

# Multidimensional Approach for Groundwater Quality Assessment of Miocene Rocks: A Case Study of Gulistan-e-Johar Area, Karachi, Pakistan

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**Abstract:** The main objective of present study is to evaluate the groundwater quality of Gulistan-e-Johar town for drinking purpose. Groundwater samples (n= 50) were collected from shallow boring wells at various depths (9-15m). The groundwater pH is acidic to basic (range: 6.7-7.8; mean: 7.2) where a large number of samples (80%) are alkaline. Geochemical data revealed that groundwater samples are highly saline (90%) where highly variable TDS content (range: 408-48192ppm; mean: 58192ppm) is reported. Major cation and anion varied in the order of Na (453 mg/l) >Ca (238 mg/l) >Mg (223mg/l) > K (29mg/l) and Cl (1435 mg/l) > SO<sub>4</sub> (1086 mg/l) > HCO<sub>3</sub> (318 mg/l) > NO<sub>3</sub> (17 mg/l) respectively. Na and Ca have more than double the concentration of corresponding WHO guideline values. On the other hand, Mg content is four times higher than its recommended value. Elevated Fe content is also detected about one third in samples (0.1-0.67mg/l). About 60% of collected samples are sewage impacted as indicated by the occurrence of fecal coliforms. Principal component analysis explained five principal components (PCs). PC1 is suggesting rock water interaction and sewage mixing. PC2 shows prevalence of anoxia properties. PC3 indicates strong Fe, Zn and turbidity relation which suggests ion exchange process. PC4 and PC5 have shown strong relation of nitrate with sewage indicating the prevalence of reducing environment. The study has concluded that intense geochemical processes and anthropogenic activities are altering the ground water quality of shallow aquifers in Gulistan-e-Johar area where high salinity and hardness are major menace.

**Keywords:** Groundwater, geochemistry, drinking quality, Gulistan-e-Johar, Karachi.

## **Introduction**

Water is one of the essential components for all forms of plants and animals' life (Vanloon and Duffy, 2005). Hence, daily demand of drinking water of a man is normally 7% of his body weight (Iqbal and Gupta, 2009). In recent decades, studies on groundwater quality have received greater importance because of increasing demand of groundwater in several parts of the world (Vetrimurugan et al., 2013). This demand is increasing due to rapid population, industrialization and excessive fertilizer and pesticides application (Babu et al., 2015). Groundwater can only be used if available in sufficient quantity with acceptable quality (Khattak and Khattak, 2013). Groundwater is safe and clean as compared to surface water and it requires less treatment (Abbas et al., 2015). According to UNESCO (2007) report, 80% of the diseases and deaths are related to water contamination but this water become threat to the continuation of life if it gets polluted with harmful or toxic substance (Abbasi and Vinithan, 1999). These toxic substances exist in water in colloidal, particulate and dissolved phases which can cause serious health effects with their symptoms depending on nature and quality of metal ingested (Alabi, 2005). Similarly, salinization is also reported as the most widespread groundwater issue impacting on the environment and economic of the country (Morries et al., 2003). In coastal region, saline water intrusion due to over pumping and marine aerosols deposited on the soil are the major source of groundwater quality deterioration (Banner et al. 1989; Rosenthal et al., 1992; Vengosh and Rosenthal 1994). Likewise, anthropogenic contamination such as irrigation return flow, industrial chemicals, domestic sewage, septic tank effluent, municipal and animal wastes are other major sources of contamination.

Karachi is the largest and densely populated city of Pakistan where more than thousand industries of various nature and size are operating. These industries are discharging untreated effluents of about 72 million gallon per day into the natural and manmade drainage networks mainly through Malir and Lyari rivers (Siddiqui, et al., 2012). The drinking water in Karachi city was mostly obtained through municipal supply (Zahir et. al., 2009). However, the shortage of water supply in Karachi is increasing day by day which is associated with rapid urbanization, increasing demand of

water for domestic use as well as leakage from pipes and transmission lines. As a result, people living in the city are more depending on the groundwater and switching over to groundwater which are accumulated in the shallow aquifers. These aquifers are recharged seldom by rainfall (Rahman et al., 1997), as the Karachi falls in semi-arid region.

The over exploitation of groundwater depletes water table and accelerates the contamination transfer from surface to aquifer depth (Shah and Roy, 2002). Similarly, domestics and industrial effluent contributes to increase in concentration of different pollutants in groundwater (Raghunath et al., 2002). Heavy dependence on the groundwater abstraction is common in Gulistan- e- Johar area but no work has been carried out so far to assess its quality for drinking purpose. Therefore, present study is aimed at assessing the groundwater quality for domestic use and its potential health risk assessment. The other objective is to find out the sources of contamination through physicochemical and biological signature.

## **Material and Methods**

### **Study area**

Gulistan-e -Johar is one of the recently developed residential and commercial area of Karachi city. Geographically, the study area is located at 24.909722° N to 67.149178° E as shown in (Fig. 1) are Gulistan-e-Johar famous for the largest flat project of the country and covers an area of about 10.84 sq.km in Karachi (Khan & Khan, 2018). Gulistan-e-Johar is surrounded by strategic settlements including Jinnah International Airport, Cantonment and Central Ordinance Depot (COD). Scarcity of municipal water supply is compelling the dwellers of Johar for switching over to groundwater for domestic purpose. The electrically pumped wells have been installed by residents of most of the flat projects to extract the groundwater for domestic use in Johar area.

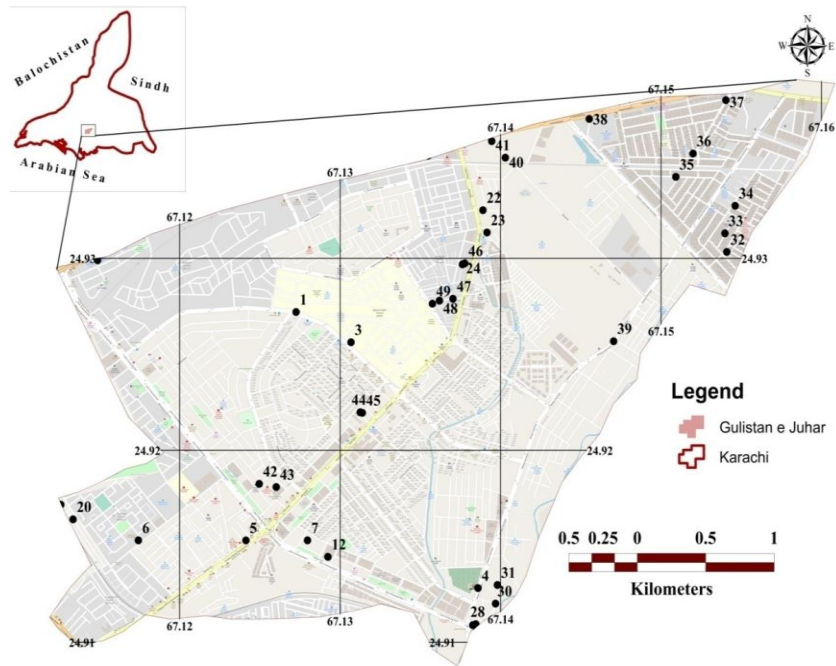


Figure 1 Sample Location map of Gulistan-e-Johar.

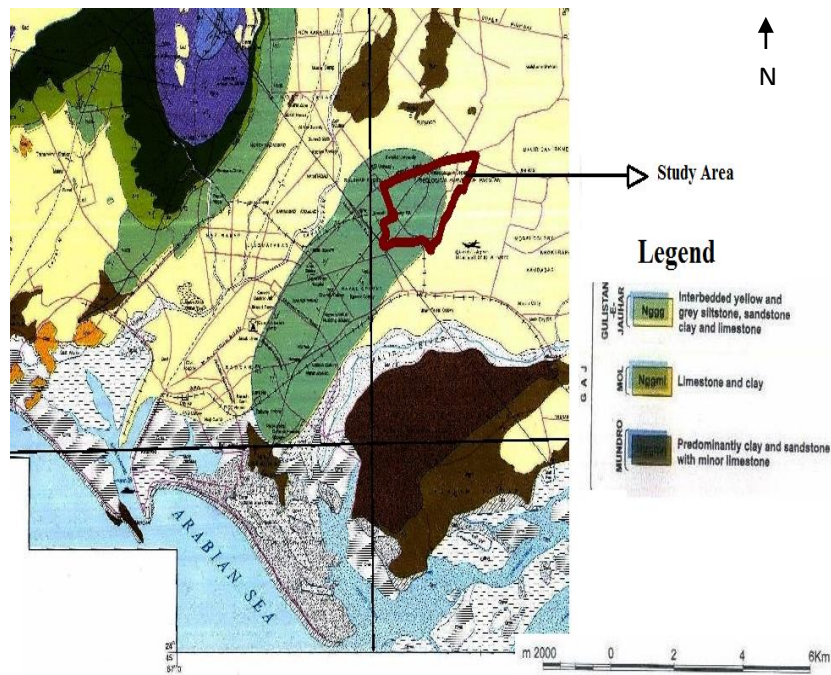


Figure 2 Geological map of study area.

The town comprises hilly region of Karachi district east. Geologically, it is resting on Gaj Formation of Miocene age which in turn is comprised of four members namely Mundro member, Mole member and Gulistan-e-Johar Member (Fig.2). Gulistan e Johar is the youngest member of Gaj Formation which) is spread over in study area (Khan et al., 2018) where it shows siltstone with interbedded shale and subordinate limestone followed by soft to hard sandstone which is highly conductive and transmissive due to the dominance of sandy silt (Pithawala and Martin-Kaye, 1946; Shah, 2009).The study area lies between two ephemeral river streams namely Lyari and Malir rivers. The Malir and Lyari rivers flow from south to east and north respectively.

### **Sampling and Analytical Procedures**

Fifty groundwater samples were randomly collected from shallow boring wells at a depth range of about 9-40m from various points of Gulistan-e-Johar town. Water was electrically pumped to remove standing water in the well column and for 2-3 minutes, to get representative sample. Location of the bore well was taken with the help of global positioning system (GPS) which were plotted on the Google image of study area. Water samples were taken in plastic bottles of 1 liter and 100 ml capacity for physicochemical analysis and nitrate determination respectively. One ml boric acid solution was added in each bottle of 100ml capacity and sample was kept in ice box (temperature: 4°C) to cease any reaction within recommended period. Physical parameters including color, taste, odor, temperature and turbidity were measured immediately after collecting the samples.

The analytical data quality was ensured through careful standardization, procedure measurements. Groundwater samples preserved in the boric acid were analyzed to determine the nitrate concentrations with Cadmium Reduction method (HACH-8171) by Spectrophotometer. Nephelometric method was used to determine turbidity of groundwater samples using turbidity meter (HANNA instruments, model HI 937073-11). The pH and electrical conductivity of collected groundwater samples (n =50) were measured with the glass electrode pH meter (ADWA AD 111) and EC meter (ADWA AD 330) respectively. Hardness was measured in terms of calcium carbonate by

EDTA titration standard method (1992). Magnesium was estimated as the difference between hardness and calcium with the help of standard formula. Soluble  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{HCO}_3$  and  $\text{Cl}^-$  in groundwater samples were measured by titration method. Flame photometer (Model: PFP-7, JENWAY, UK) was used to determine the concentration of  $\text{Na}^+$  and  $\text{K}^+$ . The gravimetric method was used to determine the sulphate concentration. Iron and manganese concentration were measured by Photometric Phenanthroline method using Spectrophotometer (Model: HACH-8171). While the other minor and trace elements were analyzed by atomic absorption spectrometer at flame mode (Model No. Analyst 400, Perkin Elmer). The membrane filtration procedure used for samples that were low in turbidity and had low bacterial counts. Before starting the procedure, all instruments were autoclaves at  $121^\circ\text{C}$ . 1-liter water sample was taken for filtration through a membrane filter paper (47mm).

## Results and Discussion

### *Physical Characteristics*

About 30% samples are yellow in color and 26% percent samples gave bad smell shown in (Table 1). Groundwater temperature is uniform ( $25\text{-}32.6^\circ\text{C}$ ) in all samples. Groundwater pH varied between acidic to basic whereas large number of samples is slightly alkaline (range = $6.7\text{-}7.8$ ; mean: 7.2). Low pH of samples seems to be controlled by geology of the area as rocks hosting these water bodies are mainly comprised of sandstone (Khan & Khan 2018). Turbidity of groundwater is generally within permissible guideline  $< 5$  NTU as assigned by WHO (2000) which widely varies between 0.03-84 NTU. Bacterial occurrence is reported in all these high turbidity samples. About 60 % of the sewage impacted samples have very high concentration of Na, K, Cl, and  $\text{SO}_4$  suggesting that unlined sanitation is responsible for high concentration of these ions (Cole et al., 2005; Husain, 2009; Husain et al., 2012). Highly variable TDS content (range= $408\text{-}8538$  mg/L; mean: 3959 mg/L) occur in the groundwater of study area. All samples have  $\text{TDS} > 500$  mg/l and about one third of total samples show  $\text{TDS} > 1000$  mg/l (Table 1). All the groundwater samples are exceeding the WHO (2011) limit. Similarly, about 84% wells violate the Pakistani guideline value of TDS content (1000 mg/l) for drinking. Such wide

variation in TDS may be related to geochemical processes and anthropogenic activities (Jeevanandam et al., 2007).

### Chemical Parameters

Concentration of sodium (range: 75-2800 mg/L; mean: 1177.66 mg/L) is highly variable in the groundwater of Gulistan-e-Johar town. Except four, all samples show Na concentrations above permissible limits of 200 mg/L for drinking water (Table 2). Amount of potassium in collected samples ranges between 9-68 mg/l with mean of 28.9mg/L. Except 3, all samples are exceeding the safe limit of potassium (Table 2). However, Generally the K content occurs in low concentration in groundwater. In study area under acidic condition causes formation of clay from feldspar decomposition. This clay in turns absorb the K from water. Similarly, high salinity favors the formation of clay minerals (Zhang et al., 2009). Calcium and magnesium contents fluctuate within the range of 36-864 and 17-1081mg/l respectively. The mean concentration of calcium (234 mg/L) in groundwater of Gulistan-e-Johar is double the prescribed limit (100 mg/L) of WHO for drinking purpose (Table 2). Sulphate content is highly variable (Range: 61-1970 mg/L) in the groundwater of Gulistan-e-Johar town. Very high sulfate content (mean: 1138 mg/L) is probably derived from weathering of sulfate and gypsum bearing sedimentary rocks (Elango, et al., 2003; Krishnakumar, S. 2004). Weak but positive correlation of Ca with SO<sub>4</sub> ( $r^2= 0.306$ ) is suggesting gypsum dissolution. Other part is attributed to sewage mixing. Bicarbonate content varies between 70-575 mg/l with mean value of 276 mg/l. Concentration of sodium (range: 75-2800 mg/L; mean: 1177.66 mg/L) and chloride (range: 71-3239 mg/L; mean: 1452 mg/l) are highly variable in the groundwater of study area.

**Table 1** Physical Characteristics of groundwater of Gulistan-e-Johar Town.

Co de	Bloc k	Depth (m)	Well age	Color	Ta ste	Od or	pH	Eh( mv)	EC (µs/c )	TDS (ppm)	Turbi dity (NTU)	Hard ness (mg/l )	Fecal colif orm	Te mp. °C
S1	B-9	9	24 months	Colorless	UO	UO	7.72	96	733	469.1	0	400	-ve	28.8
S2	B-11	31	24 months	Yellow	Bitter	UO	7.19	0	12200	7808	11.16	2930	+ve	28.8
S3	B-11	46	144 months	Colorless	Saline	UO	6.95	106	12800	8192	0.03	3300	-ve	29.7
S4	B-9	86	36 months	Colorless	Bitter	UO	7.41	-63	7520	4812.8	1.58	1480	-ve	32.6
S5	B-10	31	2 years	Colorless	UO	UO	7.39	199	1597	1022.08	0.72	600	-ve	28.8
S6	B-10	49	1 years	Yellow	Saline	UO	7.18	132	4510	2886.4	5.76	1250	+ve	28.3
S7	B-10	46	2 years	Yellow	Bitter	UO	7.54	6	1979	1266.56	9.6	620	+ve	28.5
S8	B-1	37	1 years	Colorless	UO	UO	7.18	119	6170	3948.8	0	2010	+ve	27.5
S9	B-2	31	1 years	Yellow	Bitter	UO	7.45	5	9360	5990.4	27.77	1730	-ve	29.4
S10	B-12	27	3 years	Yellow	Saline	UO	7.44	11	9370	5996.8	6.24	1530	+ve	30.4
S11	B-12	31	7 months	Colorless	Bitter	UO	7.59	137	10760	6886.4	0	1810	-ve	30.6
S12	B-13	61	5 months	Colorless	UO	UO	7.43	-24	8610	5510.4	2.43	1300	-ve	28.5
S13	B-13	46	2 years	Colorless	UO	UO	7.31	-97	7500	4800	1.26	1200	-ve	25
S14	B-11	18	3 years	Colorless	Bitter	smell	6.73	81	19350	12384	0	2500	+ve	28
S15	B-15	37	1 Years	Colorless	UO	smell	6.9	53	3970	2540.8	0	1200	+ve	28
S16	B-15	46	2 years	Colorless	UO	smell	7.25	149	2375	1520	2.3	400	+ve	27.8
S17	B-15	31	15 years	yellow	Saline	UO	7.38	152	13340	8537.6	10.92	3150	-ve	27.9
S18	B-16	51	10 years	Colorless	UO	smell	6.8	103	6375	4080	0	3100	+ve	27.5
S19	B-16	55	3 years	Colorless	Bitter	UO	6.7	106	7359	4709.76	6.23	400	-ve	27.3
S20	B-16	55	-	Yellow	Saline	smell	6.71	37	4797	3070.08	11.67	2200	+ve	30
S21	B-5	31	1 years	yellow	Bitter	UO	7.02	28	7650	4896	0	2300	+ve	31.1
S22	B-5	55	2 years	yellow	Bitter	UO	7.01	-22	8740	5593.6	4.37	2900	+ve	31.3
S23	B-5	25	5 years	yellow	Saline	UO	7.01	-17	9370	5996.8	7.39	2100	+ve	31



Code	Block	Depth (m)	Well age	Color	Taste	Odor	pH	Eh (mv)	EC (µs/cm)	TDS (ppm)	Turbidity (NTU)	Hardness (mg/l)	Fecal coliform	Temp. °C
S24	B-4	61	6 months	yellow	Bitter	UO	7.07	34	8859	5669.76	5.42	1960	-ve	30.5
S25	B-1	37	3 years	Colorless	UO	UO	7	82	8050	5152	0	1750	+ve	30.3
S26	B-9	85	2 months	Colorless	UO	UO	7.04	161	6924	4431.36	25.13	1100	-ve	29.3
S27	B-9	85	10 days	Colorless	Saline	UO	7.29	155	8559	5477.76	84	2200	+ve	29.5
S28	B-9	55	4 months	Colorless	UO	UO	7.19	145	6330	4051.2	2.58	835	-ve	29.7
S29	B-9	37	7 years	Colorless	UO	UO	7.34	157	7920	5068.8	1.28	1010	+ve	29.7
S30	B-9	107	7 months	Colorless	Saline	UO	7.18	138	6529	4178.56	2.12	1300	-ve	29.9
S31	B-9	92	4 months	Colorless	saline	UO	7.18	103	8591	5498.24	0.43	1570	-ve	29.9
S32	B-8	46	2 years	Colorless	Saline	UO	6.84	160	15309	9797.76	0.54	500	+ve	29.8
S33	B-8	46	6 years	Colorless	Saline	UO	7.21	144	9550	6112	0.69	2600	+ve	29.9
S34	B-7	66	2 years	Colorless	Saline	UO	7.18	118	1389	888.96	1.15	335	-ve	29.9
S35	B-7	66	1 years	Colorless	UO	UO	7.01	41	5570	3564.8	1.18	760	+ve	31.2
S36	B-7	49	1 years	Colorless	UO	smell	7.35	113	2840	1817.6	1.21	520	+ve	31.3
S37	B-7	31	-	Colorless	UO	UO	7.76	144	848	542.72	0.59	350	+ve	31.2
S38	B-7	46	8 months	Colorless	Saline	UO	7.34	110	5670	3628.8	5.67	810	+ve	31.2
S39	B-9	46	7 months	Colorless	UO	UO	7.38	124	5920	3788.8	1.34	900	+ve	30.4
S40	B-4	21	5 years	Colorless	UO	smell	7.08	116	3520	2252.8	2.11	950	+ve	29.7
S41	B-4	12	18 years	Colorless	UO	smell	7.05	103	1538	984.32	1.2	430	+ve	29.8
S42	B-15	54	4 years	Colorless	UO	UO	7.85	186	638	408.32	0.42	315	-ve	27.7
S43	B-15	64	3 years	Colorless	UO	UO	7.34	159	16040	10265.6	0	1790	-ve	27.6
S44	B-14	55	10 days	Yellow	Bitter	smell	7.23	-70	16790	10745.6	74	1720	+ve	27.7
S45	B-14	49	6 months	Yellow	Bitter	smell	7.41	128	18530	11859.2	46.43	1560	+ve	27.7
S46	B-4	46	1 years	yellow	Saline	smell	7.41	22	16460	10534.4	16.27	2500	+ve	27.8
S47	B-4	21	4 years	Colorless	UO	UO	6.91	69	9440	6041.6	0	2500	-ve	27.9

Co de	Bloc k	Depth (m)	Well age	Colo r	Ta ste	Od or	pH	Eh( mv)	EC (µs/c )	TDS (ppm)	Turbi dity (NTU)	Hard ness (mg/l )	Fecal colif orm	Te mp. °C
S4 8	B-4	38	2 years	Colorl ess	Sali ne	sme ll	7.14	15	75300	48192	0	1350	+ve	25.8
S4 9	B-4	21	3 years	Yello w	Sali ne	sme ll	7.1	11	3780	2419.2	26.72	5650	+ve	26.2
S5 0	B-7	21	3 years	Colorl ess	UO	UO	7.56	25	5150	3296	4.5	560	-ve	32.6
W HO li mi t	-----		-----	Color less	UO	UO	6.5-8.5	----	-----	500	0	500	-----	-----
Me an	-	45	-	30%	56 %	26 %	7.2	79.8	9049.58	5791.7	8.2	1565	-	29.22
Ma x	-	109	-	-	-	-	7.9	199	75300	48192	84	5650		32.6
Mi n	-	7	-	-	-	-	6.7	-96	638	408	0	315		25

Table 2 Major, minor and trace elements determined in the groundwater of study area.

Sample Code	Major Cations				Major Anions				Trace element						
	Ca	Na	K	Mg	SO4	HCO3	NO <sub>3</sub>	Cl	Cu	Ni	Fe	Zn	Mn	Cr	Co mg/l
GJ1	44	98	40	71	61	100	0.29	95	BDL	0.005	0.01	0.004	BDL	BDL	BDL
GJ2	556	2800	38	374	1820	225	1.21	1418	0.002	0.004	0.233	BDL	BDL	BDL	BDL
GJ3	864	2550	40	277	1870	175	29.5	1182	BDL	0.004	0.13	BDL	BDL	BDL	BDL
GJ4	200	2000	27	238	920	225	-0.05	1005	BDL	0.005	0.119	0.002	BDL	BDL	BDL
GJ5	104	200	26	83	182	190	4.36	236	BDL	0.003	0.02	BDL	BDL	BDL	BDL
GJ6	176	950	19	197	650	216	3.55	603	BDL	BDL	0.1	BDL	BDL	BDL	BDL
GJ7	64	330	13	112	240	200	1.37	768	BDL	BDL	0.113	BDL	BDL	BDL	BDL
GJ8	440	1050	49	221	1920	165	4.17	650	BDL	BDL	BDL	BDL	BDL	BDL	BDL
GJ9	336	1950	38	216	1940	190	2.89	1064	BDL	BDL	0.614	BDL	BDL	BDL	BDL
GJ10	220	2800	38	238	1880	160	1.05	1028	BDL	BDL	0.258	0.082	BDL	BDL	BDL
GJ11	344	2350	31	231	1760	240	0.79	1277	BDL	0.001	BDL	0.002	BDL	BDL	BDL
GJ12	232	2540	29	175	900	250	0.68	3073	BDL	BDL	0.124	0.001	BDL	BDL	BDL
GJ13	160	478	28	194	1300	300	1.39	709	BDL	0.001	0.109	0.001	BDL	BDL	BDL
GJ14	840	1680	68	97	1840	410	36.56	2009	BDL	0.003	BDL	0.002	BDL	BDL	BDL
GJ15	68	380	17	250	620	295	4.92	697	BDL	BDL	BDL	0.001	0.012	BDL	BDL
GJ16	82	695	9	47	395	360	17.58	426	BDL	0.003	0.514	0.076	BDL	BDL	BDL
GJ17	64	986	26	722	1570	380	119.79	2385	BDL	0.004	0.329	0.041	BDL	0.139	BDL
GJ18	86	545	37	701	1210	275	44.4	3239	0.002	BDL	BDL	0.014	BDL	0.155	BDL
GJ19	132	950	23	17	1870	300	14.48	2837	BDL	BDL	0.05	0.082	0.13	0.165	BDL

GJ20	68	375	28	493	1340	430	1.76	2606	BDL	0.019	0.401	0.105	0.424	0.0149	0.016
GJ21	360	1140	28	340	1280	395	0.72	2246	BDL	BDL	BDL	0.008	0.124	BDL	BDL
GJ22	400	1360	27	462	1310	280	-0.11	2837	BDL	BDL	0.113	0.002	0.065	BDL	BDL
GJ23	320	1480	27	316	870	295	0.05	3073	BDL	BDL	0.023	0.004	0.076	0.055	BDL
GJ24	360	1260	29	258	1368	245	-0.014	2955	BDL	BDL	0.27	0.006	0.062	0.079	BDL
GJ25	62	1240	31	388	1360	310	20.82	2329	BDL	BDL	BDL	0.006	BDL	BDL	BDL
GJ26	138	1240	33	184	1172	445	28	2128	BDL	BDL	0.029	0.033	BDL	BDL	BDL
GJ27	80	1750	33	486	1325	390	40.3	1466	BDL	BDL	0.075	0.046	BDL	0.035	BDL
GJ28	120	1200	26	130	1180	430	40	1761	BDL	0.004	BDL	0.009	BDL	0.034	BDL
GJ29	96	1640	31	187	1244	500	29.88	2482	BDL	BDL	BDL	0.01	BDL	0.02	BDL
GJ30	240	1130	26	170	816	305	1.64	2246	BDL	BDL	0.055	0.004	0.029	BDL	BDL
GJ31	360	1600	32	163	1274	370	1.02	1832	BDL	BDL	BDL	0.002	BDL	0.047	BDL
GJ32	108	2340	40	56	1638	525	32.1	3191	BDL	BDL	BDL	0.058	0.004	0.089	BDL
GJ33	96	2052	34	573	956	560	34.12	1738	BDL	0.003	BDL	0.027	0.007	0.022	BDL
GJ34	100	440	24	21	138	245	0.37	402	BDL	BDL	BDL	0.003	BDL	BDL	BDL
GJ35	160	1000	21	87	770	575	0.35	851	BDL	BDL	BDL	0.004	BDL	BDL	BDL
GJ36	80	415	17	78	381	470	0.92	1206	BDL	BDL	BDL	BDL	BDL	BDL	0.013
GJ37	60	100	15	49	90	290	1.35	236	BDL	BDL	BDL	0.197	BDL	BDL	BDL
GJ38	111	1042	22	129	564	305	8.56	1135	BDL	BDL	BDL	0.019	BDL	BDL	0.005
GJ39	120	1043	23	146	1070	386	33.63	1736	BDL	0.002	BDL	0.008	BDL	BDL	0.001
GJ40	201	480	17	109	424	365	4.01	1064	BDL	BDL	BDL	0.005	BDL	BDL	0.002
GJ41	87	240	25	52	160	385	3.7	335	BDL	BDL	0.172	0.019	0.005	BDL	BDL
GJ42	36	75	9	55	883	70	0.5	319	BDL	BDL	BDL	BDL	0.008	BDL	BDL
GJ43	350	1004	39	222	1776	280	6.38	1631	BDL	BDL	0.03	0.01	0.016	BDL	BDL
GJ44	290	1640	45	242	1970	405	6.05	1560	BDL	BDL	2.321	BDL	0.014	BDL	BDL
GJ45	286	1360	35	205	1961	415	1.21	1844	BDL	BDL	2.233	0.111	0.024	BDL	BDL
GJ46	640	430	40	219	1046	445	0.1	319	BDL	BDL	0.393	0.02	0.019	BDL	BDL
GJ47	440	410	36	340	1743	360	9.33	70.92	BDL	BDL	0.046	0.01	0.004	BDL	BDL
GJ48	400	2420	19	85	1950	400	3.63	600	BDL	BDL	BDL	BDL	BDL	BDL	BDL
GJ49	480	695	26	1081	1306	350	2.46	557	BDL	BDL	0.052	0.015	0.077	BDL	BDL
GJ50	55	950	11	75	585	410	1.428	1140	BDL	BDL	0.21	0.002	0.007	BDL	BDL
<b>WHO limit</b>	<b>75</b>	<b>200</b>	<b>30</b>	<b>150</b>	<b>250</b>	<b>300</b>	<b>10</b>	<b>250</b>	<b>0.05</b>	<b>0.02</b>	<b>0.3</b>	<b>0.005</b>	<b>0.05</b>	<b>0.01</b>	<b>0.05</b>
Mean	234	1178	29	237	1138	326	11	1459	0.002	0.019	2.321	0.197	0.42	0.17	0.016
Mini	36	75	9	17	61	70	0.1	71	0.002	0.001	0.01	0.001	0.004	0.015	0.001
Max	864	2800	68	1081	1970	575	120	3239	0.002	0.005	0.370	0.031	0.073	0.07	0.008
SD	196	762	11	205	589	114	8.3	935	0	0.009	0.977	0.084	0.175	0.076	0.008

**Quality of Groundwater based on Chloride**

To assess the groundwater quality based on Chloride, and according to Stufzand (1989) classification is widely followed and has been classified into 8 main types as given below:

**Table 3** shows Stufzand (1989) classification based on Chloride.

Chloride Type	Cl Concentration Range in mg/l	Number of Samples
Extremely fresh	<0.141	Nil
Very fresh	0.141-0.846	Nil
Fresh	0.846-4.321	Nil
Fresh brackish	4.321-8.462	Nil
Brackish –salt	28.206-282.064	11
Salt	282.064-564.127	09
Hyper-saline	>564.127	30

It is observed that most of the samples were fell into brackish salt to Hyper-saline category. The brackish-salt water type found in many locations and it could be with saline water. Hence, the water in the study area have infiltrated from recent precipitation as well as sewage impact.

**Ionic Relationship**

A strong correlation of TDS and EC is found with Na and SO<sub>4</sub> (Table 4) which shows higher concentration of these ions is responsible for high salinity in groundwater. Moderate correlation of SO<sub>4</sub> (r=0.6) with K & Na there is weathering of clay minerals with leaching of evaporate sediments rich in gypsiferous shale is present (Raup, 1966). High concentration of Cation and anions are indicating the temporary and permanent hardness in the groundwater of Johar town. As well as strong correlation of Mg (r=0.9), Ca (r=0.6) with of SO<sub>4</sub> (r=0.5) and hardness reveal that increasing concentration of hardness in groundwater is due to mainly Mg with Ca. The Mg sources in groundwater of study area may attributed to multiple sources including mica rich shale and sandstone (Tiwari et al 2013) ion exchange process and dissolution of limestone of Gaj Formation (Hem, 1985).

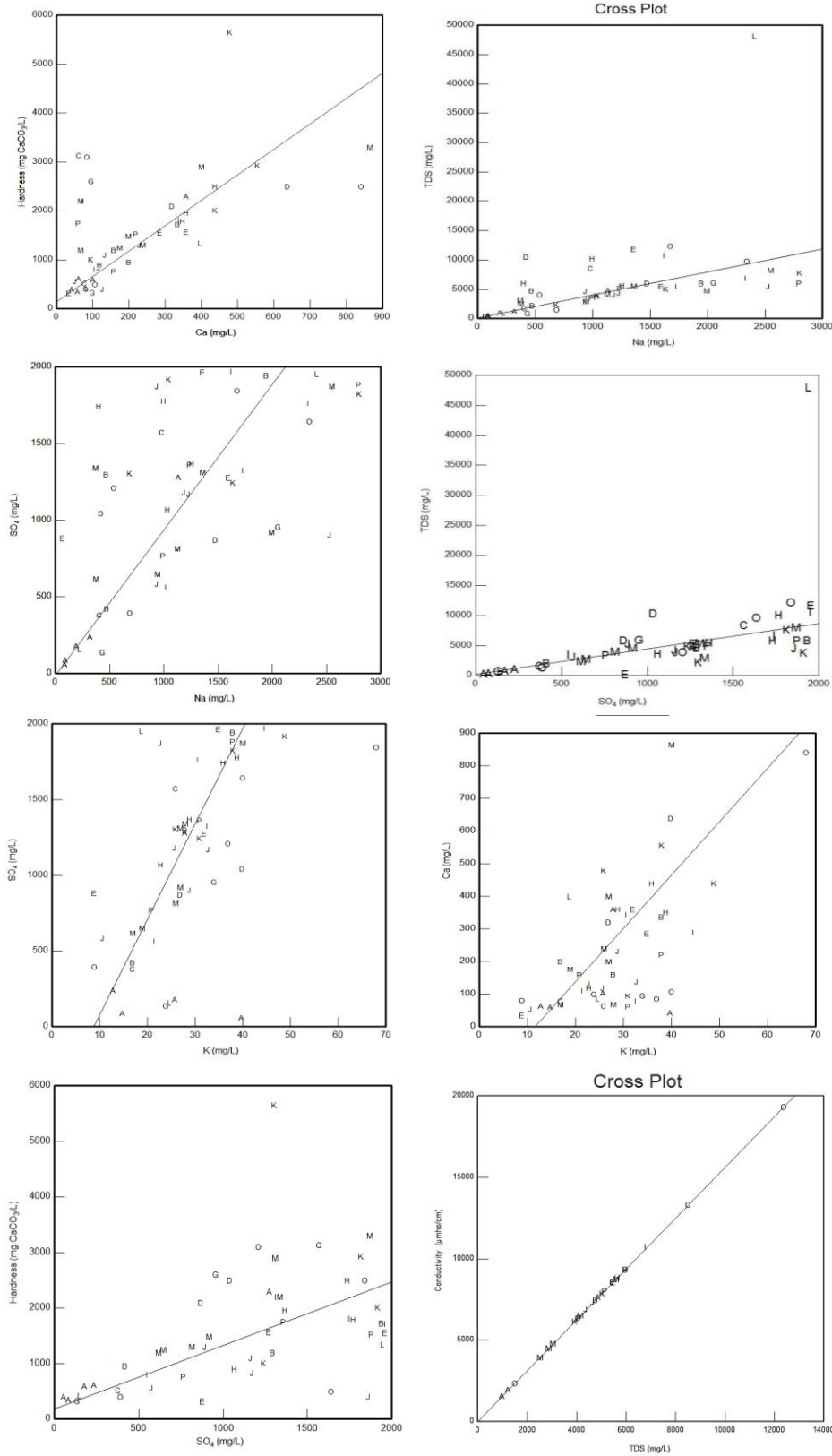


Figure 3 These graphs show the ionic relation between Cation and anion.

**Table 4** Correlation matrix of the collected samples in the study area.

	Depth	temp	pH	TDS	EC	Hardness	Turbidity	Ca	Mg	Na	K	HCO3	Cl	SO4	NO3	Sewage
Depth	1															
temp	0.12	1														
pH	-0.06	0.11	1													
TDS	-0.02	-0.34	-0.14	1												
EC	-0.02	-0.34	-0.14	<b>0.99</b>	1											
Hardness	-0.11	-0.23	-0.36	0.16	0.16	1										
Turbidity	0.23	-0.16	0.07	0.08	0.08	0.21	1									
Ca	-0.12	-0.19	-0.27	0.37	0.37	<b>0.6</b>	0.02	1								
Mg	-0.06	-0.18	-0.25	-0.02	-0.02	<b>0.88</b>	0.26	0.16	1							
Na	0.14	0.15	-0.09	<b>0.5</b>	<b>0.5</b>	0.27	0.14	0.41	0.09	1						
K	-0.08	-0.19	-0.29	0.19	0.19	0.43	0.2	<b>0.6</b>	0.18	0.41	1					
HCO3	0.11	0.12	-0.36	0.2	0.2	0.02	0.15	-0.08	0.08	0.04	0.02	1				
Cl	0.29	0.19	-0.45	0.06	0.06	0.21	0.03	0	0.26	0.38	0.23	0.27	1			
SO4	0.04	-0.31	-0.31	<b>0.51</b>	<b>0.51</b>	<b>0.5</b>	0.28	<b>0.55</b>	0.3	0.61	0.6	0.05	0.36	1		
NO3	-0.01	-0.12	-0.15	0.06	0.06	0.24	0.09	-0.11	0.36	0.1	0.17	0.28	0.33	0.21	1	
Sewage	-0.27	0.02	-0.24	0.12	0.12	0.14	0.17	0	0.18	0	0.01	0.36	0.03	-0.03	-0.04	1

### **Hydrochemical facies**

Chemical reactions and processes occurring in groundwater system define the composition of water (Guo & Wang, 2004). Hydrofacies reflect the effects of chemical processes occurring between minerals within the lithological framework and the groundwater (Back, 1966; Seaber, 1962; Pulido-Leboeuf, 2004; Nwankwoala and Udom, 2011). It depends on various factors *such as* lithology, residence time and regional flow pattern of water (Dahl, 2007). The Piper tri-linear diagram is used to show the relative concentration of the major cations and anions (Piper, 1994; Nwankwoala and Udom, 2011).

The hydrochemical characteristics of the analyzed groundwater from Gulistan-e-Johar town have been summarized in Table. These results indicate that there is no dominant hydrofacies occurring in the aquifers of Gulistan e Johar relatively Na-Cl facie is high (Fig.4). Other hydrofacies are Na-SO<sub>4</sub>, Mg-Cl, Mg-SO<sub>4</sub> and Ca-SO<sub>4</sub>. Relative abundance of the dissolved ionic species in the groundwater lies in the order of:

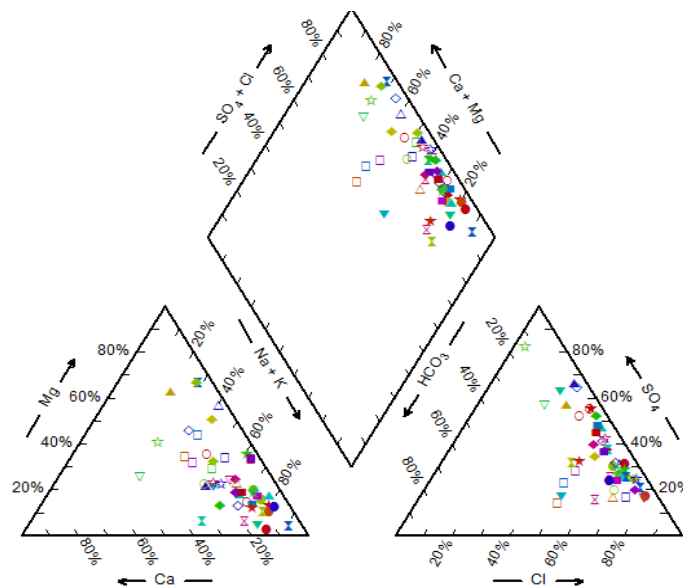
$$\text{Na-Cl} > \text{Na-SO}_4 > \text{Mg-Cl} > \text{Mg-SO}_4 > \text{Ca-SO}_4$$

**Table 5** Hydrochemical facies of groundwater from Gulistan-e-Johar.

S. No.	Hydrofacies	No. of samples	% samples
1	Na-Cl	34	68
2	Na- SO <sub>4</sub>	7	14
3	Mg-Cl	5	10
4	Mg-SO <sub>4</sub>	3	6
5	Ca-SO <sub>4</sub>	1	2

**Na-Cl hydrofacies and Mg-Cl hydrofacies**

Na-Cl is the dominant water type in the groundwater of Gulistan-e-Johar town. About 90% TDS content indicate that there is high salinity impact is present due to anthropogenic activity or high sewage contamination. Evaporative concentration is other factor for high salinity (mainly Na-Cl) in semi-arid regions like Karachi city (Raza and Bender, 1995). The occurrence of Mg-Cl hydrofacies suggests strong water-aquifer related to direct cation exchange phenomenon results from alteration of clay mineral or dolomite dissolution (Jones et al., 1999; Smith 2005; Jeong 2001, Hem 1985). Due to Cation exchange, magnesium occurring in clays is released into the water and sodium is absorbed on the surfaces of clays as a result hydrofacies is converted from Na-Cl to Mg-Cl type groundwater (Mrazovac et al., 2011).



**Figure 4** Piper diagrams of groundwater samples from Gulistan-e-Johar town.

### **Na-SO<sub>4</sub> and Mg-SO<sub>4</sub> hydrofacies:**

Na-SO<sub>4</sub> and Mg-SO<sub>4</sub> hydrofacies are reported in seven and three ground water samples respectively. Na-SO<sub>4</sub> type water is generally associated with intensive evaporation of waters, which have previously lost their Ca and HCO<sub>3</sub> to calcite precipitation and cation exchange process (Younger, 2004; Trabelsi et al., 2007).

Therefore, the weathering of carbonates, clay and gypsiferous shale in study area may significantly increase the concentration of Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> & SO<sub>4</sub><sup>-</sup> in water to form these water types (Mora et al., 2017).

### **Ca-SO<sub>4</sub> hydrofacies**

Ca-SO<sub>4</sub> hydrofacies are reported in only one ground water sample. Ca-SO<sub>4</sub> water type suggests a strong chemical weathering of gypsiferous shale & carbonate rocks of Gaj formation in Gulistan-e Johar town. It is indicating that either water was gradually deficient in Na or it has been removed from water through ion exchange with Magnesium (Khan, 2016).

### **Principal Component Analysis (PCA)**

Principal component analysis (PCA) is a statistical method it transforms all data into several principal components (PCs), which express common properties and association between different chemical components of the variables without losing information of the original data in the groundwater (Ringner, 2008; Mukherjee-Goswami et al., 2008). Table 3 shows the results of the PCA applied to the data of physicochemical variables, major ions, and dissolved trace elements in groundwater supplied to the Gulistan-e-Johar town. Five important components were significant.

PC-1 describes most of the highest (21.81%) with high positive loading for the major ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) coupled with strong positive association of hardness (0.86) and TDS (0.88). It reflects intense rock-water interaction (Khan et al., 2017). Although bicarbonate (HCO<sub>3</sub><sup>-</sup>) shows a weak relationship with other major ions in the first



component, this suggests that there is no fresh water source present. On the other hand, anthropogenic activities are also playing important role to increase these ions into the water (Panhwar, 1969). Moreover, very high hardness of water is also influenced by salts of Ca and Mg in study area. The second component (PC2) describes about 12.55% of total variance and has high positive loading for Cl, Mn, and Cr coupled with high negative loading of pH, SO<sub>4</sub> and Ca suggest that bacteria mediated sulphate reduction is causing organic soil degradation which in turn is decreasing the pH (Khan et. al., 2017).

**Table 6** Principal component analysis of groundwater in Gulistan e Jauhar area.

Component Matrix					
	Component				
	PC1	PC2	PC3	PC4	PC5
Depth	.059	.157	.196	.500	-.067
Temperature	-.249	.132	.072	.439	.578
pH	-.441	-.488	.261	.070	-.349
TDS	.898	-.204	.164	.186	.014
Hardness	.687	.044	-.370	-.481	.001
Turbidity	.387	-.072	.637	-.226	-.244
Ca	.628	-.484	-.319	-.129	.278
Mg	.488	.336	-.274	-.523	-.160
Na	.614	-.211	-.011	.438	.196
K	.755	-.303	-.124	.016	.065
HCO <sub>3</sub>	.254	.461	.356	.066	.284
Cl	.530	.564	-.045	.412	.119
SO <sub>4</sub>	.866	-.115	-.019	.060	-.072
NO <sub>3</sub>	.367	.443	-.121	.134	-.514
Sewage	.110	.228	.306	-.510	.474
Fe	.378	-.223	.733	-.173	-.148
Zn	-.017	.351	.543	-.149	-.023
Mn	.123	.508	.068	-.297	.352
Cr	.293	.658	-.160	.222	-.431
Eigen value	5.561	2.510	2.00	1.89	1.56
% of Variance	27.81	12.55	10	9.46	7.81
Cumulative %	27.81	40.36	50.36	59.82	67.64

It appears that this component is associated to redox processes controlling the solubility of Cr and Mn in groundwater. Sulphate content decreases show that anoxia is reached due to sulphate reducing bacteria start consuming it for organic matter decomposition (Chidthaisong, 2000). The third component describes the 10 % of the total variance, and it is related with the high loading of Fe and Zn and Turbidity. High turbidity is mainly caused by the mixing of sewage water with groundwater (Husain, 2009; McArthur *et al.*, 2004; Cole and Ryan, 2005; Nickson *et al.*, 2005). Naturally Fe and Mn are sourced by the weathering of minerals possessing Fe and Mn like iron sulphide, amphibolite, and iron bearing clay minerals specially found in reduced environment (Khan *et. al.*, 2017) both Fe and Mn pass through organic rich soil so it dissolved in the aquifer water (Ahmad, 2012). The PC-4 component revealed 9.46% of the total variations with positive loading temperature, depth with moderate association of Na and Cl. Negative loading of Hardness, Mg and sewage clearly indicate that major ions in the groundwater of study area suggesting source of these ions is also other than rock. It is further supported by exponentially negative relation of hardness and Mg with sewage suggesting that there is sewage mixing with groundwater (Cole and Rayan, 2005).

The PC-4 component revealed 9.46% of the total variations with positive loading temperature, depth with moderate association of Na and Cl. Negative loading of hardness, Mg and sewage clearly indicate that major ions in the groundwater of study area suggesting source of these ions is also other than rock. It is further supported by exponentially negative relation of hardness and Mg with sewage suggesting that there is sewage mixing with groundwater (Cole and Rayan, 2005). PC-5 which variance 7.8% of total variance showed very high loading of temperature, sewage and NO<sub>3</sub> with low pH. It indicates that bacterial reduction of nitrate is active in study area due to suitable temperature availability It is consistent with the fact that during sampling in the months of April to August very high temperature was present in Karachi due to lack of rainfall. The decomposition of nitrate by bacteria turns it into NH<sub>4</sub> ion which causes change in the pH of groundwater (Khan *et. al.*, 2017). It discharges from leaking sewer, septic tank, the spreading of sewage sludge and manure (Wakida & Lerner, 2005). A study carried out by Khan and Khan (2018) in Gulistan-e-Johar revealed sewage mixing was evident by draining such water into open channels and

pits. Generally mineral components are not the major natural source of nitrate in the groundwater organic matter decomposition processes are the main factors causing nitrate generation and degradation in the study area.

### Water Quality Index (WQI)

One of the most operational techniques to collect information of the water quality for the policy makers and the citizens is Water Quality Index (Yisa and Jimoh, 2010). It was first proposed by Horton in 1965 which was later generalized by Brown et al. in 1970. Water quality index (WQI) is a number that evaluates the quality of water by gathering different parameters, lower values refers to good or excellent quality while higher values refer to the bad or poor quality (Bharti, 2011).

**Table 7** Water Quality Index of collected groundwater samples from Gulistan-e-Johar Town.

Parameters	pH	TDS	Mg	Hardness	Na	K	Ca	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	NO <sub>3</sub>
	-	ppm	mg/l	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
<b>Observed Value (Vn)</b>	7.22	5792	237	1564	1177.7	28.9	234.32	325.8	1452	1137.96	11.29
<b>WHO Limits(Vs)</b>	8.5	500	150	500	200	12	75	300	250	250	10
<b>Ideal Value (Vi)</b>	7	0	0	0	0	0	0	0	0	0	0
<b>Vn-Vi</b>	0.22	5792	237	1564	1178	28.9	234.3	325.8	1452	1137.96	11.29
<b>Vs-Vi</b>	1.5	500	150	500	200	12	75	300	250	250	10
<b>Qn</b>	14.667	1158.4	158	312.8	588.8	240.83	312.4	108.6	580.8	455.184	112.9
<b>Wn=k/Vn</b>	0.4017	0.0005	0.0122	0.00185	0.002	0.1003	0.012	0.009	0.002	0.00255	0.257
<b>Qn*Wn</b>	5.891	0.58	1.9333	0.58	1.45	24.167	3.867	0.967	1.16	1.16	29
<b>Mean WQI = 88.25</b>											

Weighted arithmetic index method of WQI proposed by Brown et al (1970) was applied to evaluate the groundwater quality of Gulistan-e-Johar Town. Physicochemical parameters including pH, TDS, major cations (Ca, Mg, Na and K) and anions (SO<sub>4</sub>, Cl, HCO<sub>3</sub>, NO<sub>3</sub>, Fe, Mn and F) were used to calculate WQI of groundwater in study area.

**Table 8** WQI range, status and possible usage of the water sample (after 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 of irrigation
Above 150	Unfit for drinking	Proper treatment required for use

Water quality of collected samples is unfit for drinking purpose, as the value of WQI is 88.25 use in irrigation purpose (Table). It implies that proper treatment of groundwater is required before its use for drinking purpose.

### **Conclusion**

Present study revealed that groundwater quality is poor for drinking purpose in study area due to high salinity. Complex geochemical and microbiological processes (natural and anthropogenic) are operating in the study area. Groundwater hardness is against the WHO guideline where both temporary ( $\text{HCO}_3$ , Ca, Mg) and permanent ( $\text{SO}_4$ , Cl) hardness are reported. About 70% groundwater are chemically contaminated and 60% wells are sewage impacted as indicated by the occurrence of pathogenic bacteria. Anoxic environment due to bacteria mediated decomposition of organic matter is prevailing in the aquifers which are triggered by sewage mixing due to leaking sewer, septic tank, the spreading of sewage sludge and open drainage pits (rainfall) in the study area. Water chemistry is containing about 25% of its solute as trace elements (Fe, Cr, Mn, Cu, Zn and Co) are released from host sediments (clays and carbonate) and associated organic matter occurring in the aquifers. Out of which Fe, Mn and Cr shown higher concentration than the other trace elements. About 24% Fe content double the WHO guideline limit (0.3 mg/L) followed by 38% Mn content is also exceed the desirable limit (0.05 mg/L) and 12 % Cr is more than double the WHO guideline (0.05 mg/L) for drinking purpose. The sediment

decomposition is releasing the absorbed load into the water leading to increase the groundwater salts.

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