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Hydro Geochemical Characterization of Groundwater in Alluvial Plains of Lyari and Malir Rivers in Gulshan-e-Iqbal, Karachi

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Abstract. Gulshan-e-Iqbal and its surrounding area is studied to reveal the influence of geological factors, anthropogenic activities and weathering of aquifer rock material. Inter ionic relationship of groundwater with rocks of Nari and Gaj formation proves its unsuitability for drinking purpose. Mainly groundwater samples values are higher than the allowable limit of WHO guide line values. The graphical inter ionic association involving Ca^{2+} + Mg^{2+} and SO_4^{2-} + HCO_3^- evidence the presence of carbonate and silicate weathering in the region. Municipal supplied water samples parameters are in permissible limits but biologically contaminated. Water samples from treated water plant contain nutrients with in limit with no biological contamination. Inter ionic ratio of Ca/Mg and Na/Cl reflect sea water intrusion and is responsible for groundwater pollution due to intimacy of study area to Arabian sea. Groundwater of the study area contains substantial level of salinity and thereafter requires purification before using it.

Keywords: alluvial plane, physico-chemical indicators, coastal area, sea intrusion, geo spatial

Introduction

Groundwater is a vital requirement for the existence of living organisms due to its role in biological, physico-chemical and in environmental processes (Patil *et al*., 2012). In Alluvium plains groundwater utilized for many purposes, like intake and irrigation, domestic and in trade etc. Generally, studies show that 65% of the water which is used globally for domestic purpose comes from groundwater, 20% accounts for irrigation and 15% is consumed in industrial purposes (Admilla *et al*., 2019). Geochemical composition of groundwater in study area depends on the setting of sub-ordinate rock stratum, quality of recharge water, soil and water contact chemical process. The presence of anions and cations in groundwater reflects the contact of water with underlying rock in unsaturated zone and residence time of water in an aquifer (Bouchaou *et al*., 2008). Externally groundwater is vulnerable to contamination in unconfined alluvial aquifers due to surface and groundwater interaction Thakur *et al*. (2015). Geological information is an essential tool for the hydro geochemical characterization and to access the contamination source of groundwater Mustapha *et al*. (2013) and Panno *et al*. (2006). The excessive anthropogenic activities, natural resources exploitation, development of the modern societies and development of the industrial system threatened the quality of water and become source of the air, groundwater pollution. Some toxic elements (Pb, Arsenic, Ag and Cd etc.) reaches to groundwater. Singh *et al*. (2011) are produced from the anthropogenic activities and industrial waste and these are the source of waterborne disease for living organisms Alanis (2005).

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Therefore, many researches have been done to provide safe and secure water Wang *et al*. (2019). European council on 6th May 1948 in Strasbourg, noticeably described the Significance of groundwater for human and environment in European charter. Villholth *et al*. (2017) and assumed that the requirement of water is increasing day by day in metropolitan areas as compared to rural areas and to meet the demand of water, dependence on local water resources is rising gradually.

Current population of Pakistan is 224,641,266 in May 19, 2021 which is equivalent to 2.83% of the total world's population (World Population Prospects, 2019).

Karachi is a big metropolitan city of Pakistan and its population is exponentially increasing from last few decades. In 2020, population of Karachi was estimated to be around 16.1 million (16,093,786) and in 2021 it is 16,459,472 with growth rate of 2.27% (World Population Prospects, 2019). About 60% Population of Pakistan use groundwater for drinking and domestic purpose (Solangi *et al*., 2017; Alanis, 2005). According to PCRWR and survey reports of hospitals, in Sindh province 44% population have deficiency of safe drinking groundwater and therefore become victim of water borne disease (ulcer, liver, hypertension, hepatitis, kidney failure) (Alamgir *et al*., 2016; PCRWR, 2004-2003).

Karachi University and Gulshan-e-Iqbal area of Karachi were selected to monitor the quality of ground, municipal and treated plant water. Study area located in coastal belt of Karachi city, where quality and quantity of water is degrading. Groundwater recharging in area mostly dependent on the rainy season and intimacy of Arabian sea force leading to an increasing trend of salinity here. Available resources in study area are not completely suitable regarding quality and quantity for human health. Groundwater data reflects the urbanization impact and geological interaction, sea water intrusion and over pumping and water logging effects. It is vital to discover the ground and sea water contact particularly in the coastal areas due to the increasing inhabitants Mondal *et al*. (2010).

Quality of groundwater is unsuitable for drinking purpose. Locals mainly acquire water from hydrants or tankers (muncipal supply water) for domestic use. There are many small water treatment plants installed in various parts and supplying de-mineral water. Hutchings and Tarbox (2008). Analytical results show that water samples from treated water plant contained required nutrients and are according to WHO guidelines values and there is no presence of toxic elements. Municipal water is also with in the permissible limit of the WHO guidelines but it is biologically contaminated due to old pipelines and poor management. Chemical parameters in groundwater reflect contact of water with underlying rocks in unsaturated zone and residence time of water in an aquifer Bouchaou *et al*. (2008). Salinity factor of available groundwater data reflects that there is precipitation and geological influence on groundwater composition.

Geologically Karachi city directly sets on folded tertiary strata with a patchy alluvial cover and has both sandy and rocky shoreline. The coastal zone faces several environmental hazards such as difficult foundation conditions, saline water, encroachment, rising sea level and risk of seismic shocks, both offshore and onshore. The city is located on a Malir and Lyari river gravel plain with the neutral harbour in the Arabian sea. Gravelly plain is surrounded by a series of longitudinal hills and valleys, in the north and the north west extending to the coast (Fig. 1).

Stratigraphically, in study area, Rocks type of momani group is found and relating with Nari formation and Gaj formation. Gaj formation is lying over the Nari formation (Table 1).

According to Shah (1977a and b) these group contain dominancy of sea sediments with a few estuarine and fluvatile rudiments in the upper part. Nari formation near base consists of limestone following the sandstone and shale, which in turn is overlain by gypsiferous shale, calcareous sandstone and argillaceous limestone Gaj formation. The Gaj formation of Miocene age is covered by Alluvial. Only Gaj formation is uncovered and exposed in study area and consist of enormous limestone, irregular with fine grained sandstone and conglomerate Shah (1977a and b). It has thickness of about 50 m and exists above the Nari formation of

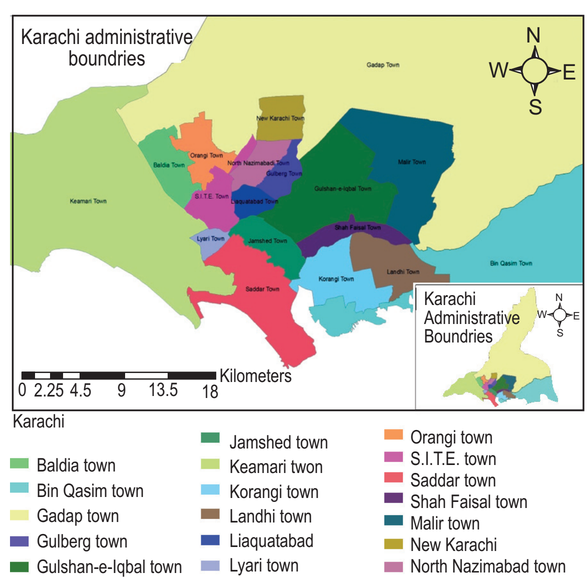

Fig. 1. Administrative boundaries of Karachi.

Table 1. Litho-stratigraphic scheme of the study area (after Ahmed *et al*., 1986)

Epoch	Formation	Unit	Description
Miocene	GAJ	Drigh road clay	Multi-coloured clay with few bands of limestone
		Talawa limestone	Golden thin bedded, sandy, limonitic and fossilierous limestone
		Jhilli stone	Cream white, hard, thick bedded l. stone rich in forams, corals and algae
		Metan clay	Greyish-brown, soft, nodular clay containing thin limestone intercalations
Oligocene	NARI	Orangi sandstone	Multi-coloured ferrogenious sandstone, soft, friable medium to coarse grained, gritty
		Ghoralaki limestone	Cream to light brown, hard, nodular
		Halkani sandstone	Grey to rusty brown, soft, silky sandstone with few thin calcareous bands rich in fossils
		Pirmangho limestone	Dark brown ,thick bedded limestone with yellowish green sandy shale
		Tobo limestone	Grey to brown coloured medium bedded fossiliferous limestone with minor shale

Oligocene age JICA (1981). Rest of the area is covered by recent to sub-recent alluvium material, which largely contains sand, silt and clay. The homogeneity of the sub recent deposits is reasonably more thick, compacted and harder than top alluvium. In Karachi, depth of alluvium deposits is generally 2-25 m. The composition of groundwater is reflected in data as mentioned in lithography Shah (2009). Depositional environment of these Nari and Gaj formations is shallow marine in the former Karachi trough Malkani *et al.* (2017).

Groundwater was encountered in the depth range of 0.76 m to 1.82 m below the existing ground level in all the boreholes and test pits executed at the site at the time of this investigation. However, this may fluctuate due to seasonal and other environmental variations. The topography of the area is plan with no major changes in elevation observed across the site. Fill material was also encountered till highest depth of 3.5 m lower than the existing ground plane shown in Table 2.

Materials and Methods

Description study area. Administratively Karachi is divided in to the eastern and western part (Fig. 2). Study of groundwater was carried out in eastern part. Eastern part is divided into two towns og Gulshan-e-Iqbal and Jamshed town. The study area is located at a distance of 19 km away from the coastal area at 24°55′0″ N to 67°5′0″ E. Different sort of water samples were taken from the surroundings of Gulberg and Gulshan-e-Iqbal which have a semi-arid climate with precipitation of (174 mm). In summer area temperature reaches to 35 °C during rain showering and during dry season the temperature hit the value of 42 °C PMD, (2012).

Table 2. The sub-surface deposits upto the explored depth consist of the following units

Fill material	Clay	Sand
Silt	Sandstone	Limestone
Clay stone	Siltstone	Mudstone

Sampling and laboratory analysis. ***Sample collection.*** Sampling has been carried out by using standard methods randomly, total (22) water samples were collected from different locations of the study area (Fig. 2). Out of 22 water samples the eight (8) samples of groundwater were collected from hand pump, well and tube wells at different locations marked with sample ID as (GW-1 to GW-8) with red dots in map. Ten (10) samples were collected from municipal supplied which marked with sample ID (MW-1 to MW-12) and present on map with sky blue dots (Fig. 3). Two samples were collected from water plant for checking the quality and quantity comparison and these represented with TW-1 and TW-2 sample ID also shows with green dots in location map (Fig. 2).

Method of sample collection and analysis. Plastic bottles with capacity of one litre used for the collection of water samples. These plastic bottles were initially cleaned by detergent and rinsed with diluted hydrochloric acid. After cleaning, the bottles washed with de-ionized water thoroughly and dried. At the time of sample collection from the source these bottles were rinsed

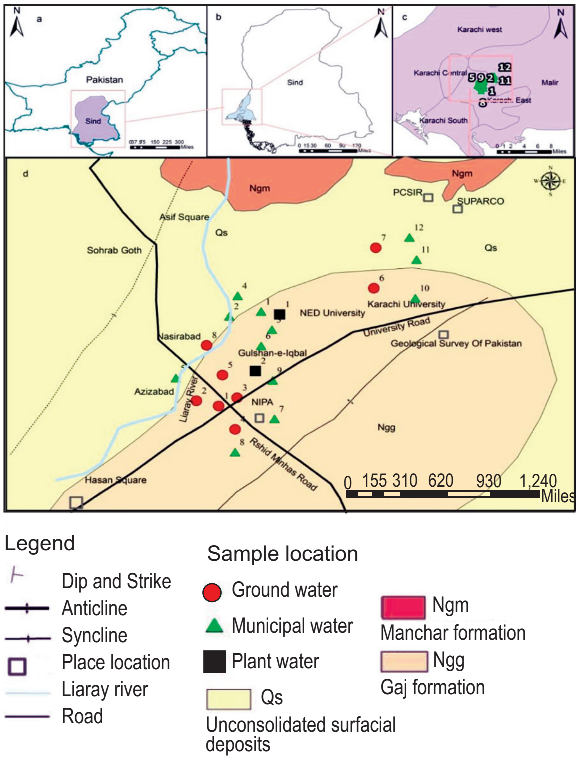

Fig. 2. Location and geological map of study area.

thrice with sample water for the purpose of removal of contamination. Aesthetic characters of water samples (odour, colour and taste) were checked *in-situ*, while other parameters such as temperature, conductivity, TDS were measured by using portable HINNA Calibrated Electrode. Bicarbonate estimated by Argentometric titration method. The analysis of metals sample were acidified and collected in separate plastic bottles. All the major cations (Ca, Mg, Na and K) and anions (chlorides, bicarbonates sulphates and nitrates) and minor elements were analyzed in the lab using standard methods (APHA,1992).Cl was measured by the Argentometric method. The SO_4 measured by Gravimetric method, F is estimated by fluoride electrode and Ca and Mg was determined by EDTA titration method. Description of different elements estimated from study area and its possible natural sources are shown in Table 3.

Results and Discussion

Physio-chemical parameter analysis. Current study appraise the level of groundwater contamination and effect of geological aspect with anthropogenic contamination around Gulshan-e-Iqbal, Karachi for this purpose, physico-chemical analysis were performed for groundwater, municipal water and water treated plant samples. Biological analysis was performed only for municipal water samples and water plant treated sample because their physico-chemical parameters concentration was ~~within the WHO guideline values shown in Table 4-5.~~ Data revealed that the worth of water samples depend on site and supervision of the water resource. Contaminated samples reveal the anthropogenic discharge and geological effect on the properties of groundwater in study area.

pH. The solubility calculation and geochemical equilibrium is an important factor that effect on the value of pH Saalidong *et al*. (2022). The pH values of samples collected from groundwater, municipal supplied water and water treatment plant the pH is from 7.02 to 8.15 and it is laying in permissible limit of WHO. pH values indicate the geochemical processes of constant equilibrium. The pH data is in the range and reflect that rock water interaction process never contribute acidity or basicity.

There is no any such type of mineral or anthropogenic source, which enhances or decreases the pH of water

Table 3. Description of elements and its expected natural sources in study area

Chemical constituents in water	Expected major natural sources
Calcium (Ca)	Feldspars, gypsum, calcite, dolomite, clay minerals
Magnesium (Mg)	dolomite, clay minerals
Sodium (Na)	Feldspars (albite), clay minerals, evapourates such as halite (NaCl)
Potassium (K)	Feldspars (orthoclase and microcline), feldspathoids, some micas, clay minerals
Carbonate (CO_3) and Bicarbonate	Limestone, dolomite
Sulphate (SO_4)	Gypsum, anhydrite
Chloride (Cl)	sedimentary rocks (evapourates)
Nitrate (NO_3)	Atmosphere, plant debris, legumes, animal excrement
Fluoride	Anthropogenic activities

Table.4. Chemical parameters analyzed data of samples (a) groundwater (b) municipal water (c) treated water

Sample ID	EC µS/cm	pH -	TDS mg/L	Hard. mg/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	CO_3 mg/L	HCO_3 mg/L	SO_4 mg/L	Cl mg/L	NO_3 mg/L	F^- mg/L	Alk. m.mol/L	Arsenic ppb	Salinity
(a) Chemical data of ground water samples																	
	NGVS	6.5-8.5	<1000	500	200	150	200	30	NGVS	NGVS	250	250	10	1.5	NGVS	50	
GW-1	7366	7.88	5150	1325	245	112	2512	65.2	Nil	512	578	1012	36	3.04	15	15	1.82833
GW-2	3130	7.25	2003	600	140	61	414	35.5	Nil	330	340	547	18.98	1.09	6.6	10	0.988238
GW-3	2912	7.12	2650	793	194	87	548	45	Nil	476	450	753	33	1.5	8	5	1.360407
GW-4	6712	8.05	4699	1060	312	122	1597	75	Nil	766	502	1312	58	2.03	12	23	2.370325
GW-5	5989	7.85	4192	913	291	102	1278	65	Nil	645	389	1088	46	1.08	10	10	1.965635
GW-6	3460	7.51	2214	450	96	51	582	9	Nil	350	380	687	0.816	1.98	7	0	1.241169
GW-7	1990	7.64	1274	450	112	41	246	11.2	Nil	240	164	415	1.378	0.82	4.8	35	0.74976
GW-8	5340	8.05	3738	905	245	82	532	65	Nil	610	312	1102	45	2.01	12	12	1.990928
(b) Municipal supply water samples																	
MW-1	691	8.15	442	170	36	19	82	6.7	Nil	140	51	103	1.175	0.36	2.8	0	0.186085
MW-2	686	8.12	439	170	36	19	81	6.4	Nil	140	48	105	1.601	0.35	2.8	0	0.189698
MW-3	822	7.74	526	190	40	22	96	7.2	Nil	130	88	125	1.412	0.52	2.6	0	0.225831
MW-4	775	7.83	496	180	40	19	92	6.4	Nil	130	80	120	1.164	0.57	2.6	0	0.216798
MW-5	816	7.64	522	200	40	24	94	6.8	Nil	130	92	125	1.189	0.41	2.6	0	0.225831
MW-6	678	7.83	434	170	36	19	81	6.5	Nil	130	53	105	1.24	0.32	2.6	0	0.189698
MW-7	701	7.72	449	170	32	22	81	6.3	Nil	140	54	103	1.091	0.32	2.8	0	0.186085
MW-8	696	7.82	445	170	32	22	80	6.5	Nil	140	51	105	1.2	0.48	2.8	0	0.189698
MW-9	638	7.74	408	150	32	17	74	5.3	Nil	130	56	90	1.276	0.41	2.6	0	0.162599
MW-10	698	7.55	447	170	40	17	82	6.9	Nil	140	55	105	1.182	0.29	2.8	0	0.189698
MW-11	695	7.64	445	170	40	17	81	6.1	Nil	140	53	103	1.182	0.51	2.8	0	0.186085
MW-13	696	7.65	445	170	40	17	80	6.6	Nil	140	55	105	1.117	0.4	2.8	0	0.189698
(c) Water treated plants samples																	
TW-1	338	7.76	216	100	20	12	29	3.3	Nil	40	13	78	1.492	0.11	0.8	0	0.140919
TW-2	378	7.61	242	110	24	12	35	2.8	Nil	80	17	60	1.931	0.35	1.6	0	0.108399

in study area. Statistically, the pH is independent and not effected by anion and cations concentration. There is no positive correlation of pH with measured parameters (Table 8). The values less than 6.5 or more than 8.5 can impair the portability of drinking water Saalidong *et al*. (2022). For example, toxicity of cyanides and sulphides increases with decrease in pH and ammonia becomes more toxic with increase in pH Rattner *et al*. (2003). Hence, occurrence of slightly alkaline pH means pH=7.7 in groundwater samples, municipal supply water and water treated plant samples favour its use for drinking purpose.

Electrical conductivity (EC). groundwater purity and quality can be evaluated with the electrical conductivity and also reflect concentration of total ion dissolved in water due to anthropogenic intensity, soil interaction and rock water interaction. The average electrical conductivity values in study area are as under in Table 6.

The average groundwater EC value is greater than the limit as prescribed by WHO (<1000 mg/L). It is related with elevated concentration of ionic salts exists in the water body and cannot be used for irrigation purposes because of high ionic salts. The Average EC value of municipal supplied water samples is laying in permissible limit of WHO but biologically not fit for drinking purpose (Table 4 and 5) and not used for drinking purposes. Statistically among the electrical conductivity and total dissolved substance a strong and positive relation is found (Fig. 3). The average EC value of water samples collected from water treatment plant is 358 μS/cm, not biologically contaminated and also safe for drinking purpose (Table 5 and 6).

Table 5. Biological analysis of Muncipal and water treated plants from study area

Sample no. Unit Permissible limits	Total coliform cfu/mL 0/100mL	*E. coli* cfu/mL 0/100 mL	Remarks
MW-1	3	0	Unfit
MW-2	25	0	Unfit
TW-3	0	0	Fit
MW-4	21	1	Unfit
MW-5	19	0	Unfit
MW-6	4	0	Unfit
MW-7	73	2	Unfit
MW-8	12	0	Unfit
MW-9	62	0	Unfit
TW-10	0	0	Fit

Table 6. Average value of electrical conductivity

treated	Ground water	Municipal supply water	Water plant water
Electrical conductivity μS/cm	4612.375	716	358

Total dissolved solids (TDS). Total dissolved solids are related to total dissolved substance that leached to groundwater bodies due to interaction with the soil, rocks. Water having TDS more than 500 mg/L is not suitable for intake. TDS values of groundwater is above than the permitted limits. Sources of soluble salts in groundwater may be accredited to suspension of mineral deposits from foundation rock Raju *et al*. (2012) and Hynes (1983). The groundwater is highly mineralized and containing toxic elements and biological contamination, it is not suitable for drinking purpose. High TDS depicts sea water control as incorporation of seawater with groundwater disturbs the hydro-geochemistry by rising TDS Rani and Bahu (2008). This water may be used after treatment. Low recharge of aquifers due to inadequate rainfall and the re-treating rivers also causes seawater intrusion. Since groundwater is not over abstracted by the dwellers of study area the latter phenomenon is more possible for the seawater intrusion in the coastal parts of Karachi. categorization of collected samples on TDS criteria revealed in (Table 7). TDS is usually estimated from EC, which necessitates the discovery of highly significant relationships between the two. Statistically TDS have direct relation with conductivity and total number of ions (Fig. 3).

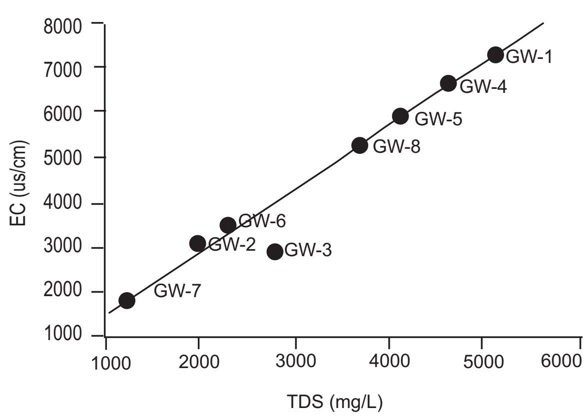

Fig. 3. Relationship between EC and TDS.

Table 7. Classification of water samples based on TDS (Robinove, Langford and Brookhart, 1958)

Classification of groundwater	Total dissolved solids (ppm)	No of samples/ type of samples
Non saline	< 1000 ppm	14 Collected from munciple water and treated water plant
Slightly saline	1000-3000 ppm	4 Groundwater samples
Moderately saline	3000-10,000 ppm	4 Groundwater samples

Total alkalinity. Alkalinity predicts presence of the usual salts in water. The source of alkalinity is the occurrence of minerals, which liquefy in water from soil. Alkalinity causing ions in groundwater are bicarbonate, hydroxide, phosphate and organic compounds Malkani *et al*. (2017). In study area, alkalinity of the groundwater is greater than the alkalinity of samples obtained from them municipal supplied water and its reason is removal of the dissolved ions and which is causing the alkalinity. Alkalinity values are much less than the values of total hardness, impartial salts of calcium or magnesium such as sulfates and chlorides may be present because of the intrusion of sea water. Data shows presence of halite, sand stone and clay minerals in study area. Graphical studies show that there is strong positive correlation of alkalinity with hardness (Fig. 5).

Total hardness. Hardness boosts the boiling point and decreases the lather development with soap (Yadav *et al*., 2012; Patil and Patil, 2010). Hardness of samples which are taken from groundwater is greater than hardness of the municipal supplied water and treated plant water respectively. Values of total hardness is maximum in groundwater samples and higher from permissible border approved by WHO. Municipal and treated plant water falls in the WHO range. Statistically, Ca^{2+} and Mg^{2+} are the key constituents and accountable for the raise in hardness shown in Fig. 4 and 6 and hardness have positive correlation with bicarbonate (Fig. 7) and with sulphate (Fig. 8). It shows the groundwater interaction with the carbonate minerals e.g. lime stone, dolomite and calcite Basavarajappa and Manjunatha (2015). The deep aquifers of study area occur in the nearest Karachi coastal areas and the excessive amount of Ca and Mg are incorporated by carbonate rocks and seawater or could be contributed from the calcareous soil and limestone in sub surface Naeem, (2015). In the study area there is dominance of calcite over the dolomite because the ratio of Ca/Mg (>1) Rafi *et al*. (2019). Litho-stratigraphic scheme indicate that aquifers are overlain by the limestone units (Table 1). Suspension of Ca and Mg in the groundwater ultimately increases the hardness in the aquifers of study area.

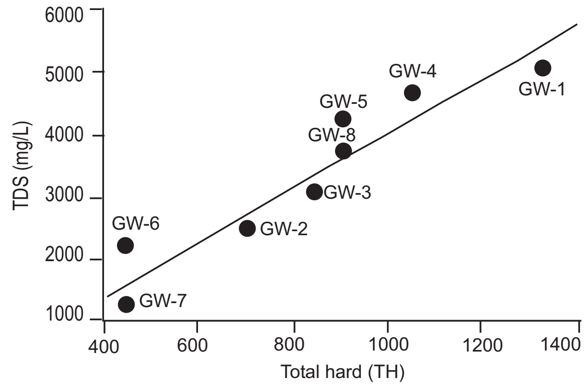

Fig. 4. Relationship between TDS and hardness.

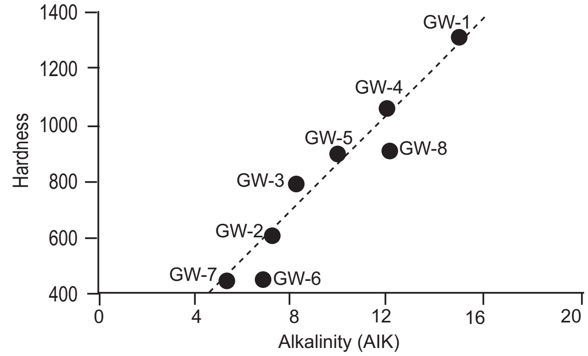

Fig. 5. Relationship between hard and alkalinity.

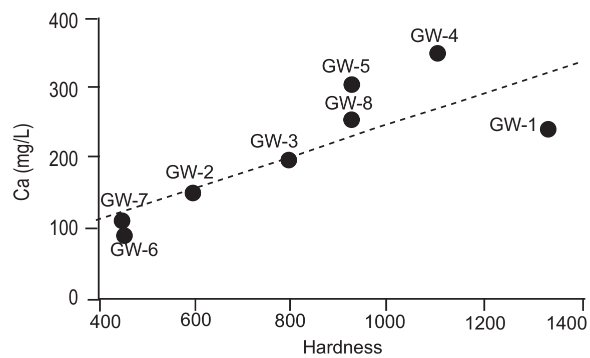

Fig. 6. Relationship between hardness and calcium.

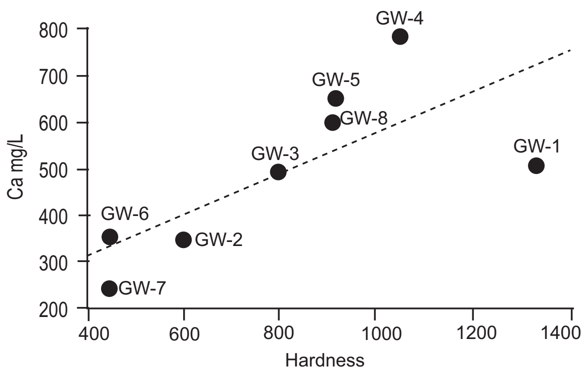

Fig. 7. Relationship between bicarbonate and hardness.

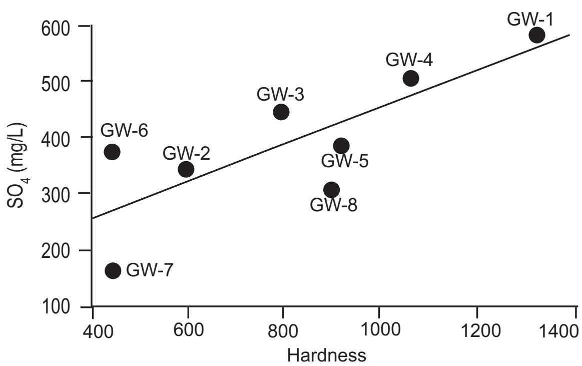

Fig. 8. Relationship between hardness and SO_4.

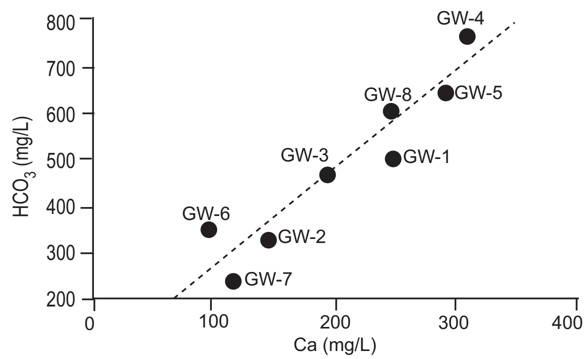

Fig. 9. Relationship between Ca and HCO_3.

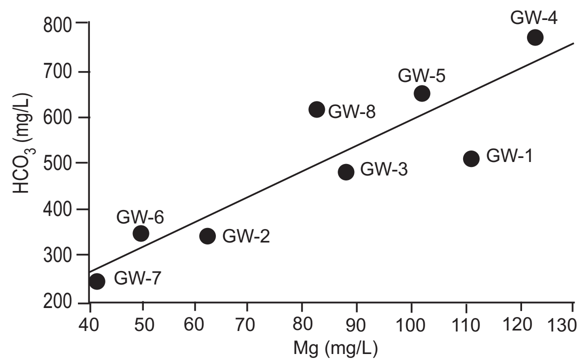

Fig. 10. Relationship between Mg and HCO_3.

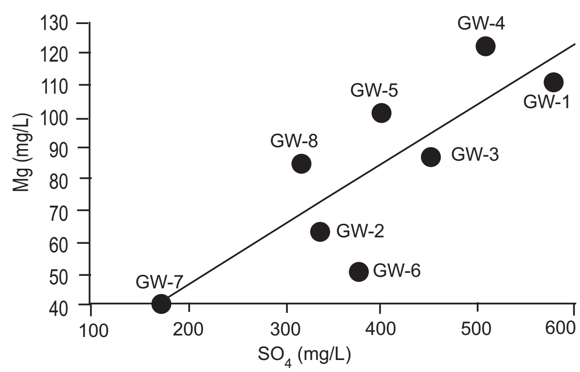

Fig. 11. Relationship between Mg and SO_4.

Calcium and magnesium. Calcium and magnesium in groundwater is crossing the WHO limits and increasing the total hardness of groundwater. However, their values in municipal supply and water treated plant samples are within the permissible limits. Different kind of rocks in sub surface, industrial waste and manure are possible sources. Values of calcium and magnesium varied, ranges from 96 to 312 mg/L and from 41 to 122 in groundwater samples. In municipal water calcium ranges from 20 mg/L to 40 mg/L and Mg from 17 mg/L to 24 mg/L, whereas in water-treated plant, it is about 12 mg/L. Statistically calcium and Mg have positive correlation with total hardness shown in (Fig. 6) and strong correlation with bicarbonate shown in (Fig. 9, 10 and 11). Correlation of magnesium with sulphate shown in (Fig. 12) and chloride shown in (Fig. 13) for Ca and Mg ion in water samples.

Sodium, potassium and chloride. Sodium, potassium and chloride concentration is highly variable in groundwater, municipal supplied water and in treated plant water. Source of chloride, sodium, calcium, magnesium in groundwater are usually from the dissolution of NaCl, $CaCl_2$ and $MgCl_2$ salts coming from sea water intrusion and carbonate rocks interaction. Concentration variation in chloride is due to evapourite dissolution. Bikundia and Mohan (2014), sub-surface salt domes intrusion of seawater are possible sources of high chloride content.

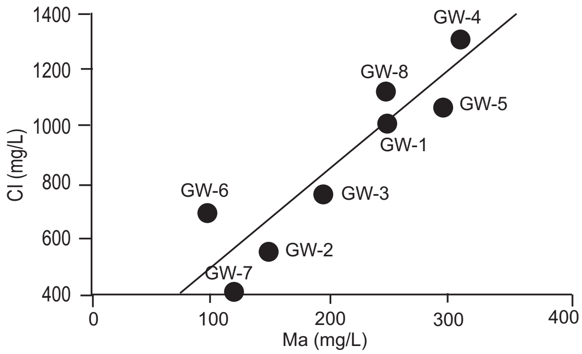

Fig. 12. Relationship between Ca and Cl.

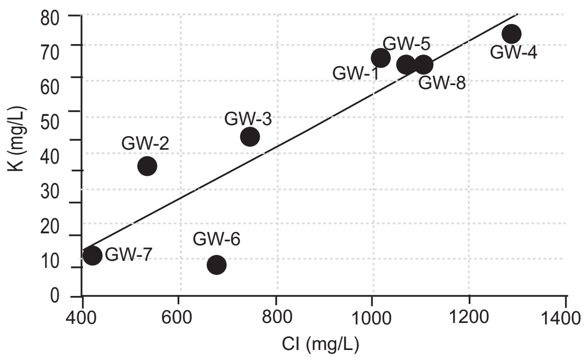

Fig. 13. Relationship between K and Cl.

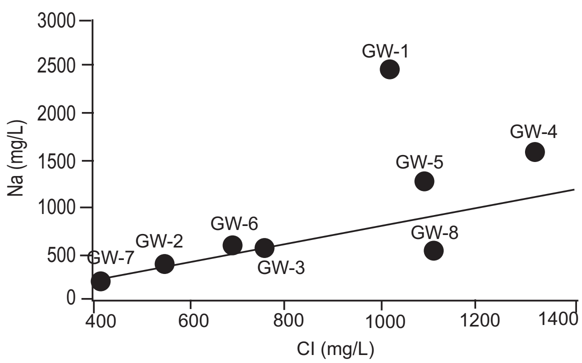

Fig. 14. Relationship between Na and Cl.

Study area is nearest to coastal area of Arabian sea and sodium content in the groundwater is contributed by the active and ancient seawater intrusion Rafi *et al.* (2019). Values of sodium, potassium and chloride in groundwater sample, crossing the WHO level. There is positive correlation of Ca and chloride (Fig. 12), potassium and sodium with Cl (Fig. 13 and 14). There is weak correlation of K with SO_4 and NO_3 describe in

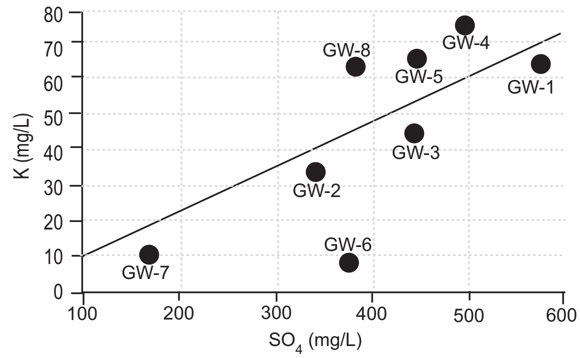

Fig. 15. Relationship between K and sulphate.

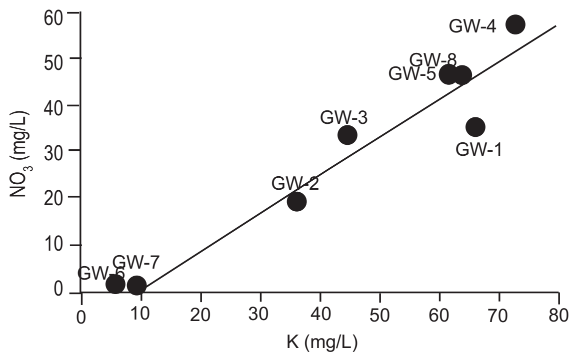

Fig. 16. Relationship between K and NO_4.

Fig. 15 and Fig. 16, coefficient correlation between different parameters of water samples is shown in Table 8.

Hydro geochemical evaluation. Groundwater classification is studied graphically by Piper diagram using the hydro-geochemical parametrs Piper (1944) and Bashir *et al*. (2017). The Piper diagram was generated using the data to evaluate the type of hydro facies, mixing of different water source and salinity intrusion Korfali and Jurdi (2015). Diagram reflects mostly sample are lying in the Na+ K and Cl water type category. There is dominanacy of alkalies (Na+K) over the alkaline (Ca+Mg) Fig. 17. The presence of the anions of the sample along sulphate and chloride faces in Piper diagram reflect strong acid anions (SO_4+ Cl) dominance over the weak acidic anions (HCO_3 + CO_3). The dominancy of Na-Cl indicate the sea water intrusion in study area (Korfali and Jurdi, 2015; Rani and Bahu, 2015; Demetriades, 2010).

Ionic interrelationships. Certain ionic sources in groundwater can be categorized with finding the ratio

Table 8. Coefficient correlation between groundwater parameters

		Correlation coefficient									
		pH	Ca	Cl	SO_4	TDS	Mg	Na	K	HCO_3	NO_3
pH		1	0	0	0	0	0	0	0	0	0
Ca	mg/L		1	0.93	0.567	0.892	0.935	0.648	0.966	0.954	0.973
Cl	mg/L			1	0.626	0.916	0.892	0.646	0.899	0.978	0.913
SO_4	mg/L				1	0.78	0.813	0.823	0.62	0.575	0.569
TDS	mg/L					1	0.941	0.879	0.899	0.854	0.839
Mg	mg/L						1	0.809	0.931	0.893	0.914
Na	mg/L							1	0.653	0.549	0.543
K	mg/L								1	0.91	0.978
HCO_3	mg/L									1	0.954
NO_3	mg/L										1

Table 9. Ratio of Ions for prediction of sea intrusion in groundwater

Ca	Mg	Ca/Mg	Na	Cl	Na/Cl	Cl	HCO_3	Cl/HCO_3	Cl	SO_4	Cl/SO_4
245	112	2.18	2512	2012	1.24	2012	512	3.92	2012	578	3.480969
140	61	2.29	414	547	0.75	547	330	1.65	547	340	1.608824
~~194~~	~~87~~	~~2.22~~	~~548~~	~~753~~	~~0.72~~	~~753~~	~~476~~	~~1.58~~	~~753~~	~~450~~	~~1.673333~~
312	122	2.55	1597	1312	1.21	1312	766	1.71	1312	502	2.613546
291	102	2.85	1278	1088	1.174	1088	645	1.68	1088	389	2.796915
96	51	1.88	582	687	0.84	687	350	1.96	687	380	1.807895
112	41	2.73	246	415	0.59	415	240	1.72	415	164	2.530488
245	82	2.98	532	1102	0.48	1102	610	1.80	1102	312	3.532051

between major ions have been sorted. Summary of these ratios given in (Table 9). Concentration ratios of an ion with reference to other ions are linked to the aquifer (host rock). Statistical relationship in groundwater data also predict the rock water interaction, the grade of replenishment of groundwater or its incorporation with seawater Park *et al*. (2008).

Ca/Mg. Fresh water is categorized by the dominancy of Ca^{2+} and seawater with dominancy of Mg^{2+} Mondal *et al*. (2010). The ratio of Ca/Mg in all samples give a picture of seawater intrusion in study area.

Na/Cl. Na and Cl dominancy in groundwater reflect the seawater effect *via* direct combination or by marine salt Patil and Patil (2010). The ratio between Na and Cl is greater than one it designate that there is no single source of Na and Cl. Greater ratio point out that aquifer is probably polluted by the seawater intrusion Park *et al.* (2008).

HCO_3/Cl. HCO_3 and chloride ratio is observed in less amount in study area.Less ratio of HCO_3/Cl than the Ca/Mg ratio specify the alteration of fresh groundwater in brackish water Mondal *et al*. (2010).

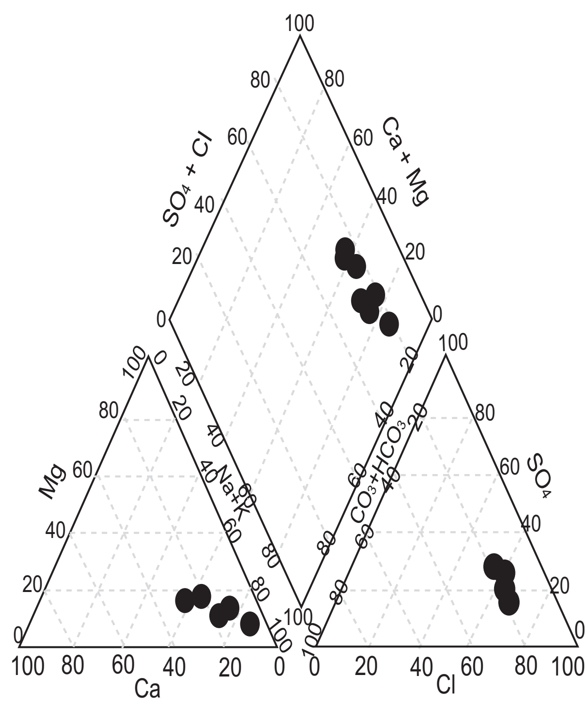

Fig. 17. Piper diagram of groundwater samples from Gulshan-e-Iqbal and its surroundings.

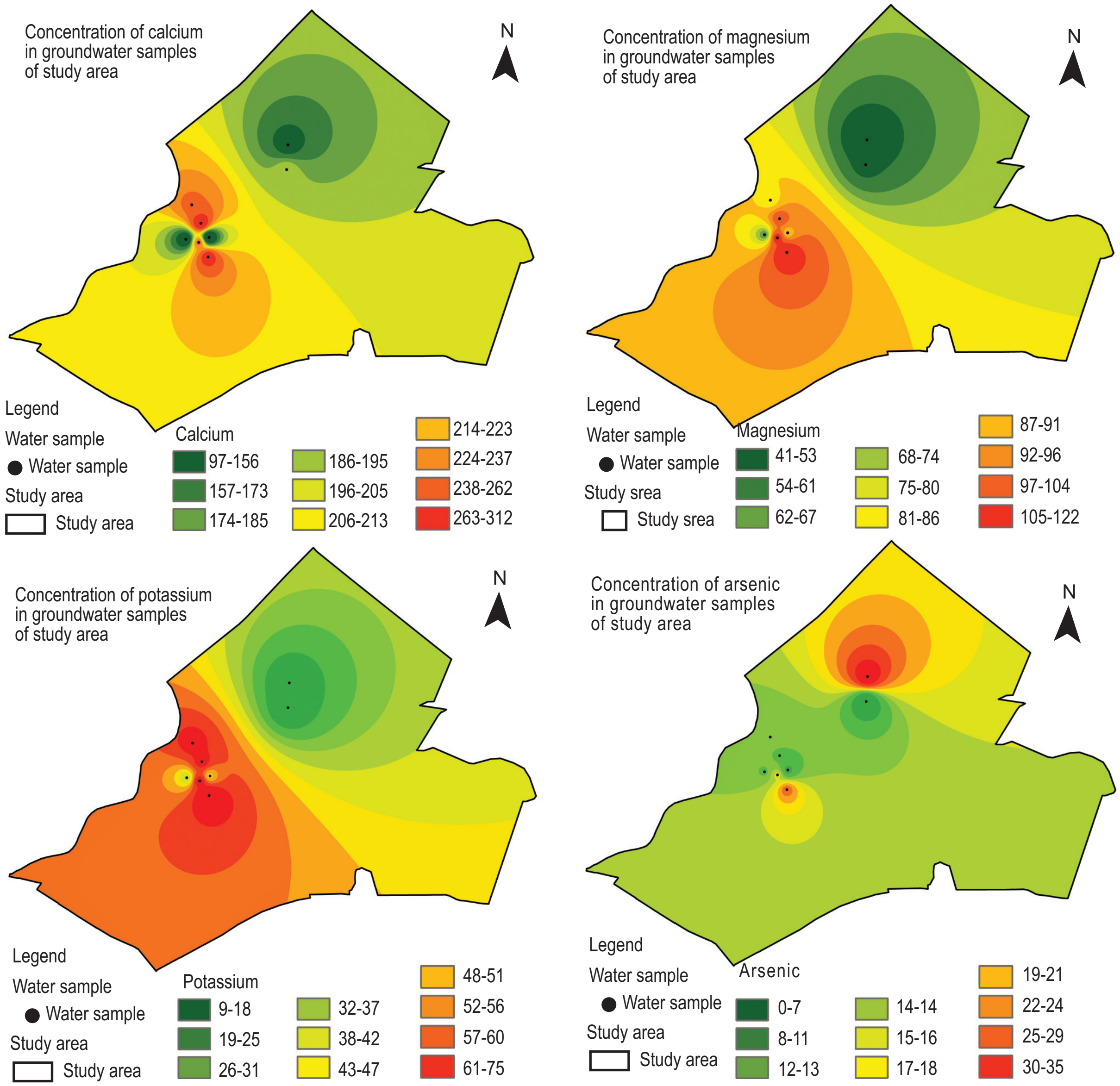

Fig. 18. Spatial distribution of Ca, Mg, K and As.

Cl/SO_4. There is another factor for differentiation of seawater from the fresh water that is sulphate content. The excess of sulphate in fresh water is higher as compare to seawater and marine water contains very high absorption of chloride as compared to fresh water. The Cl/SO_4 ratio is extremely high which is 3.532051 and clearly specifies the role of sea water intrusions as explained by other workers somewhere else Park *et al.* (2008).

Impurities concentration due to crossing the WHO limit in groundwater samples through interpolation technique has shown in Figs. 18 and 19.

Conclusion and Recommendations

Quality and quantity of groundwater is threatened with the unnecessary utilization of natural resources due to urbanization, construction of new societies and industrial growth. Some substances like arsenic, find their way naturally in to the groundwater which is carcinogen for health. Study reveals that quantity and quality of groundwater completely unfit for because it is crossing the limits of WHO guide line values such as Na, Cl, SO_4,, Ca, Mg, hardness, TDS and EC. Municipal supply water is close within the range of WHO guideline values but it is biologically contaminated. It contains microbes,

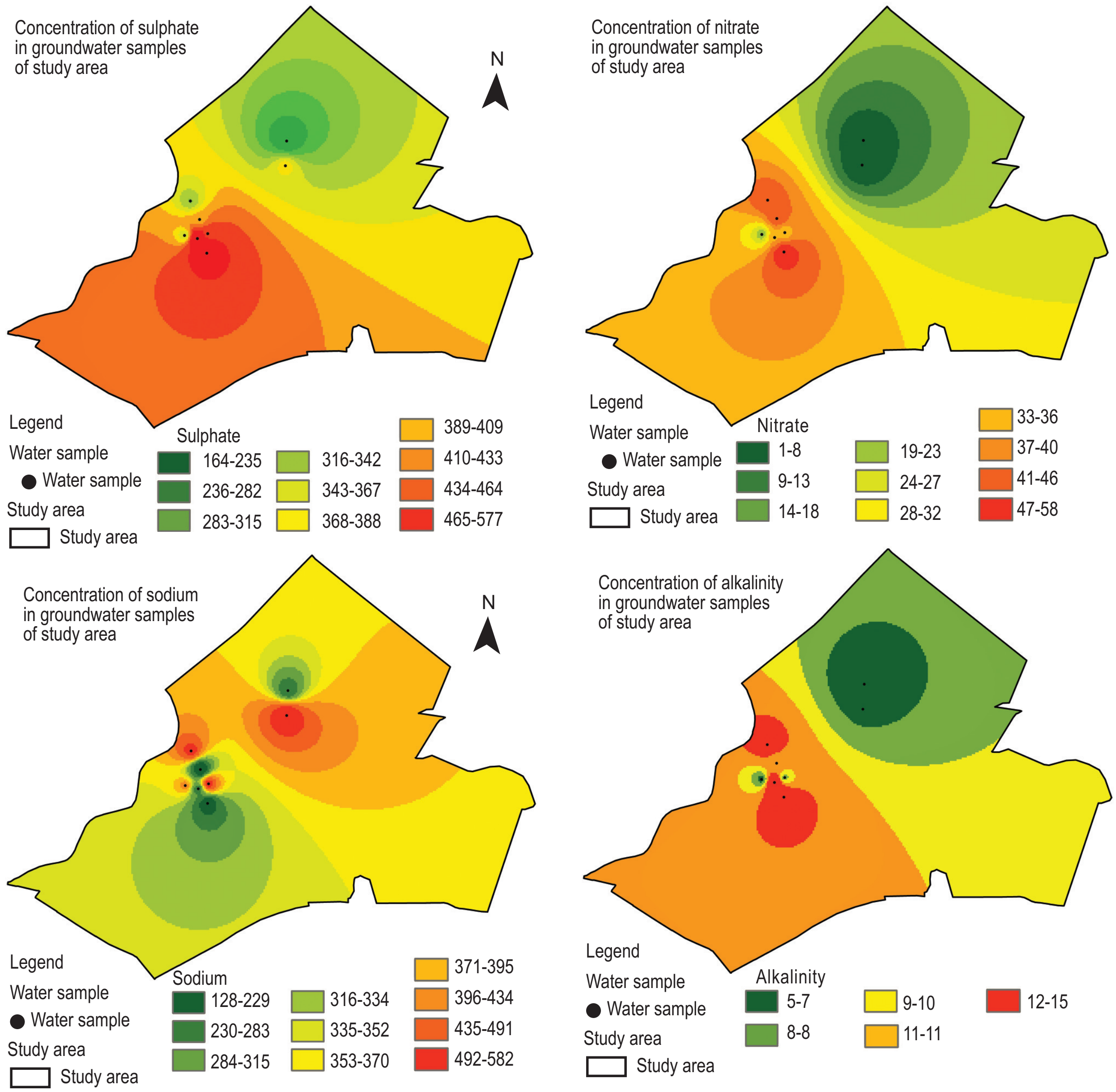

Fig. 19: Spatial distribution of SO_4, NO_3, HCO_3 and As.

poisonous and physiologically surplus biological substances and causing pathogenic disease. Hence, groundwater needs physical, chemical and biological treatment, according to WHO standards depending on the chemical composition. Existing pollutants and biological microbes in groundwater are now a day's treated in private water plants containing osmo-memberane and resin with ultra violet light.

It is suggested that constantly control and monitoring of the quality of water is must to ensure the healthy life. Groundwater resources protection in study area is challenge for the government and also it is a universal problem. This problem can be managed with cooperation between governmental and non-governmental organizations.

Conflict of Interest. The authors declare that they have no conflict of interest.

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