

Hydrogeochemical Evaluation of Groundwater of SITE Area, Karachi, Pakistan

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Summary: In Karachi city presence of elevated concentration of various pollutants from natural and anthropogenic sources has caused the acute shortage of safe drinking water. The physicochemical data of different aquifers of Karachi were examined to elucidate the geochemistry and identify natural and anthropogenic processes controlling the quality of groundwater. Twenty four groundwater samples were collected from different localities of SITE area of Karachi. Physical and chemical characteristics of groundwater were determined using standards methods. Minor and trace metals (Fe, Zn, Co, Cu, Ni, Cr) were also determined to know the geochemical conditions of aquifers. Data was interpreted using multivariate statistical analysis. Groundwater of the area is mainly saline and 80 % water samples contain TDS above 500 ppm. Aquifers are dominated by HCO₃ and Ca-Cl hydrofacies, which shows impact of seawater intrusion. Lateral distribution of groundwater pollution was investigated using Inverse Distance Weighting (IDW) technique using ArcMap, which indicates displacement of freshwater with seawater. In addition calcite and gypsum dissolution were also played a vital role to increase the salinity of the water. At few places mixing of sewage water and leaching through surface solid waste were also evident. Zinc concentration was high in 88% water samples. Lateral distribution of physicochemical parameters shows great heterogeneity, which indicates influence of local geology and land use pattern.

Keywords: Groundwater pollution, Hydro-geochemical investigation, Water quality, Karachi.

Introduction

Next to the air we breathe, water is probably the most vital asset for the survival of all forms of life [1, 2, 3]. Groundwater and surface water are the two main reservoirs, used by human being due to their easy accessibility; therefore, about 65% of the groundwater in the world is used for drinking purpose [4-6]. In urban areas of developing countries about 50% of the drinking water is derived from wells, springs and bore holes and around 1000 million residents in Asia rely on such water resources [7]. Unfortunately, these precious groundwater resources are depleting day by day due to over-extraction, climate change and pollution. According to WHO, nearly 80% of the health hazards are caused by drinking polluted water [8-11].

Usage of groundwater depends upon its availability and quality; it can be used only if it is available in sufficient quantity with suitable quality. In Pakistan for 216 million population 128300 million m³ surface and 50579 million m³ groundwater is available per year, which is attained by recharge from natural precipitation, flow from rivers, seepage from canals and its accumulation [12, 13]. Almost one-sixth of the total population does not have easy access to safe drinking water which ultimately leads people to over-extract groundwater [14]. Due to sporadic precipitation and improper fresh water storage in arid and semi-arid regions of Pakistan, groundwater is the most significant source of fresh water and 60% of its population mainly depends upon groundwater for drinking and irrigation purpose. Groundwater demand has also been raised

with rapid increase in unplanned and unorganized urbanization. In future it is expected that this water consumption will rise as the country's population of 216 million is projected to increase to 384 million in 2050.

Karachi is one of the biggest metropolitan cities of Pakistan situated in semi-arid region, facing severe scarcity of domestic water supply due to rapid urbanization and industrial activities. Large-scale industrial activities, worst solid and liquid waste management, inappropriate sewerage system in Karachi city continually deteriorates groundwater sources in terms of its quality and quantity. As a result, majority of inhabitants rely on unsafe groundwater without maintaining World Health Organizations (WHO) standards. Current study was carried out in densely populated SITE Town of Karachi (Fig 1). Site town is one of the biggest industrial zone of Karachi, having giant industrial structure has been facing severe shortage of municipally supplied water, therefore majority of residents use ground water to fulfil their daily domestic water needs. As the understanding of groundwater geochemistry is important to ensure its quality for drinking purpose, [15] The current study has been emphasized to detect groundwater status of Site town to classify its groundwater quality for drinking purpose according to WHO standard and to evaluate the natural and anthropogenic factors responsible to deteriorate the groundwater quality in the area.

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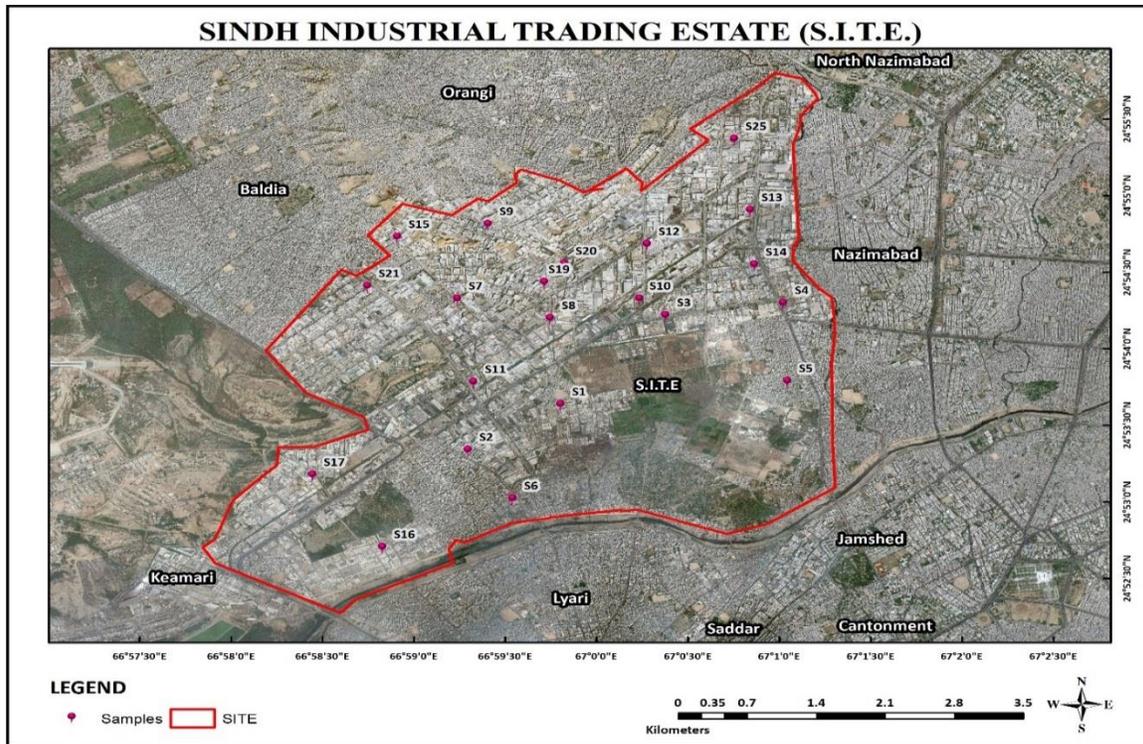


Fig. 1: Location and sampling map of S.I.T.E. area.

In present study ArcMap 10.5 was also used to observe the spatial distribution of pollutants as it is the most emerging and useful tool used in water quality assessment. Hence these research findings would be highly helpful for local government to develop strategies to locate pollutants and schemes to save groundwater resources.

Experimental

To determine the groundwater quality status of SITE town, total twenty-four groundwater samples were collected randomly from various locations of study area. This sampling was carried out in post monsoon season in the month of September, 2016. All samples were taken from the depth range of 100-150ft. Global Positioning System (GPS) was used to mark accurate bore hole location of each sample (Fig. 1). Groundwater samples were collected in three plastic bottles of 1000 ml, 500 ml and 100 ml capacities. 1.0 ml boric acid was added in each 100-ml bottle for nitrate preservation whereas 1000 ml bottle was used for general physicochemical analyses, while in 500 ml capacity bottle 1% HNO_3 was added to preserve the sample for trace metal analysis. Bottles were properly washed and rinsed thoroughly with distilled water and then with representative sample at sampling site. Highly fluctuating parameters like pH, total dissolved solids

(TDS) and temperature were determined on the site just after the sampling by using Adwa® (AD 111) pH meter and Adwa® (AD 330) Multimeter. Furthermore, remaining parameters were analyzed in the lab by using standard methods which are summarized in Table-1. Replicate samples were used to minimize the chance of cross contamination. All instruments were calibrated and all chemical reagents were of analytical grade to ensure accuracy of data. Flame photometer (JENWAY EFP7) was used for determination of sodium and potassium concentration. EDTA standard titration method (1992) was used for calcium and magnesium concentration. Chloride concentration of each sample was determined by argentometric titration method, while sulphate by using gravimetric method. Standard titration method (1992) was also adopted for bicarbonate determination. Spectrophotometer (HACH-8171) was used for Nitrate determination. All trace elements including iron, zinc, cobalt, copper, nickel, and chromium were analyzed by Atomic Absorption Spectrometer (Analyst 400 Perkin Elmer). Quality control was insured by adding duplicate and spiked samples and calculating ionic balance for each sample. Spatial mapping was done using in ArcMap10.5 software. The hydro-chemical facies are the function of ground water interaction with aquifer matrix and water residence time as hydrogeochemical facies also reveal the effects of

chemical processes occurring between minerals within the lithological framework and the groundwater [16-18]. To assess the hydro-chemical character of groundwater of study area, Piper and Durov diagrams were used, constructed by using Aqua chem software. In Arc GIS deterministic and geostatistical interpolation techniques has been widely used to provide the information in holistic manner without losing the spatio-temporal variability which are often critical in data assessment and helpful to understand the spatial and temporal variation in groundwater pollutants in groundwater [19-21]. In present study an interpolation technique of ordinary IDW (Inverse distance weighting) was used for generating thematic layers of the relevant factor of each parameter. IDW is an interpolation process in which missing values are calculated by combining other nearby sample values, with the assumption that closer values are more comparable than the farthest value, and it is used here to approximate the uncertain stations' value. Therefore, IDW has a strong ability to predict the overall trend of groundwater contamination when a dataset is autocorrelated [22-26].

Study Area

Study area is a part of Karachi city, which is situated at the coast of Arabian sea and as an important port, is a central point of trade and main hub of oil refineries, textile, pharmaceutical, polymer, plastic, cement, cotton, heavy chemicals, petrochemicals, edible oil and leather industries (Fig.1). S.I.T.E town is named after the Sindh Industrial and Trading Estate (SITE), situated in west of Karachi and lies at 24°92'95" to N 24°87'71" N latitude and 66°96'46" E to 67°01'80" E longitude. Geographically the town is bordered by Gadap town to the north, Liaquatabad Town and North Nazimabad Town to the east across the Orangi Nala stream, Lyari and Saddar to the south across the Lyari River and Kiamari to the west (Fig.1). SITE town is one of the largest industrial area in Pakistan with more than 2,000 industrial units and covers approximately 4,500 acres (18 km²) of land and is densely populated with population of 0.45 million.

Karachi city mainly gets municipal supply water from 122 km far Keenjhar Lake, which originates from the Indus River. Second source of water is Hub Dam in north-west of Karachi city which supplies water to the population of Karachi since 1980. However, these two reservoirs are unable to fulfill the requirement of twenty five million population of Karachi that needs 1,100 million gallons water per day. Karachi only gets 450-480 million gallons per day water, therefore rest of the water requirement is fulfilled by extracting groundwater.

Karachi and its surroundings are covered by Nari and Gaj Formations of Tertiary age [27]. Nari Formation of the Oligocene age forms the lowermost part, which is overlain by Miocene rocks of Gaj Formation and the lower Manchar series of Upper Miocene age (Fig. 2). Gaj Formation is well exposed in Karachi and comprised of four members namely Mundro member, Mole member and Gulistan-e-Johar Member. A huge area of this city is built upon these rocks and the study area is primarily covered by Gulistan-e- Jauhar member of Gaj Formation. Small units of Mundro (Pleistocene age) and Mol member (Pliocene age) are exist in northern part of study area, while rest of the area is covered by Recent and Sub-Recent deposits (Fig. 2), which overlies the Nari Formation of Oligocene age [28]. Gaj Formation having 50 m thick bed in the Karachi region comprising predominantly soft to hard sandstone and argillaceous limestone. The most important anticlines in the topography of Karachi include Pir Mangho, Landhi-Korangi, and Drigh Road.

Shallow aquifers in the area reside in alluvium, while deeper aquifers are in fractured limestone of Gaj Formation. Karachi is a part of Hub and Malir River Basin. Malir and Lyari rivers receive all the industrial and domestic waste and drains directly into Arabian sea within an area of 336 km. Recharge from polluted Malir and Lyari Rivers contribute to the recharge systems of the aquifers of Karachi through seepage. However, coastal aquifers of the city are highly saline and are affected by active seawater intrusion.

Table-1: Equipment/methods used to analyze groundwater samples collected from S.I.T.E.Town.

S.No.	PARAMETER	STANDARD METHOD
1	pH	pH meter (AD 111)
2	TDS (mg/l)	EC meter, Adwa (AD 330)
3	CONDUCTIVITY (mS/cm)	EC meter, Adwa (AD 330)
5	CALCIUM (mg/L)	EDTA Titration Method, Standard Method (1992)
6	MAGNESIUM (mg/l)	
7	POTASSIUM (mg/l)	Flame photometer JENWAY EFP7
8	SODIUM (mg/l)	
9	CHLORIDE (mg/L)	Titration (Silver Nitrate), Standard Method (1992)
10	BICARBONATE (mg/L)	Titration Method, Standard Method, (1992)
12	NITRATE mg/L	Spectrophotometer, HACH-8171
13	IRON	Atomic Absorption Spectrometer (Aanalyst 400 Perkin Elmer)
14	TRACE ELEMENTS	Atomic Absorption Spectrometer (Aanalyst 400 Perkin Elmer)

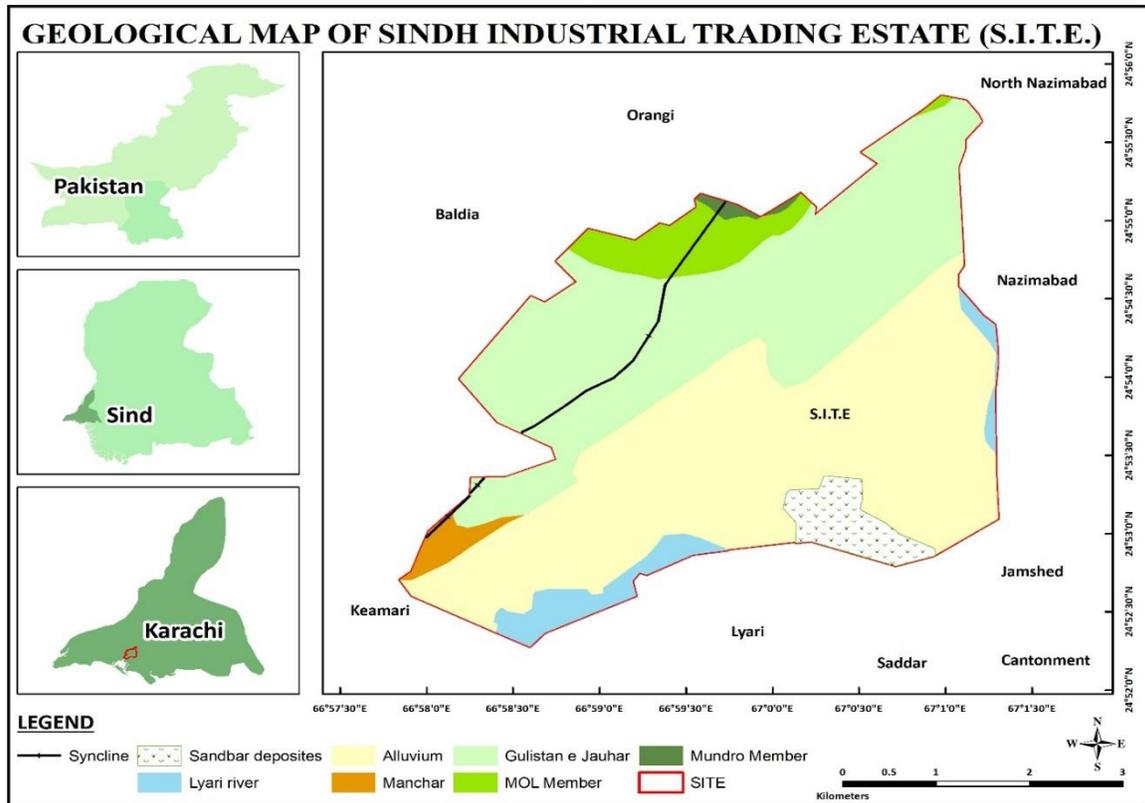


Fig. 2: Geological Map of S.I.T.E Town.

Study area lies within moderate climate region with generally high relative humidity ranges from 58% in December (the driest month) to 85% in August (the wettest month) with an average temperature of 21°C. The average annual rainfall is 256 mm, but in certain years rainfall is higher and it may rain heavily within a short span of 48 hours.

Results and Discussion

The concentrations of different constituents in groundwater are the result of anthropogenic and geogenic hydrogeochemical processes, which makes the understanding of their origin difficult. Results of physicochemical analysis of site town showed that water was safe in terms of color, odor and turbidity. Analysis reveals that pH of groundwater of study area lies within the circum-neutral range (6.5-8.5) prescribed by WHO (Table-2). However, groundwater of site town contains extremely elevated concentration of Electrical conductivity (EC) and Total Dissolved Solids (TDS), ranges widely between 4050-35600 $\mu\text{S}/\text{cm}$ and 2020-17800ppm respectively. The electrical conductivity of most freshwaters ranges from 10 to 1,000 $\mu\text{S}/\text{cm}$ but may exceed 1,000 $\mu\text{S}/\text{cm}$, especially in polluted waters. However, most of the samples show high EC, which could be

the resulted from the interplay of semi-arid climate, low rate of precipitation and low recharge of aquifers, seawater intrusion, leaching from solid waste and mixing of sewage water. Pearson correlation among EC and TDS ($r=0.99$) (Table-3) indicates that the source of high values of EC & TDS may be associated with over pumping of groundwater, because the study area faces excessive extraction of groundwater for various industrial uses [29]. Sodium content in the analyzed samples ranged from 123-707 ppm (mean of 528 ppm). Around 83% of the representative samples lies far beyond the desired limit of (WHO 200 ppm). Data indicates that groundwater of site town contains extremely high chloride concentration (mean=3488 ppm). As the study area is mainly an industrial hub of Karachi, where huge amount of effluents is directly discharged in open spaces, which directly percolates in the groundwater and become responsible to rise the concentration of Na and Cl in groundwater. Calcium and Magnesium concentration widely fluctuates and lies above the WHO Standard (Ca=75 ppm, Mg=150 ppm) for drinking purpose in the groundwater of study area. Calcium and magnesium are the two major ions which are responsible for water hardness. Groundwater of study area is categorized as very hard (Mean=6562) and shows input of effluent from

industries. Sample analysis also depicts the usual trend of high Ca content over Mg, indicates that groundwater is interacting with limestone [30]. About 99% of the samples exhibit Ca/Mg ratio >1 (Table-4), ultimately suggests the calcite dissolution over dolomite [31] as study area is mainly covered by Jauhar member of Gaj Formation (Fig. 2) however,

calcite dissolution is the main but not only the single factor for elevated Ca, Mg concentrations and it is also triggered by input of industrial and domestic waste as it is indicated by strong positive correlation of Ca (0.86) and Mg (0.96) with TDS (Table-3).

Table-2: Physico Chemical Analysis of Groundwater of S.I.T.E Town.

SAMPLE NO	EC	TDS	pH	Ca	Mg	Na	K	Cl	HCO ₃	SO ₄	NO ₃	Ionic Balance
Unit	µS/cm	ppm		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%
S-1	6220	3110	7.75	610	261	930	30	2304	2100	147	53.78	4.32
S-2	6200	3100	7.77	560	253	834	29	2198	1890	122	55.73	4.96
S-3	4700	2360	7.32	1320	176	593	17	1507	4150	212	86.63	1.41
S-4	4660	2330	7.33	620	207	612	17	1507	2250	220	92.58	4.1
S-5	6920	3460	7.4	550	223	624	17	1524	2150	195	96.44	4.2
S-6	4720	2370	7.36	530	221	621	17	1542	2010	260	92.23	4.4
S-7	4960	3580	7.71	570	185	668	27	1737	1790	155	46.18	4.7
S-8	4940	2470	7.81	340	196	679	28	1719	1190	122	44.82	5.0
S-9	35600	3990	7.11	470	210	547	35	1536	1740	1083	50.86	4.8
S-10	35200	17600	7.02	8260	1467	570	67	1980	2000	1890	57.54	3.5
S-11	35600	17800	7.07	7300	1452	579	68	14216	1975	2262	60.68	3.4
S-12	35600	17800	7.11	5350	1595	593	68	15421	1900	521	61.8	5.3
S-13	7710	3850	7.84	750	276	127	19	1410	1450	513	65.3	5.3
S-14	32300	16200	7.29	4030	1140	480	46	10580	2400	700	35.52	4.8
S-15	4100	2350	6.95	800	299	534	17	1276	2850	1115	142	3.36
S-16	32200	16100	7.25	5040	1079	506	45	12585	2500	961	34.5	6.0
S-17	7570	3790	7.73	850	282	124	19	1643	1070	773	64	5.2
S-18	7590	3800	7.76	750	295	123	19	2198	1120	538	63	6.2
S-19	4810	2400	7.71	490	213	570	11	1160	1080	415	189	6.8
S-20	7970	4000	7.6	450	251	707	11	1241	2320	456	160	4.2
S-21	4120	2330	7.57	490	194	136	26	1080	980	340	125	5.8
S-22	4050	2020	6.99	940	286	446	11	1028	4575	155	227	2.8
S-23	4710	3160	7.61	650	245	702	11	1134	1250	374	147	2.3
S-24	4810	3500	7.62	430	245	380	10	1205	1150	415	162	1.9
Average	12803	5978	7	1756	469	529	28	3489	1995	585	92	
Min	4050	2020	7	340	176	123	10	1028	980	122	34	
Max	35600	17800	8	8260	1595	930	68	15421	4575	2262	227	
WHO LIMITS (2017)	1500	500	6.5-8.5	75	150	200	12	250	300	250	10	

Table-3: Pearson's correlation matrix among Physico-chemicals Parameters.

	TDS	EC	Ca	Mg	Na	K	Cl	HCO ₃	SO ₄	NO ₃
TDS	1.00	0.89	0.95	0.98	0.03	0.91	0.86	0.04	0.68	-0.44
EC		1.00	0.86	0.86	0.03	0.88	0.76	0.02	0.72	-0.49
Ca			1.00	0.96	0.04	0.90	0.74	0.12	0.78	-0.37
Mg				1.00	0.04	0.92	0.85	0.07	0.69	-0.37
Na					1.00	0.13	0.06	0.26	-0.14	-0.06
K						1.00	0.78	-0.03	0.67	-0.60
Cl							1.00	0.07	0.46	-0.41
HCO ₃								1.00	-0.04	0.23
SO ₄									1.00	-0.24
NO ₃										1.00

Around 33% of the total samples lies within the permissible range of WHO (250 ppm) while rest of the samples contain extremely high sulphate concentration (mean=581 ppm). Gypsum dissolution is considered as the principal source of high sulphate content in groundwater as it shows strong positive correlation with Ca & Mg ($r=0.78$ & $r=0.69$ respectively) which is catalyzed by sewerage and domestic waste input [32].

Chlorides and sulphates are the most sensitive indicators of anthropogenic input. In natural groundwater low concentrations of these constituents indicates unpolluted fresh water [33]. Moreover, Cl/SO₄ between 0.63-29.20, while Cl/SO₄ molar ratio more than 19 indicates, mechanism of sulphate reduction, however, in the area only one sample shows Cl/SO₄ ratio 29.60, which indicates sulphate reduction phenomenon at small scale (Table-4). Eventually anthropogenic influence is seems to be dominant mechanism as it is evident by positive

correlation between SO_4 and Cl and these constituents have same anthropogenic source. Groundwater of Site town has excessive concentration of bicarbonate with the mean of 1995 ppm, as it's the most abundant anion but in the current study it does not have direct relation with other anions and cations, therefore it can be concluded that bicarbonate concentration is high due to anthropogenic activities. In the study area effluent from textile, pharmaceutical and food processing

industries and broken sewage lines percolates into the aquifer and oxidation of organic matter may have resulted in high concentration of HCO_3 in the groundwater. Data reveals that except 20% of the samples, remaining all the collected samples have exceeding potassium content compared with WHO (10 ppm). Potassium is mainly derived from clayey units of Gaj Formations as the water is mainly pumped from aquifers of Gaj member.

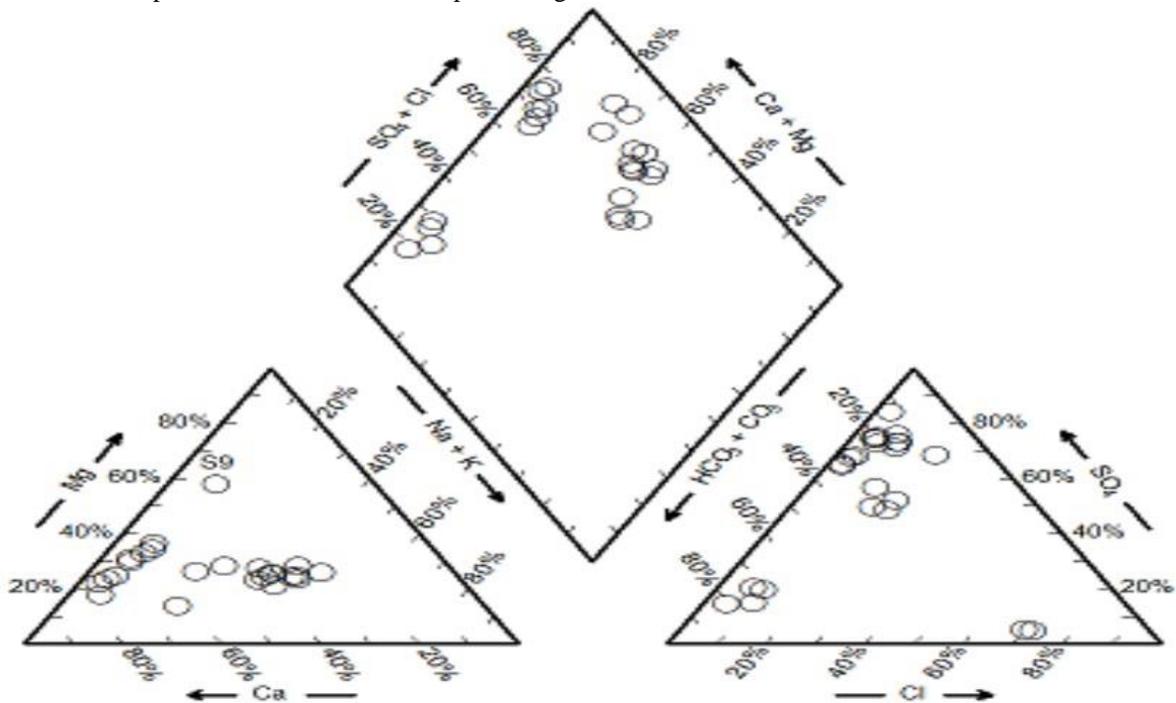


Fig. 3: Piper Diagram showing hydrofacies in the study area.

Table- 4: Geochemical ratios of analyzed ions in Groundwater of S.I.T.E Town.

S.No.	Cl/HCO ₃	Na/Cl	Ca/Mg	TDS/EC	Cl/SO ₄
S-1	1.097	0.404	2.341	0.50	15.73
S-2	1.163	0.379	2.216	0.50	18.00
S-3	0.363	0.394	7.493	0.50	7.12
S-4	0.670	0.406	3.002	0.50	6.86
S-5	0.709	0.409	2.467	0.50	7.80
S-6	0.767	0.403	2.403	0.50	5.92
S-7	0.970	0.385	3.076	0.72	11.23
S-8	1.445	0.395	1.738	0.50	14.08
S-9	0.883	0.356	2.238	0.11	14.03
S-10	0.990	0.288	5.632	0.50	0.70
S-11	7.198	0.041	5.028	0.50	0.63
S-12	8.116	0.038	3.355	0.50	29.60
S-13	0.972	0.090	2.713	0.50	3.46
S-14	4.408	0.045	3.534	0.50	17.47
S-15	0.448	0.418	2.677	0.57	1.14
S-16	5.034	0.040	4.671	0.50	13.10
S-17	1.536	0.075	3.009	0.50	2.38
S-18	1.962	0.056	2.545	0.50	2.62
S-19	1.074	0.491	2.298	0.50	2.90
S-20	0.535	0.570	1.794	0.50	2.72
S-21	1.102	0.126	2.526	0.57	3.69
S-22	0.225	0.434	3.292	0.50	6.65
S-23	0.908	0.619	2.655	0.67	3.03
S-24	1.048	0.315	1.755	0.73	2.90

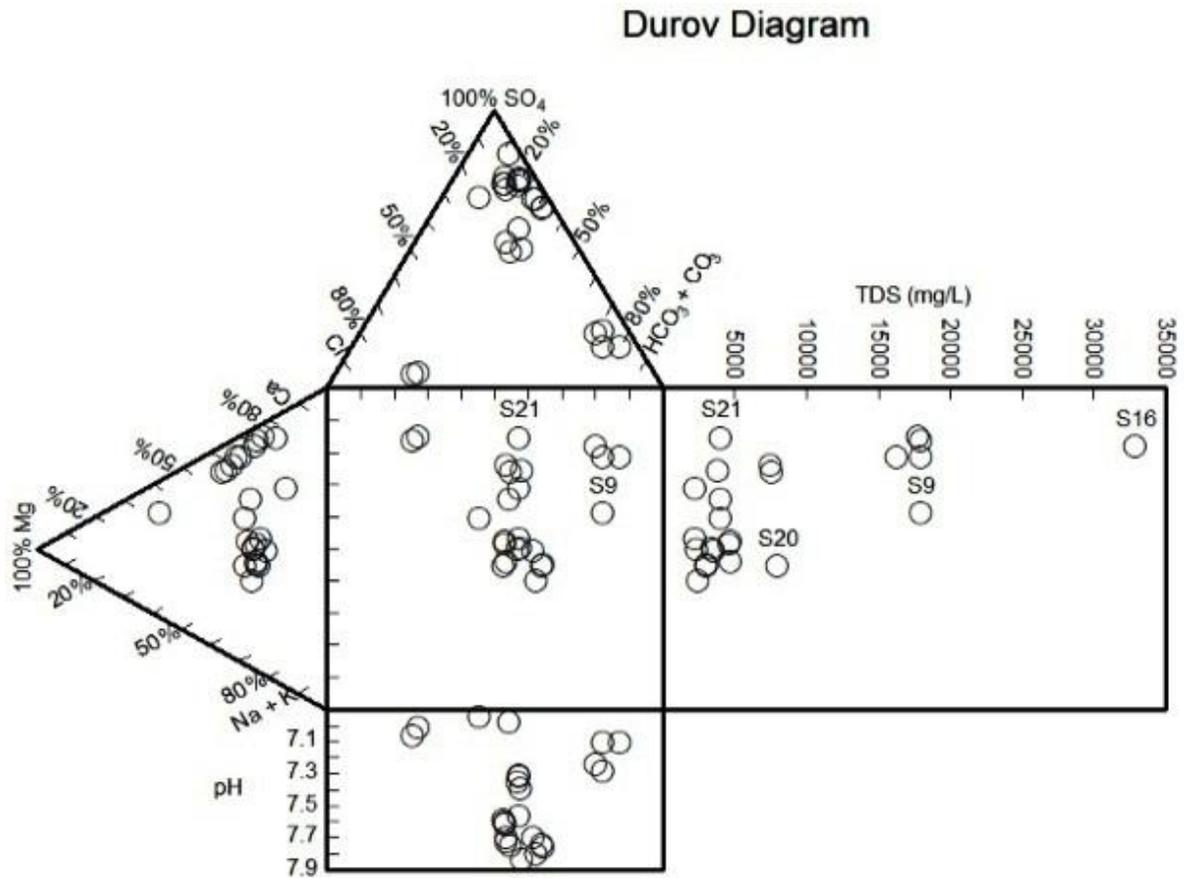


Fig. 4: Durov's Diagram of collected groundwater samples.

Table-5: Groundwater analyses of trace elements in S.I.T.E Town. (BDL: below detection limit).

SAMPLE NO	Fe	Mn	Zn	Cu	Ni	Cr	Co
Unit	ppb						
Detection limit (ppb)	5	1.5	1.5	1.5	6	3	9
S-1	BDL	BDL	37	BDL	BDL	BDL	BDL
S-2	BDL	BDL	32	BDL	BDL	BDL	BDL
S-3	BDL	BDL	283	BDL	BDL	BDL	BDL
S-4	BDL	BDL	192	BDL	BDL	BDL	BDL
S-5	BDL	BDL	171	BDL	BDL	BDL	BDL
S-6	BDL	BDL	167	BDL	BDL	BDL	BDL
S-7	BDL	BDL	67	BDL	BDL	BDL	BDL
S-8	BDL	BDL	73	BDL	BDL	BDL	BDL
S-9	122	BDL	348	BDL	BDL	BDL	BDL
S-10	41	BDL	222	BDL	BDL	BDL	BDL
S-11	53	BDL	255	BDL	BDL	BDL	BDL
S-12	52	BDL	294	BDL	BDL	BDL	BDL
S-13	BDL	BDL	89	BDL	BDL	BDL	BDL
S-14	79	BDL	1359	BDL	BDL	BDL	BDL
S-15	64	BDL	32	BDL	BDL	BDL	BDL
S-16	79	BDL	1288	BDL	BDL	BDL	BDL
S-17	BDL	BDL	91	BDL	BDL	BDL	BDL
S-18	BDL	BDL	83	BDL	BDL	BDL	BDL
S-19	BDL	BDL	747	BDL	BDL	BDL	BDL
S-20	43	BDL	784	BDL	BDL	BDL	BDL
S-21	BDL	BDL	84	BDL	BDL	BDL	BDL
S-22	BDL	BDL	83	BDL	BDL	BDL	BDL
S-23	BDL	BDL	1638	BDL	BDL	BDL	BDL
S-24	BDL	BDL	814	BDL	BDL	BDL	BDL
Average	66.625	-	9233	-	-	-	-
Min	41	-	32	-	-	-	-
Max	122	-	1638	-	-	-	-
WHO LIMITS	300	0.4	50	2000	70	50	40

Table-6: Statistical summary of Hydrogeochemical parameters of Groundwater of Study area.

S:No	Parameters	Unit	No. of samples	Minimum	Maximum	Mean	SD	SD Error	Variance
1	EC	$\mu\text{S/cm}$	24	4050.0	35600.0	12802.5	12826.9	2618.3	164529523.9
2	TDS	ppm	24	2020.0	17800.0	5977.9	5871.1	1198.4	34469512.9
3	pH	ppm	24	7.0	7.8	7.4	0.3	0.1	0.1
4	Ca	ppm	24	340.0	8260.0	1756.3	2345.0	478.7	5498920.1
5	Mg	ppm	24	176.2	1594.6	468.7	470.6	96.1	221475.1
6	Na	ppm	24	123.0	707.0	528.5	216.0	44.1	46650.9
7	K	ppm	24	10.0	68.0	27.7	18.3	3.7	335.6
8	Cl	ppm	24	1028.1	15420.8	3488.8	4514.3	921.5	20378960.7
9	HCO ₃	ppm	24	980.0	4575.0	1995.4	896.5	183.0	803771.6
10	SO ₄	ppm	24	122.1	2262.0	581.0	549.5	112.2	301945.6
11	NO ₃	ppm	24	34.5	227.1	92.2	53.0	10.8	2805.4

Sample analysis (Table-5) shows that all determined trace and minor elements are below the detection limit, except zinc. Zinc concentration varies within the range of 32-1638 ppb (Mean=9233ppb), around 88% of the samples exceed the desired limit of WHO (50 ppb), which may be attributed to dumping of domestic waste, sewage sources or industrial effluents [34]. High concentration of Zn can pose the serious health issue to the local population.

Piper diagram classified that groundwater of SITE town mainly falls in the category of Ca-HCO₃ and Ca-Cl hydrofacies (Fig. 3). These two hydrofacies indicates two evolutionary stages, in early stage low salinity (Cl < 1000 ppm) and later stage of seawater intrusion. Ca-HCO₃ type hydrofacies represents freshwater water recharge through surface run off [35-37]. While Ca-Cl hydrofacie represents cation ion exchange phenomenon as the aquifer material mainly comprised of clay unit of Gaj Formation therefore when saline/sea water comes in contact with these clayey units, ion exchange may take place and Ca is released and Na is adsorbed on clayey unit and results in Ca-Cl hydrofacies. Rest of the samples represent no dominant

groundwater type, this is also evidenced by durov diagram (Fig. 4).

The map represents that almost all analyzed parameters including TDS, EC, Ca, Mg, Na, K, HCO₃, SO₄, NO₃, shows variable distribution pattern and indicates the hydrogeochemical zoning due to natural and anthropogenic influence and overlapping of these two process at some places (Fig 5 a,b,c.). Distribution of Mg, K and Cl shows four distinct zones with high concentration, while Na shows relatively high concentration from east to north of study area, indicating that input of Na is mainly related to point and non-point anthropogenic sources (Fig 5 b). Moreover, TDS and EC show the heterogeneous distribution of salinity in the groundwater. It shows four high salinity zones with low salinity areas, indicating that freshwater resources are at risk in the area and freshwater is gradually replacing with saline water due to over pumping and low surface water recharge. (Fig 5 a,) Spatial distribution of NO₃ and SO₄ revealed that study area is not widely affected by nitrate, while only central part of study area is under the influence of high SO₄ concentration (Fig 5 c).

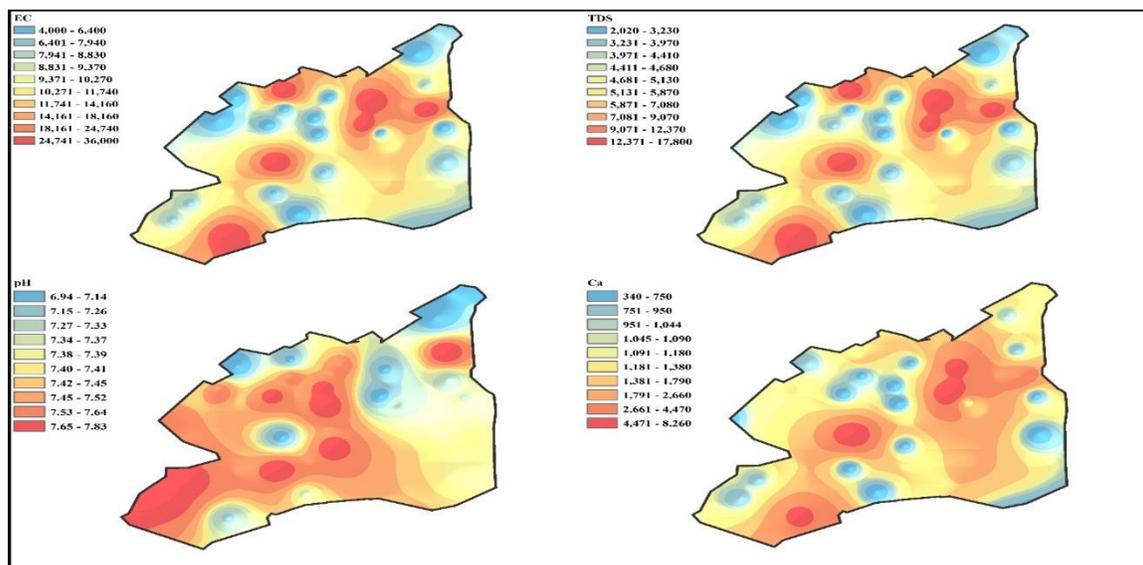


Fig. 5: (a) Spatial Distribution pattern of EC, TDS, pH and Ca in the study area.

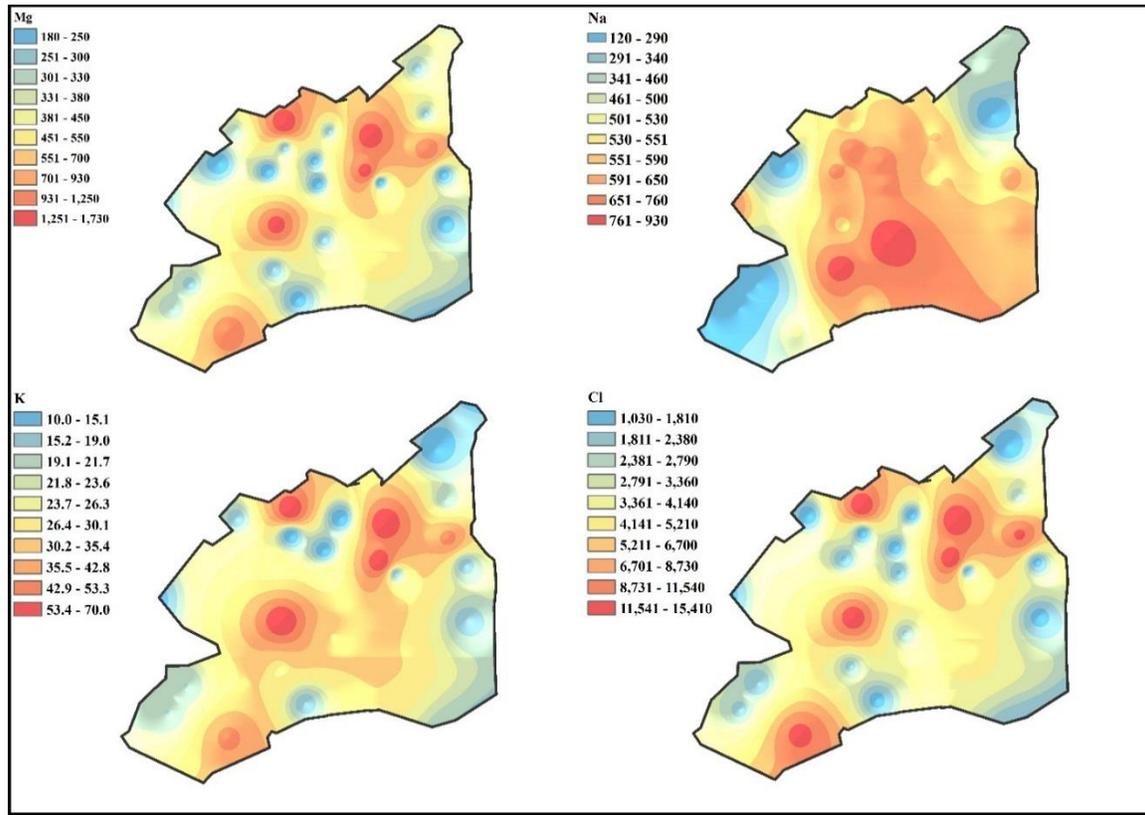


Fig. 5: (b) Spatial distribution pattern of Mg, Na, K and Cl in the study area.

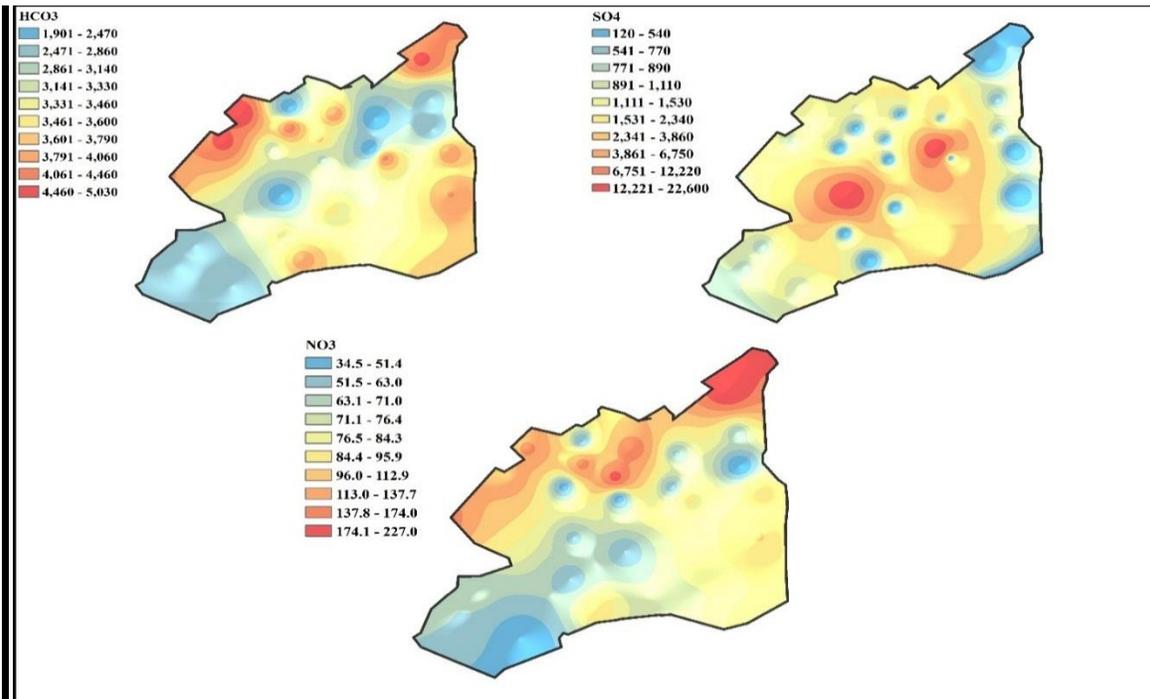


Fig. 5: (c) Spatial distribution pattern of HCO₃, SO₄ and NO₃ in the study area.

Conclusions

- Interpretation of the groundwater data of SITE town indicates that water geochemistry is controlled by complex interaction between evaporation, mineral dissolution, seawater intrusion, leaching from waste dumps and incorporation of sewage in the aquifers.
- Groundwater of site town is highly saline and show high concentration of EC (4050-35600 $\mu\text{S}/\text{cm}$) and TDS, (2020-17800 ppm).
- In nearly all samples Ca/Mg ratio >1 , indicating calcite dissolution over dolomite from Jauhar member of Gaj Formation. Strong positive correlation ($r = 0.78$) between Ca and sulphate show gypsum dissolution as main phenomenon.
- Main hydrofacies of groundwater of SITE town are Ca-HCO₃ and Ca-Cl shows evolutionary trend of groundwater from fresh to saline due to seawater intrusion. Hydrogeochemistry of aquifers of the area was characterized using lateral distribution maps of TDS, EC, Ca, Mg, Na, K, HCO₃, SO₄, NO₃, which indicates that aquifers are affected by natural and anthropogenic processes and contains zones of fresh and saline water, while over pumping and seawater intrusion is a contributing factor to displace the fresh groundwater with saline seawater.
- Concentration of Fe, Mn, Cu, Ni, Cr and Co are below detection limit, while Zn concentration ranges from 32-1638 ppb around 88% of the samples show Zn concentration above WHO standard of 50 ppb, which shows influence of anthropogenic pollution.

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