use patterns, influence groundwater chemistry (Saha and Kumar, 2006). However, modern agricultural practices, urbanization, and industrialization have contributed to the alarming situation of water pollution, resulting in alterations to the physicochemical properties of water bodies and environmental contamination. Therefore, it is crucial to analyze the quality of the water in order to maintain and improve the natural ecosystem (Dohare et al., 2014).

The escalating pollution of groundwater has become a significant cause for concern due to its increasing use for both human consumption and industrial activities. The World Health Organization (WHO, 1993) has reported that approximately 80% of human diseases are caused by consuming contaminated or toxic water, leading to various waterborne illnesses. Consequently, the establishment of water quality standards is crucial to determining the suitability of groundwater for its intended purposes.

Karachi, the largest and most densely populated city in Pakistan with a population exceeding 30 million, has been grappling with a chronic shortage of municipally supplied water for many decades. As a result, the residents of Karachi have rapidly turned to groundwater as an alternative for drinking and other domestic uses. The focus of present study is the Moach Goth and its surrounding area that is part of Baldia Town (industrial zone housing numerous minerals processing plants and warehouses). Mineral and chemical processing plants in study area consume a significant amount of water (both surface and ground) for mineral processing, leading to the leaching of various elements into the ground resulting in groundwater contamination. This contamination poses a high risk to the surrounding population that can become a prevalent issue, which can cause various ailments among the affected population. Despite such calamitous vulnerability, no comprehensive investigation has been carried out so far to assess the groundwater quality and potential sources of contamination in this industrial part of Karachi. Therefore, the present study is aimed at assessment of groundwater quality using the water quality index (WQI) and statistically analyzing the factors influencing the chemistry of groundwater in the study area using principle component analysis.

Study Area

The study area encompasses Moach Goth, Naval Colony and Gulshan-e-Mazdoor, located in the Baldia Town of the Kemari district, situated in the western part of Karachi, Sindh. Moach Goth primarily serves as a residential area, yet it hosts numerous mineral processing plants and warehouses. Conversely, Gulshan-e-Mazdoor and Naval Colony are entirely residential neighborhoods. The Hub River lies approximately 8 kilometers northwest of the study area. sewage system of Moach Goth is in dire circumstances and getting worsen every day. Pipelines for sewage have been damaged in the study area. Sewage water comes up and spills out in the study area when the drains are clogged. Roads suffer severe damage (cracks or pitting) or are consequently completely washed away. Majority of the paved sections of the roads are washed out as a result of poor maintenance. it becomes more aggravated during the rainy season where huge amount of water is infiltrating through unpaved surfaces and reaches the shallow aquifers.

Material and Methods

Sample Collection

Groundwater samples (25) were collected from boring wells at a depth range of 55-250 feet for physiochemical analysis from study area. The deepest well reached a depth of 250 feet, while the shallowest is occurring at 55 feet. To ensure representative samples, groundwater was electrically pumped for a duration of 2-3 minutes. Plastic bottles with a capacity of 1 liter were utilized for sample collection, while smaller bottles (200 ml) added with boric acid were specifically used for nitrate analysis to prevent further reactions. Prior to collection, the bottles were washed thoroughly and rinsed properly with distilled water, and finally with groundwater from the sampling site. Locations of the boreholes were determined using the Global Positioning System (GPS) and marked on a Google image (Fig.1).

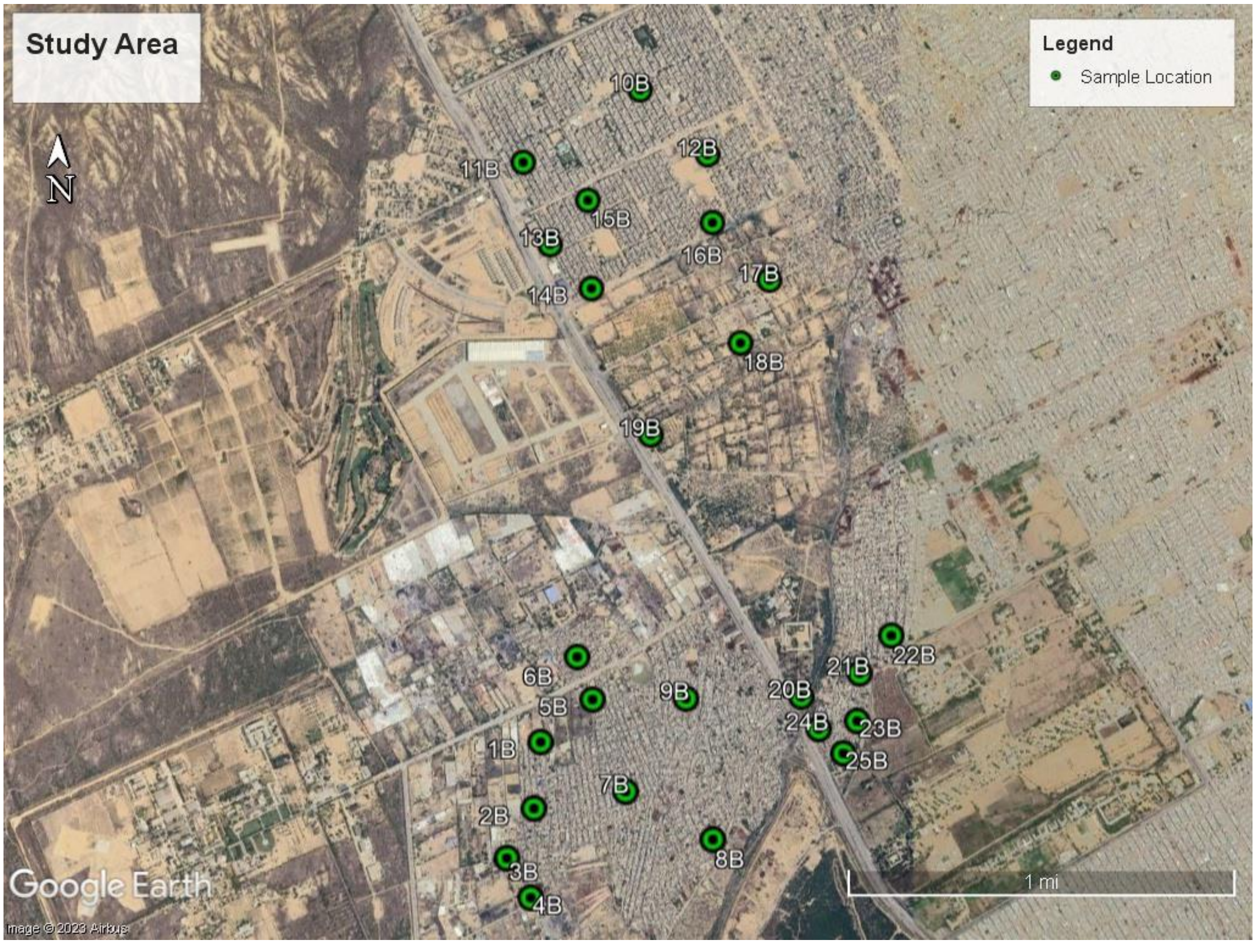

Fig.1: Sample location sites marked on the map of study area.

Groundwater Analysis

All samples were analyzed for physicochemical parameters in the laboratory of Department of Geology, University of Karachi. The pH, EC and total dissolved solids (TDS) of the collected samples were measured using specific instruments: a glass electrode pH meter (ADWA AD 111) for pH measurement and an EC meter (ADWA AD 330) for EC and TDS measurement. Sodium and potassium concentrations were determined using a flame photometer (model: PFP-7, JENWAY, UK). Bicarbonate and chloride ions were measured using argentometric titration. The standard EDTA titration method (1992) was employed to determine calcium and total hardness.

Magnesium content was estimated by calculating the difference between hardness and calcium using a standard formula. The sulfate content was determined through a gravimetric method. Nitrate was measured using the Cadmium Reduction Method (HACH-8171) through a spectrophotometer after groundwater samples were preserved in boric acid to stop any reactions that might have reduced the nitrate content. Furthermore, the analysis of chromium (Cr), cobalt (Co), copper (Cu), manganese (Mn), iron (Fe), and lead (Pb) was carried out using an atomic absorption spectrometer in flame mode (Model No. Analyst 400, Perkin Elmer). Microbial activity was semi/quantitatively analyzed by using a microbial testing kit with color change from transparent to black grading from negative to very high.

Determination of Water Quality Index (WQI)

According to Yisa and Jimoh (2010), the Water Quality Index (WQI) is a highly efficient means of conveying information about water quality to both concerned citizens and policy makers. Weighted arithmetic index method of WQI proposed by Brown et al (1970) was used to evaluate the groundwater quality status of study area. Physicochemical parameters including pH, TDS, hardness and major cations (Na, Ca, Mg, and K) and anions (Cl, HCO_3, SO_4 and NO_3) were used to calculate WQI of groundwater in study area. WQI is calculated by using following formula.

$$WQI=\sum QnWn/ \sum Wn$$

Where, Qn is the quality rating of nth water quality parameter. Wn is the unit weight of nth water quality parameter.

$$Qn=100*[(Vn - Vi) / (Vs- Vi)]$$

Where, Vn is the actual amount of nth parameter present. Vi is the ideal value of the parameter, Vi = 0, except for pH (Vi = 7). Vs is the WHO standard permissible value for the nth water quality parameter.

Unit weight (Wn) is calculated using the formula

$$Wn= k / Vn,$$

Where, k is the constant of proportionality, and it is calculated using the equation

$$K= 1 / \sum Vs= 1, 2, \ldots, n$$

Results and Discussion

Physical Parameters

The field observations indicate that the water samples were colorless. The field tests and lab measurements of pH, TDS, major Cations, major Anions and depth of the water samples, are presented in Table 2. Variations in pH values have an indirect impact on groundwater quality, including the solubility of heavy metal ions and microbial growth (Mohamadi et al., 2011). The pH of collected samples ranges Between 6.49 - 7.31 with a mean of 6.86. Thus, the pH of groundwater is within the WHO permissible range of 6.5 - 8.5. One of the most important factors that can affect a variety of changes in water, including bacterial growth, color, taste, odor, and corrosion issues (Jones et al., 1999; WHO, 2008), is the temperature of the groundwater. Groundwater temperature varied in the range of 26.6-27.6°C mean temperatures of 27.1°C reported in study area. The degree of pollution is indicated by the turbidity of the water (Momba et al., 2006). Water turbidity depends on the suspended load, which includes organic particles, bacterio-plankton units, colloids, air bubbles, and other non-uniformities in the water samples (WHO 2008). Turbidity of collected groundwater samples ranges between 0-1.35 NTU with mean value of 0.45 NTU. All samples were found under permissible limit <5 NTU by WHO (2011). About 52% samples is showing positive response for Microbial Activity.

The TDS content in the collected groundwater samples ranges from 2070 to 6650 mg/l, with an average of 3768 mg/l. All the samples have high TDS content above guideline values set by the Pakistan Environmental Protection Agency (1000 mg/L) and the World Health Organization (500 mg/L) for drinking water. The TDS content is primarily composed of inorganic salts, including bicarbonates, chlorides, and sulphates. The significant variation in TDS levels may be mainly attributed to both human activities and natural geochemical processes (Jeevanandam et al., 2007) that are prevalent in the region.

Table 1. TDS classification of study area groundwater (after Prakash and Soma)

Classification	TDS in mg/l	No. of Samples
Non – saline	< 1000	0
Slightly saline	1000 – 3000	8
Moderately saline	3000 – 10000	17
Very saline	> 10000	0

The redox potential of collected samples varies from +199 to +267 mV with a mean of +473 mV. All samples showed positive Eh suggesting the recent recharge. Extremely variable content of hardness is reported (range: 1000–3200 mg/L, mean: 1900 mg/L). The hardness of all samples in the study area is above the WHO permissible limit (500 mg/L) for drinking purposes. Hard water can cause a variety of health issues, including artery calcification (Saleem et al., 2016).

Chemical Parameters

Major Cations

Sodium has highly variable in concentration (range: 460-1406 mg/l; mean 982 mg/l). All samples have sodium concentration above permissible limit (200 mg/L) prescribed by WHO for drinking purpose. It is observed that all the collected samples are exceeding the safe limit of potassium 12 mg/l, (range: 15-58 mg/l; mean 28 mg/l). According to Sayyed and Bhosle (2011), sewage mixing and agricultural activities seem to be the main causes of the rise in potassium levels in groundwater. Furthermore, because feldspars are more susceptible to weathering and alteration than quartz in silicate rocks, K may have formed from the weathering of feldspar and clay minerals from the aquifer matrix (Kenneth, 2014). Calcium and magnesium contents range between 128-700 and 63-437 mg/l respectively. The mean value of calcium (378 mg/l) is five times the permissible limit of 75 mg/l set by the WHO. Sample 17B is taken from a graveyard and shows the highest concentration (700 mg/l) of Calcium. The mean concentration of Mg (232 mg/l) in the groundwater of the study area is above the WHO permissible limit (150 mg/l). All samples have a higher magnesium concentration than the permissible limit (200 mg/L) prescribed by the WHO, except four samples.

Table 2. Physical characteristics of collected groundwater samples.

Serial No	Well Depth	Microbial Activity	Turbidity	Temperature	Eh	pH	TDS	Hardness
	(m)		(NTU)	(°C)	(mv)		mg/l	mg/l
1B	150	+ve	0.5	27.6	202	6.99	5150	2,800
2B	180	+ve	0.7	27.6	204	6.6	4700	2,600
3B	200	-ve	0.32	27.5	306	6.54	4220	2,200
4B	150	+ve	0.42	27.6	246	6.49	5640	3,000
5B	170	+ve	1.01	27.6	216	6.71	5450	2,600
6B	180	-ve	0	27.5	473	6.76	3830	1,200
7B	150	-ve	0	27.4	326	6.76	4190	2,400
8B	120	-ve	0	27.5	297	7.14	4320	2,200
9B	150	-ve	0	27.5	298	7.04	5490	3,200
10B	200	-ve	0	27.4	278	7.10	3280	1600
11B	250	-ve	0	26.8	292	6.74	2110	1,300
12B	200	-ve	0	26.8	277	6.73	2280	1,000
13B	160	-ve	0	26.9	258	6.91	2560	1,200
14B	200	-ve	0	26.9	254	6.82	3690	1,600
15B	170	+ve	0	26.6	223	7.09	2070	1,000
16B	150	+ve	1.01	26.9	280	6.65	3330	1400
17B	200	+ve	0.65	26.9	246	7.02	6650	3200
18B	230	+ve	1.05	26.7	236	6.54	4640	2,400
19B	200	+ve	1.07	27	207	6.98	2620	1,000
20B	180	+ve	1.03	26.9	220	6.8	2420	1,200
21B	150	+ve	1.35	26.9	209	7.15	3560	2,000
22B	220	+ve	0.99	27	200	6.88	3600	1,800
23B	95	+ve	1.26	27	199	7.31	2350	1,600

Table 2. Continuing

Serial No	Well Depth	Microbial Activity	Turbidity	Temperature	Eh	pH	TDS	Hardness
24B	150	-ve	0	26.9	406	7.15	2700	1,000
25B	55	-ve	0	27	320	6.71	3349	2,000
WHO Limits	-	-	<5 NTU	-	-	**6.5-8.5**	**500**	**500**
Mean	170	-	0.45	27.1	267	6.86	3768	1900
Min	55	-	0	26.6	199	6.49	2070	1000
Max	250	-	1.35	27.6	473	7.31	6650	3200
St dev.	195	-	1.35	1	274	0.82	4580	2200

Major Anions

The concentration of chloride (range 780-4433 mg/L; mean: 2122 mg/L) is highly variable. All collected samples have chloride concentration above WHO standard (250 mg/L) for drinking water. Nitrate concentration ranges between 9.7-98 mg/l with a mean of 45 mg/l. Except two, all collected samples has higher nitrate content as against WHO compliance (10 mg/l). Bicarbonate concentration ranges between 200-580 mg/l with a mean of 393 mg/l. About 90% of total collected samples are unfit for drinking in terms of bicarbonate content as against WHO compliance (300 mg/). The biodegradation of organic matter can cause the release of bicarbonate from the dissolution of carbonate minerals (Jeong, 2001). All of the total collected samples have sulphate content above the permissible limit (250 mg/l). Sulphate concentration shows large deviation (range: 334 – 1026 mg/l; mean: 572 mg/l). Discharge of domestic sewage and industrial waste may be the cause of the high concentration of SO_4^{2-} in ground water (Srivastava et al., 2012).

Table 3. Chemical characteristics of collected groundwater samples

Chemical Parameters															
	Major Cations				Major Anions				Minor/trace elements						
Serial No	Na	K	Ca	Mg	Cl	NO3	HCO3	SO4	Cr	Cu	Co	Mn	Ni	Pb	Fe
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
1B	1,210	27	600	316	3,121	59.82	400	658	0.097	BDL	0.001	0.01	BDL	0.001	BDL
2B	1090	22	580	279	2694.26	49.6	380	667	0.1	BDL	0.002	0.001	BDL	0.003	BDL
3B	1,052	27	500	231	2,482	49.5	420	529	0.111	BDL	0.003	0.001	BDL	0.005	BDL
4B	1,231	40	620	352	3,121	98.1	380	716	0.11	0.099	0.001	0.001	0.625	0.002	0.386
5B	1272	15	560	292	3,262	59.4	400	814	0.111	BDL	0.001	0.002	BDL	BDL	BDL
6B	1053	25	376	63	2,199	32.76	500	463	0.073	BDL	0.001	0.001	BDL	BDL	0.302
7B	1,005	33	400	340	2,447	59.64	380	562	0.074	BDL	0.002	0.001	BDL	BDL	0.135
8B	1,100	27	440	267	2,660	38.76	370	545	0.083	BDL	0.001	0.003	BDL	BDL	0.402
9B	1,232	33	560	437	3,546	49.3	230	673	0.102	BDL	0.002	0.004	BDL	BDL	0.347
10B	960	38	296	209	2,057	9.7	340	490	0.03	BDL	BDL	BDL	BDL	BDL	0.374
11B	890	20	240	170	851	52.92	420	440	0.023	0.019	0.001	BDL	BDL	BDL	0.244
12B	560	26	232	102	1063.8	19.36	400	383	0.017	BDL	BDL	BDL	BDL	BDL	BDL
13B	730	20	216	160	1,348	38.32	420	334	0.002	BDL	BDL	BDL	BDL	BDL	BDL
14B	1,071	28	288	214	2,057	30.64	400	440	0.005	BDL	BDL	BDL	BDL	BDL	BDL
15B	460	16	240	97	780	38.52	380	375	0.007	BDL	BDL	BDL	BDL	BDL	BDL
16B	1048	24	312	151	1737.54	56.82	400	422	0.003	BDL	BDL	0.017	BDL	BDL	BDL
17B	1406	24	700	352	4,433	58.56	200	830	0.094	0.01	0.001	0.001	BDL	BDL	BDL
18B	1,116	20	560	243	2,943	34.72	280	512	0.081	BDL	0.001	0.001	BDL	BDL	BDL
19B	910	58	192	126	1241	32.75	500	512	0.064	BDL	BDL	BDL	BDL	BDL	BDL
20B	785	42	232	151	1,170	9.77	580	358	0.036	BDL	BDL	BDL	BDL	BDL	BDL
21B	1,000	26	312	296	1950.3	35.28	380	841	0.077	BDL	BDL	BDL	BDL	BDL	BDL
22B	1,032	26	320	243	2056.7	35.8	360	614	0.043	BDL	BDL	BDL	0.244	BDL	0.088
23B	550	23	240	243	1028.34	57.12	340	614	0.113	0.011	BDL	BDL	BDL	BDL	BDL

Table 3. Continuing

Chemical Parameters															
	Major Cations				Major Anions				Minor/trace elements						
Serial No	**Na**	**K**	**Ca**	**Mg**	**Cl**	**NO3**	**HCO3**	**SO4**	**Cr**	**Cu**	**Co**	**Mn**	**Ni**	**Pb**	**Fe**
	mg/l	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**
24B	885	24	128	165	1347.5	29.31	460	479	0.06	BDL	BDL	0.071	BDL	BDL	BDL
25B	900	38	304	301	1453.9	88.8	500	1,026	0.1	0.001	BDL	0.047	BDL	BDL	BDL
WHO Limits	**200**	**12**	**75**	**150**	**250**	**10**	**300**	**250**	**0.05**	**2**	**0.05**	**0.1**	**0.07**	**0.01**	**0.3**
Mean	982	28	378	232	2122	45	393	572	0.065	0.028	0.001	0.012	0.435	0.003	0.285
Min	460	15	128	63	780	9.7	200	334	0.002	0.001	0.001	0.001	0.244	0.001	0.088
Max	1406	58	700	437	4433	98.1	580	1026	0.113	0.099	0.003	0.071	0.625	0.005	0.402
St dev.	946	43	572	374	3652	88.4	380	692	0.111	0.098	0.002	0.07	0.381	0.004	0.314

***BDL** = Below Detection Limit

Minor and Trace Elements

The quality and composition of groundwater appears to be dependent on recharge and discharge, but the study area shows recharging of collected groundwater samples from wells that are influenced by human activities and direct inputs from the surrounding environment. The concentrations of Fe^{2+} in collected groundwater samples ranges between 0.088-0.402 mg/L with a mean of 0.285 mg/l. It is observed that, mean iron concentration is within the permissible limit (3 mg/l) set by WHO. The chromium concentration in the collected samples ranged from 0.002 to 0.113 mg/l. The average concentration of chromium was found to be 0.065 mg/l, which is above the permissible limit set by the World Health Organization (WHO). However, it is worth noting that approximately 64% of the collected samples exceeded the prescribed limit of 0.05 mg/l for chromium established by the WHO.

The nickel content in the collected samples ranged from 0.244 to 0.625 mg/l, with an average concentration of 0.435 mg/l. However, all of the samples exceeded the recommended limit set by the World Health Organization (WHO), which is 0.07 mg/l. On the other hand, the copper concentration varied between 0.001 and 0.099 mg/l, with a mean of 0.028 mg/l. Fortunately, all of the samples fell within the permissible limit of 2 mg/l for copper in drinking water, as stated by the WHO.

All of the samples collected were found to have manganese concentrations within the safe limit of 0.1 mg/l. The range of manganese content observed in the samples was 0.001-0.071 mg/l, with an average concentration of 0.012 mg/l. The concentrations of lead and cobalt ranged from 0.001 to 0.005 mg/l and 0.001 to 0.003 mg/l, respectively. The WHO limit for lead is 0.01 mg/l and the limit for cobalt is 0.05 mg/l, and both of these elements are found within these limits.

Water Quality Index of Study Area

The weighted arithmetic index (WQI) method is used to assess the quality of groundwater in study area. This method aims to provide a single value that represents the overall water quality by considering various parameters and their concentrations in a sample. The resulting value offers a comprehensive interpretation of water quality and its suitability for different purposes such as drinking, irrigation, and industrial use (Abbasi and Abbasi, 2012).

To calculate the WQI for groundwater, the first step involves estimating the quality rating (Qn) for each parameter using the formula: Qn = 100 * [(Vn – Vi) / (Vs – Vi)]. A quality rating of Qn = 0 indicates the absence of pollutants, while 0 < Qn < 100 suggests that the pollutants are within the prescribed standards. A Qn value greater than 100 indicates that the pollutants exceed the standards (Gungoa, 2016). In the collected groundwater samples, the quality ratings (Qn) for parameters such as TDS, Hardness, Na, K, Ca, Mg, HCO_3, NO_3, SO_4, and Cl are all above 100, as mentioned in Table 4. This indicates that these components are the main factors contributing to the deterioration of water quality in study area.

The second step is to calculate the unit weight (Wn) for all the physico-chemical parameters using the formula: Wn = k / Vn, as shown in Table 4. The calculated WQI results (Table 4) indicate that the groundwater in study area is unfit for drinking purposes as suggested by Brown et al. (1972). The water quality of the collected samples is bad for drinking, with a WQI value exceeding 100 (WQI = 109). This implies that proper treatment of the groundwater is necessary before it can be used for any purpose.

Table 4. Water Quality Index of collected groundwater samples

	pH	TDS	Hardness	Na	K	Ca	Mg	Cl	NO3	HCO3	SO4
Parameters	**-**	**mg/l**	**mg/l**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
Observed Value (Vn)	6.86	3768	1900	982	28	378	232	2122	45	393	572
WHO Limits (Vs)	8.5	500	500	200	12	75	150	250	10	300	250
Ideal Value (Vi)	7	0	0	0	0	0	0	0	0	0	0
Qn	-9.04	753.6	380	491	234	504	154.7	848.8	450	131	229
Wn=k/Vn	0.427	0.001	0.0015	0.0030	0.104	0.008	0.013	0.0014	0.065	0.0075	0.005
Qn*Wn	3.859	0.586	0.586	1.465	24.417	3.907	1.953	1.172	29.3	0.977	1.172
∑Wn = 0.636 , ∑QnWn = 69.39 ,									**WQI = 109**		

Table 5: WQI range, status and possible usage of the water sample (Brown et al., 1972)

WQI	*Status*	*Possible usages*
0–25	Excellent	Drinking, irrigation and industrial
25–50	Good	Domestic, irrigation and industrial
51–75	Fair	Irrigation and industrial
76–100	Poor	Irrigation
101–150	Very poor	Restricted use for irrigation
Above 150	Unfit for drinking	Proper treatment required before use

In order to understand a regional pattern of water quality deterioration, a WQI map of study area has been constructed (Fig. 2). This WQI map revealed the occurrence of three main categories of WQI classes i.e. a) poor (WQI range: 81-94) b) very poor (WQI range: 95-106) and c) extremely bad (WQI range: 107-119). From WQI map, it can be observed that main part of study area is affected by very poor category of WQI for groundwater. Likewise, extremely bad category of WQI occupies the southern part and couple of pockets in center and northeastern part (Fig. 2). On the other hand, two small pockets of poor category lie on the Northwest and Southeast of study area beside one big pocket on the north. This distribution pattern suggests that water quality is mainly hampered in the southern part that is generally increasing northward.

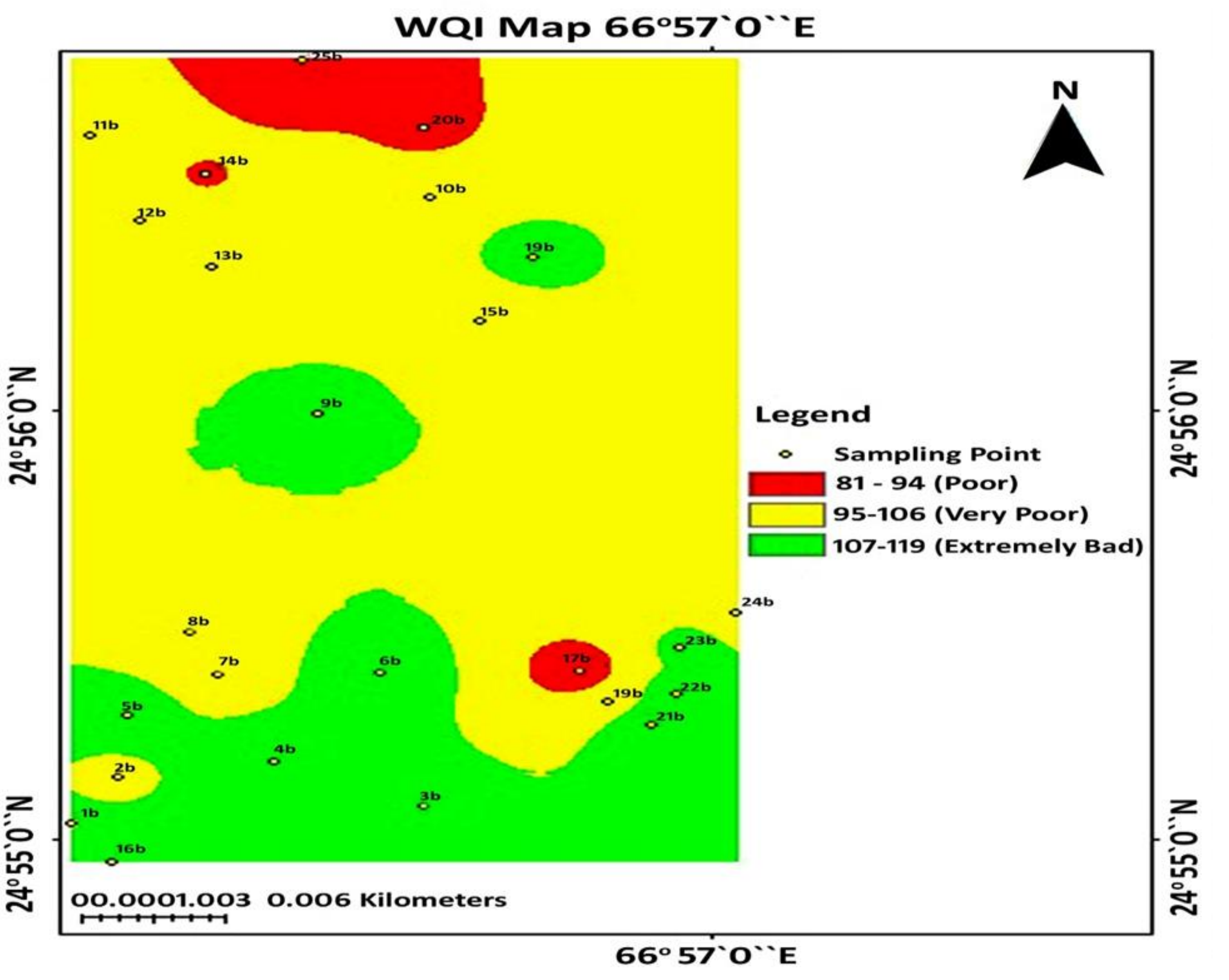

Fig 2: Groundwater water quality index (WQI) of the study area

Ionic Interrelationship

A moderately negative correlation of well depth is observed with NO_3^-(-0.48), SO_4^{2-}(-0.46), and Mn^{2+}(-0.45), suggesting that the reducing condition is increasing with well depth. Microbial/faecal activity is showing a strong positive correlation with turbidity (0.84), Fe^{2+}(0.40) and a strong negative correlation with Eh (-0.72) indicating that microbial activity is increasing with turbidity and Fe^{2+} with decreasing Eh such that no freshwater recharge occurs with appearing anoxic environment. Temperature shows moderate and significant correlations with TDS (0.60), hardness (0.58), Na^+(0.56), Ca^{2+}(0.59), Mg^{2+}(0.48), Cl^-(0.57), Cr^{2+}(0.62), Co^{2+}(0.64), Pb^{2+}(0.48) and Fe^{2+}(0.50) showing chemical reactions with percolating water with rock as water rock interaction with temperature change in shallower wells. Eh(mv) also shows significant correlation with Mn^{2+}(0.45) and Fe^{2+}(0.40) suggesting more infiltration of meteoric water increases dissolution of minerals comprises Fe^{2+} and Mn^{2+} particulates. Similarly, significant correlation exists with pH and Ca^{2+}(0.40), Co^{2+}(-0.41) and Pb^{2+}(-0.47) suggesting anthropogenic environment as warehouses with chemical use leaches into the ground towards selected wells. TDS shows strong to moderate correlation with hardness(0.93), Na^+(0.90), Ca^{2+}(0.95), Mg^{2+}(0.76), Cl^-(0.99), NO_3^-(0.47), negative correlation with HCO_3^-(-0.57), positive with Cr^{5+}(0.65), SO_4^{2-}(0.59) and Co^{2+}(0.59) and Moderate to strong correlation occurs with hardness in relation to Na^+(0.78), Ca^{2+}(0.93), Mg^{2+}(0.92), Cl^-(0.91), NO_3^-(0.57), HCO_3^-(-0.62), Cr^{5+}(0.72), SO_4^{2-}(0.67) and Co^{2+}(0.63) signifying importance of dissolution of minerals, water rock interaction and anthropogenic activities like sewage impact as well as Cr^{5+} deposits infiltrate into available wells. Very strong to moderate correlation occurs with Na^+ and Ca^{2+}(0.80), Mg^{2+}(0.65), Cl^-(0.90), NO_3^-(0.40), Cr^{5+}(0.50), SO_4^{2-}(0.51), Co^{2+}(0.51) and negative with HCO_3^-(-0.40) showing similar rock water interaction. Moderate to significant correlation exists between Ca^{2+} and Mg^{2+}(0.70), Cl^-(0.93), NO_3^-(0.49), negative with HCO_3^-(-0.57), positive with Cr^{5+}(0.66), SO_4^{2-}(0.51), Co^{2+}(0.68) and Pb^{2+}(0.42) exhibiting influence of calcareous rock beds along with release of trace element into the surrounding aquifers that exposed to possible contamination due to geogenic and anthropogenic matter. Moderate to significant correlation occurs between Mg^{2+} and Cl^-(0.74), NO_3^-(0.57), negative with HCO_3^-(-0.58), Cr^{5+}(0.67), SO_4^{2-}(0.73) and Co^{2+}(0.48) similar with correlations of TDS, hardness, Na^+, and Ca^{2+} interpretation for sources. Significant correlation exists between Cl^- and NO_3^-(0.40), negative with HCO_3^-(-0.62) and positive with Cr^{5+}(0.60), SO_4^{2-}(0.51) and Co^{2+}(0.59) which implicitly shows sewage impact (Ali and Adnan, 2021) with release of Cr^{5+}, SO_4^{2-} and Co^{2+} through anthropogenic matter (waste) in the studied environment. Significant correlation also occurs between NO_3^- and Cr^{5+}(0.55), SO_4^{2-}(0.64), Cu^{2+}(0.58) and Ni^{2+}(0.47) implicitly suggests release of such ionic species from geological matter as deposits above and beneath the surface along with Ni^{2+} added from corrosive pipelines (WHO, 2011). Cr^{5+} strongly and moderately correlates with HCO_3^-(0.73), Co^{2+}(0.57) and Pb^{2+}(0.41) where Cr^{5+} and Pb^{2+} may release from anthropogenic sources with few industrial units that uses chrome plating as product through metal usage and tail pipe emitting materials (Kumar et al., 2016; Zhang et al., 2023) while decomposition of organic matter releases HCO_3^- (Ali and Adnan, 2021). Cu^{2+} shows very strong correlation with Ni^{2+}(0.90) and significant correlation with Fe^{2+}(0.42) indicating release from municipal pipelines (WHO, 2011) that may corrode due to salinity and acidic pH in some wells. Co^{2+} moderately correlates with Pb^{2+}(0.68) showing same source origin whilst Ni^{2+} significantly correlates with Fe^{2+}(0.40) that explicitly indicates corrosive pipelines as their sources (WHO, 2011). However, Pb^{2+} could potentially affect nervous system and kidney of individual (Xiao et al., 2019; Li et al., 2023).

Table-6. Correlation matrix of physicochemical parameters

	Well Depth	Microbial Activity	Turbidity	Temp.	Eh	pH	TDS	Hardness	Na	K	Ca	Mg	Cl	NO3	HCO3	Cr	SO4	Cu	Co	Mn	Ni	Pb	Fe
Well Depth	1																						
Microbial Activity	0.06	1																					
Turbidity	0.05	**0.84a**	1																				
Temperature	-0.21	-0.11	-0.13	1																			
Eh	-0.11	-0.72b	-0.63	0.15	1																		
pH	-0.29	-0.01	0.01	-0.18	-0.08	1																	
TDS	-0.02	0.21	0.10	**0.60c**	-0.07	-0.24	1																
Hardness	-0.14	0.21	0.12	**0.58c**	-0.22	-0.19	**0.93a**	1															
Na^+	0.12	0.12	0.12	**0.56c**	0.04	-0.28	**0.90a**	**0.78b**	1														
K^+	-0.11	-0.02	0.06	0.14	-0.03	0.00	-0.06	-0.05	0.05	1													
Ca^{2+}	0.05	0.28	0.12	**0.59c**	-0.16	-0.40c	**0.95a**	**0.93a**	**0.80a**	-0.15	1												
Mg^{2+}	-0.31	0.11	0.10	**0.48c**	-0.24	0.00	**0.76a**	**0.92a**	**0.65b**	0.06	**0.70b**	1											
Cl^-	0.05	0.17	0.09	**0.57c**	-0.06	-0.18	**0.99a**	**0.91a**	**0.90a**	-0.08	**0.93a**	**0.74b**	1										
NO_3^-	-0.48c	0.16	0.01	0.32	-0.04	-0.32	**0.47a**	**0.57c**	0.40c	-0.02	**0.49c**	**0.57c**	0.40c	1									
HCO_3^-	-0.14	-0.13	-0.04	-0.05	0.24	-0.19	-0.57c	-0.62b	-0.40c	0.35	-0.57c	-0.58	-0.62	-0.16	1								

Table-6. Continuing

	Well Depth	Microbial Activity	Turbidity	Temp.	Eh	pH	TDS	Hardness	Na	K	Ca	Mg	Cl	NO3	HCO3	Cr	SO4	Cu	Co	Mn	Ni	Pb	Fe
Cr^{2+}	-0.37	0.20	0.26	0.62c	-0.03	-0.06	0.65b	0.72b	0.50c	0.10	0.66b	0.67b	0.60c	0.55c	-0.23	1							
SO_4^{2-}	-0.46c	0.23	0.25	0.33	-0.16	0.00	0.59c	0.67b	0.51c	0.08	0.51c	0.73b	0.51c	0.64c	-0.26	0.73c	1						
Cu^{2+}	-0.06	0.19	-0.01	0.22	-0.08	-0.31	0.28	0.31	0.20	0.21	0.30	0.27	0.19	0.58c	-0.08	0.24	0.18	1					
Co^{2+}	0.13	-0.18	-0.17	0.64c	0.18	-0.41c	0.59c	0.63b	0.51c	-0.12	0.68b	0.48c	0.59c	0.32	-0.29	0.57c	0.18	0.08	1				
Mn^{2+}	-0.45c	-0.25	-0.23	-0.14	0.45c	0.12	-0.14	-0.16	-0.05	0.02	-0.28	-0.02	-0.18	0.17	0.27	0.07	0.21	-0.09	-0.22	1			
Ni^{2+}	0.00	0.26	0.07	0.24	-0.14	-0.32	0.28	0.29	0.23	0.23	0.27	0.26	0.20	0.47c	-0.06	0.19	0.18	0.90a	0.01	-0.09	1		
Pb^{2+}	0.10	0.02	0.00	0.48c	-0.05	-0.47c	0.28	0.32	0.21	0.00	0.42c	0.17	0.24	0.27	0.03	0.41c	0.09	0.24	0.68b	-0.11	0.23	1	
Fe^{2+}	0.00	-0.39c	-0.44c	0.50c	0.37c	0.05	0.22	0.22	0.28	0.21	0.20	0.22	0.24	0.08	-0.19	0.12	-0.02	0.42c	0.24	-0.19	0.39c	-0.05	1

PCA (Principal component Analysis)

Principal component analysis allowed to have a comparative approach about contaminants (anthropogenic or natural) whether emission sources affecting rainwater (Haider et al., 2022) and inland sources contributing in groundwater contamination (Ali and Adnan, 2021). It comes in one of the source apportionment models to predicts potential pollution sources (Li et al., 2023). PCA determines the possible contaminants along with their sources and here groundwater contamination with relative sources can be visualized within semiarid environment showing that collected samples of groundwater with different physicochemical and trace elements are evenly or closely involved in fluctuating groundwater quality. For further visualization, (Table 7) elaborates principal components and screening of groundwater quality parameters.

Factor 1 explains 36.368% of total variance (Table 7). A strong relationship of TDS (0.942) and hardness (0.969) is clustered with major cations Na^{+} (0.822), Ca^{2+} (0.938), Mg^{2+} (0.849) anions Cl^{-} (0.902), NO_3^{-} (0.632), SO_4^{2-}(0.672). Similarly, the strong association of trace metals like Cr^{5+} (0778), Cu^{2+} (0.416), Co^{2+} (0.674), Ni^{2+} (0.400), Pb^{2+} (0.427) indicates industrial processing impacts. It is consistent with the fact that mineral ware houses and ore processing sites are frequent in study sites. These are expected to contribute major fraction of dissolved trace metals in the groundwater of the study area.

Factor 2 described 13.407% of total variance (Table 7) where sewage impact in terms of fecal bacteria (-0.875) and turbidity (-0.851) due to fecal organics that are controlled by the delicate balance of oxygen and aerobic bacteria. This is consistent with the strong relation with Eh (0.850) and dissolved iron (0.584) (Ferrous).

Factor 3 expresses 10.709% of total variance where well depth (-0.81) strongly influence the redox conditions as indicated by a good negative relationship with NO_3^{-} (0.63), SO_4^{2-} (0.507) and Mn^{2+} (0.607) along with positive relationship with Co^{2+} (-0.400). It means that bacterial respiration increases with depth where main oxidants are nitrate, sulfate and manganese reducing bacteria.

Factor 4 explains 10.039% of total variance where three parameters pH (-0.555), Cu^{2+} (0.723), Ni^{2+} (0.745) are strongly associated. Negative relationship of pH with Cu^{2+} and Ni^{2+} concentration clearly indicate the role of acidity in metal solubilization from host minerals and enrichment in associated groundwater.

Factor 5 only explains 7.542% of total variance. This factor reveals a strong inverse association of Fe^{2+} (-0.603) and Pb^{2+} (0.606). The geochemical behavior of both these ions are strongly influenced by the occurrence of oxidants as seen in (Ali and Adnan, 2021). Both are base metals and chalcophile in nature. The cooccurrence of both in the groundwater is positive in accordance that suggest the same source. However, However, the situation is opposite in the present study. It clearly indicates that the source of both elements is different. It is consistent with the fact that lead based battery manufacturing is quite common in the study area. Hence, lead is incorporated into the groundwater from industrial sites. On the other hand, iron is sourced from natural sediments of aquifers where oxygen is extensively respirated by the bacteria by means of organic matter decomposition (Ali and Adnan, 2021; Haider et al., 2022). It is evident by the positive association of HCO_3^- (0.457) with this factor.

Factor 6 described 5.459% of total variance in which only 3 parameters Temp (0.411), K^+ (0.682), NO_3^- (-0.400) are clustered in this factor but very important to explain water rock interaction which is bacterial mediated. The cooccurrence of K^+ and NO_3^- in inverse relationship suggests that both are from the same source like sewage (Ali and Adnan, 2021). The 2 parameters are strongly controlled by temperature as the bacterial activity is mainly influenced by temperature (Haider et al., 2022). As the groundwater temperature increases, the nitrate content is respirated that the results into decrease in available nitrate. On the other hand, Na^+ and K^+ are the main cation in sewage. Where Na^+ is adsorbed on the sediments due to pH changes. However, potassium remains in the groundwater due to its higher solubility at wide pH ranges (Ali and Adnan, 2021; Haider et al., 2022).

Table 7: Principal components of collected groundwater samples.

Parameters	Principal Component Analysis						
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7
Well depth	-0.122	-0.188	**-0.813**[a]	0.289	-0.069	-0.041	0.270
Microbial	0.220	**-0.875**[a]	0.074	0.207	0.051	0.031	0.062
Turbidity	0.133	**-0.851**[a]	0.069	0.083	0.170	0.226	0.121
Temperature	**0.680**[b]	**0.401**[c]	-0.010	0.074	0.110	**0.411**[c]	-0.149
Eh	-0.135	**0.850**[a]	0.054	-0.146	0.069	-0.103	0.258
pH	-0.284	-0.147	0.230	**-0.555**[c]	**-0.468**[c]	0.269	-0.284
TDS	**0.942**[a]	-0.011	-0.134	-0.130	-0.063	-0.029	0.206
Hardness	**0.969**[a]	-0.069	-0.029	-0.144	-0.064	-0.032	-0.034
Na^+	**0.822**[a]	0.061	-0.162	-0.089	-0.052	0.072	**0.466**[c]
K^+	-0.003	0.083	0.341	0.342	-0.119	**0.682**[b]	0.257
Ca^{2+}	**0.938**[a]	-0.064	-0.237	-0.032	0.040	-0.069	0.034
Mg^{2+}	**0.849**[a]	-0.063	0.194	-0.238	-0.164	0.012	-0.100
Cl^-	**0.902**[a]	-0.006	-0.236	-0.199	-0.113	0.011	0.211
NO_3^-	**0.632**[b]	0.038	**0.514**[c]	0.175	0.125	**-0.400**[c]	-0.121
HCO_3^-	**-0.525**[b]	0.198	0.319	0.347	**0.457**[c]	0.296	0.202
SO_4^{2-}	**0.672**[b]	-0.177	**0.507**[c]	-0.264	0.070	-0.003	0.082
Cr^{5+}	**0.778**[b]	-0.006	0.294	-0.134	0.250	0.224	-0.141
Cu^{2+}	**0.416**[c]	0.059	0.301	**0.723**[b]	-0.299	-0.228	-0.065
Co^{2+}	**0.674**[b]	**0.400**[c]	**-0.400**[c]	-0.007	**0.401**[c]	0.066	-0.229
Mn^{2+}	-0.156	0.298	**0.607**[b]	-0.300	0.242	-0.252	0.345
Ni^{2+}	**0.400**[c]	-0.011	0.271	**0.745**[b]	-0.309	-0.168	0.026
Pb^{2+}	**0.427**[c]	0.154	-0.185	0.359	**0.606**[b]	0.054	-0.309
Fe^{2+}	0.284	**0.584**[c]	-0.047	0.215	**-0.603**[b]	0.213	-0.098
Eigen values	8.365	3.084	2.463	2.309	1.735	1.255	1.007
%Variance	36.368	13.407	10.709	10.039	7.542	5.459	4.378
%Cumulative	36.368	49.774	60.483	70.522	78.064	83.523	87.901

Conclusion

The occurrence of high salinity, hardness, and bacterial contamination is significantly deteriorating the water quality of study area. Most of the physiochemical parameters do not meet the compliance standards set by the World Health Organization (WHO). Moreover, both physicochemical and trace elements are contributing to the deterioration of groundwater quality. The calculated value of WQI falls into unfit category. It is concluded that groundwater of study area is physio-chemically and biologically unfit for drinking purpose. Industrial pollution is also responsible for water chemistry imbalance. This implies that the water is not suitable for drinking, irrigation, or industrial purposes. Proper treatment is necessary before using the groundwater for any intended uses.

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