

## Water Quality Degradation of Al-Mukalla Groundwater Aquifer/Yemen

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**Abstract:** This study investigates the natural and anthropogenic processes that influence the chemistry of groundwater within the Al-Mukalla Aquifer. Seventeen ground water samples were collected during August 2010 from different fields around Al-Mukalla City and analyzed for their physico-chemical constituents. The groundwater in the study area falls under brackish water type (TDS > 1000 mg/l). The order of major cations are Ca > Mg > Na > K. The total hardness (TH) as CaCO<sub>3</sub> ranges from 623 to 1168 mg/l. Water with TH greater than 80 mg/l cannot be used for domestic purposes. In the study area there are two groundwater facies: earth alkaline type water in the first nine wells and alkalis in the other wells. These groundwater types in the study area is predominately indicative of the lithology of aquifer and the role of evaporation in the water composition as the loss by evaporation results in the transfer of salts from soil water to the soils. The saturation Indices of groundwater lie under saturation degrees except saturation Indices of dolomite. The study area has high to very high salinity with low sodium water types, which need adequate drainage to overcome salinity problems for irrigation purposes.

**Key words:** Groundwater Quality (GWQ) • Groundwater • Al-Mukalla • Yemen

### INTRODUCTION

Yemen is a developing country with limited drinking water supplies. Like most of the Arabian Gulf countries, Yemen depends on groundwater as the main source of water supply for domestic needs [1]. Surface and groundwater quality assessment is a major issue having profound impact on our lives. The major ionic components present in natural waters are generally considered to come from two main sources. One of these is atmospheric, with ions dissolving in rainwater and the other is a result of the weathering of soils and base rocks in the catchment [2]. The transport of aqueous phase contaminants depends on the permeability of in-situ rocks, the geological setting of the hydrogeology of the area.

The water quality is affected by both macro and micro scale factors. Macro scale factors include climate, landscape and parent material of the area, while micro scale factors include land use and management at field or farm level. Past studies have indicated that there is a strong relationship between land use and quality of both surface and ground water in the area [3]. Uncontrolled hazardous waste sites are major environmental and public health concerns in many countries. Groundwater pollution is one of the most common environmental problems nowadays [4]. Leachates from landfills and uncontrolled industrial effluents disposal cause significant deterioration in the water quality of many aquifers throughout the world [5, 6].

The rapid and growing agricultural, industrial and municipal development in and around Al-Mukalla city

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lead to substantial accumulation of toxic matter and a significant environmental impact has been imposed on the ambient conditions. Water quality investigations are carried out to provide information on the health of water bodies and for developing strategies that help in better management of catchment and water resources [7].

This study was therefore designed to investigate the natural and anthropogenic processes that influence the chemical composition of groundwater.

## MATERIALS AND METHODS

Groundwater samples were collected from seventeen representative open wells during August 2009 from different fields around Al-Mukalla City (Fig. 1). Temperature, electrical conductivity (EC) and pH were measured using digital meters immediately after sampling. Water samples collected in the field were analyzed for chemical constituents such as Na, K, Ca, Mg, Cl, HCO<sub>3</sub>, SO<sub>4</sub>, NO<sub>3</sub> and fluoride using recommended methods of analysis as suggested by the [8] at the Laboratory of marine pollution, faculty of environmental sciences and marine biology, Hadhramout University and the local water and sanitation authority. The accuracy of the chemical analysis was verified by calculating ionic balance error, which is generally with 5%. Quality-assurance was used to evaluate potential contamination problems and included replicate, field blank and Laboratory blank. The Piper diagram and salinity diagram were constructed using Aquachem Scientific Software (AquaChem 4). The PHREEQC 2.8 was used to calculate saturation Indices [9].

**Description of the Study Area:** Al-Mukalla city is the capital of Hadhramout Governorate. The study area is located in the north east of Al-Mukalla city between latitude 14.29 °N and 15°N and longitude 49°E and 50°E (Fig.1). Water supplies of the study area are based on groundwater abstraction from Jeza Formation (Quaternary aquifer). This groundwater is used as an essential source for drinking water, agricultural irrigation and industrial usages. The topography is generally low-lying with elevations ranging from sea level to about 200 m. The region is located within the arid belt with a humid climate. The average monthly relative humidity is about 70%. Rainfall distribution is typically bimodal with about 80% of rainfall recorded between July and September. The average annual rainfall is 50 mm. The mean temperature for the hottest months (April/July) is 38.5°C while that of the coolest month (January) is 20°C. Agriculture is not the main occupation of the inhabitants of this area. It is also home to numerous oil exportation, fishery and a seaport. Along the Aden Gulf coast there are a few narrow basins that open to the sea and present rift filled with Oligocene-Quaternary series. Al-Mukalla is one of these basins. The major aquifers in this study area are made up from the Quaternary series filling the wadis. The upper aquifer consists of Quaternary sands and gravels. Generally, the Quaternary alluvial (Jeza Formation) are the main source of groundwater for Al-Mukalla water supply. This aquifer is in parts underlain by the upper Oligocene-Miocene series [10]. The lower aquifer consists typically of limestone and shale interbeds. High Ca, Na and SO<sub>4</sub> [11]. The occurrence of groundwater is controlled by a fissure-flow system,

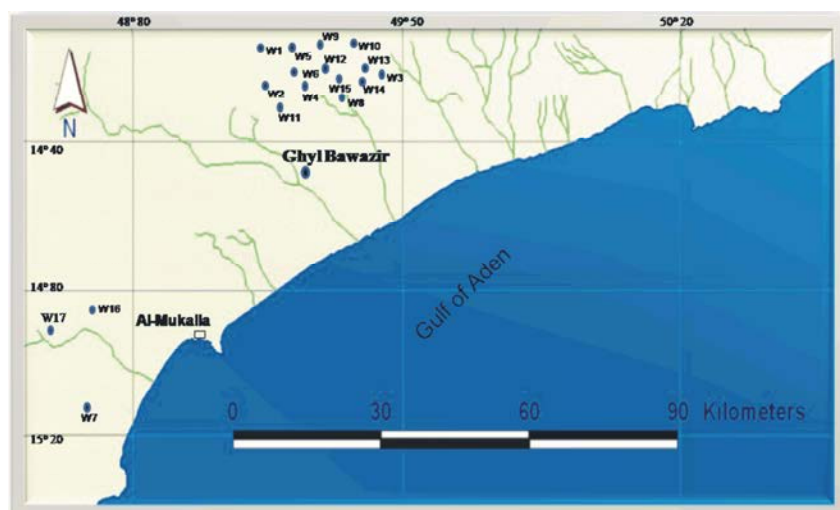


Fig. 1: Location map of the study area.

which determines the movement of water throughout the variously developed karst structures. Recharge of the hydrogeological system originates from precipitation, which is estimated to be up to 250 mm/year. Falling on the heavily fractured Jawl plateau infiltrates into Paleocene Um-er-Raduma limestone. Groundwater movement through the underlying less permeable Eocene strata is enhanced by the presence of strike-slip cross faults [11].

The groundwater body commences its flow southward. The surface catchment area stretches for about 20 km north Al Naga'a area. Agriculture and untreated wastewater have both indirect and direct effects on the quality of ground waters and are one of the key activities causing water quality degradation in the study area. Yemen still utilizes amounts of some organochlorine pesticides, such as DDT, dieldrin, HCB and heptachlor. Hence, they were generally found in marine organisms and shore sediments in the Gulf of Aden coast, but at low concentrations. The pesticides used in those areas contain a wide range of chemical compounds. Phosphoric pesticides are the highest percentage (40%). Pyrethroidic, carbonic and mylathion pesticides account 30, 20 and 24% respectively of the total pesticides used. Hexachlorocyclohexanes (HCH) was less than 0.5% [1].

## RESULTS AND DISCUSSION

**Groundwater Chemical Composition:** The results of analysis of the groundwater samples are presented in Table 1. The pH values of groundwater samples range

from 7.3 to 7.9 with an average value 7.6, while the field temperature varies between 26°C to 30°C with an average 27.9°C. Electrical conductivity (EC) indicates the amount of materials dissolved in water and its values of the studied samples range from 1672 to 2670  $\mu\text{S}/\text{cm}$  with an average value of 2172  $\mu\text{S}/\text{cm}$ . TDS range from 1049 to 1623 mg/l. All of the TDS values obtained in the study area are beyond the permissible limits (WHO, 1997), making the water unsuitable for various domestic activities. The groundwater in the study area falls under brackish water type (TDS > 1000 mg/l) [12].  $\text{SO}_4$  is the dominant anion followed by  $\text{Cl}$ ,  $\text{HCO}_3$  and  $\text{NO}_3$ .  $\text{SO}_4$  constitutes 49-75% of the equivalent of the anions in the samples. It ranges from 420 to 960 mg/l. The high values of  $\text{SO}_4$  reflect the lithology of the study area and increasing the weathering and dissolution of  $\text{SO}_4$  bearing minerals.  $\text{SO}_4$  is unstable if it exceeds the maximum permissible limit of 400 mg/l and causes a laxative effect on human system with the excess Mg in groundwater [13]. All the studied samples have  $\text{SO}_4$  concentration exceed the maximum permissible limit. The concentrations of  $\text{Cl}$ ,  $\text{HCO}_3$  and  $\text{NO}_3$  lie between 136 to 276, 120 to 256 and 2.5 to 43 mg/l in respective order. They fall within the maximum permissible limit for drinking as per the WHO international standards. Among the cations, the concentrations of Na, K, Ca and Mg ions ranged from 78-115, 8-18, 140-245 and 36-136 mg/l, respectively. Ca is a dominant cation. The order of abundance is  $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$ . The total hardness (TH) as  $\text{CaCO}_3$  ranges from 623 -1168 mg/l. water with TH greater than 80 mg/l cannot be used for domestic

Table 1: The results of analysis of the groundwater samples in the study area

Samples	T °C	pH	E.C	TDS	F	$\text{NO}_3$	CL	$\text{SO}_4$	$\text{HCO}_3$	Ca	Mg	Na	K	TH
W1	28.00	7.50	2551.00	1562.78	1.72	3.10	275.50	745.30	208.20	215.60	126.75	83.63	8.80	1061
W2	27.00	7.40	2269.00	1387.20	1.72	3.20	220.00	718.10	120.00	140.00	120.00	115.00	10.90	844
W3	27.00	7.84	2131.00	1336.60	1.65	5.10	210.30	680.00	127.00	160.00	100.90	105.00	11.80	815
W4	28.00	7.78	2370.00	1511.10	1.75	3.00	160.60	853.40	126.00	215.00	125.60	79.20	11.30	1054
W5	29.00	7.50	2230.00	1441.70	1.71	2.50	159.20	810.00	155.20	145.00	136.70	96.00	14.70	925
W6	28.00	7.52	2670.00	1623.80	1.75	3.20	139.60	960.80	164.00	224.50	110.80	90.00	12.90	1017
W7	27.00	7.9	2550.00	1606.10	1.33	3.30	245.70	820.00	160.00	224.80	130.00	91.00	11.30	1097
W8	26.00	7.82	2656.00	1590.60	1.44	5.10	239.80	776.00	196.00	245.00	135.00	78.90	12.80	1168
W9	29.00	7.73	2421.00	1557.07	1.53	3.30	160.50	870.50	178.00	202.24	124.23	94.80	12.50	1017
W10	28.00	7.72	2341.50	1468.10	1.58	3.70	135.90	840.00	170.00	179.40	116.60	96.00	11.50	928
W11	29.00	7.43	2202.00	1436.50	1.80	4.70	150.00	808.00	150.00	178.90	105.90	97.00	17.00	883
W12	30.00	7.44	1686.00	1058.00	0.99	2.80	160.00	505.00	150.00	160.00	55.20	88.00	12.00	627
W13	28.00	7.3	1793.00	1107.10	0.95	3.70	170.00	530.00	150.00	170.00	56.40	87.00	15.00	657
W14	27.00	7.3	1786.00	1049.20	0.68	5.10	172.00	420.00	256.20	160.00	60.00	88.00	16.00	647
W15	27.00	7.52	1672.00	1073.10	0.97	32.60	160.00	450.00	207.00	190.00	36.00	87.00	14.00	623
W16	28.00	7.53	1813.00	1179.92	0.99	35.10	182.00	489.00	246.44	176.00	64.60	96.00	14.00	706
W17	28.00	7.72	1794.00	1147.86	0.92	43.40	179.00	470.00	202.52	188.00	55.20	93.00	18.00	697

Units mg l/l except pH, T (°C), EC ( $\mu\text{S}/\text{cm}$ ).

Table 2: Saturation Indices and SAR of groundwater samples in the study area

Samples	SI anhydrite	SI calcite	SI dolomite	SI fluorite	SI gypsum	SI halite	CA-I	CA-II	SAR	Na%
W1	-0.9	0.5	1.1	-0.48	-0.66	-6.3	0.56	0.23	1.1	15.4
W2	-1	0.02	0.33	-0.62	-0.8	-6.2	0.24	0.09	1.7	23.8
W3	-0.99	0.5	1.2	-0.58	-0.77	-6.3	0.284	0.10	1.6	23
W4	-0.8	0.6	1.3	-0.46	-0.61	-6.6	0.304	0.07	1.1	15
W5	-0.98	0.26	0.8	-0.67	-0.78	-6.5	0.154	0.03	1.4	19.7
W6	-0.75	0.45	0.9	-0.45	-0.55	-0.66	0.09	0.01	1.2	17.3
W7	-0.83	0.8	1.7	-0.68	-0.61	-6.3	0.479	0.16	1.2	16.2
W8	-0.82	0.85	1.7	-0.56	-0.6	-6.4	0.54	0.19	1	13.9
W9	-0.83	-0.6	1.5	-0.62	-0.63	-6.5	0.16	0.03	1.3	17.9
W10	-0.88	0.5	1.3	-0.62	-0.68	-6.4	-0.01	-0.002	1.4	19.4
W11	-0.88	0.26	0.6	-0.5	-0.68	-6.5	0.10	0.02	1.4	20.9
W12	-1	0.3	0.5	-0.98	-0.83	-6.5	0.22	0.07	1.5	24.8
W13	-1	0.16	0.2	-0.97	-0.8	-6.4	0.29	0.10	1.4	24.1
W14	-1.12	0.36	0.65	-1.27	-0.91	-6.4	0.29	0.11	1.5	24.7
W15	-1	0.5	0.7	-0.87	-0.8	-6.5	0.24	0.08	1.5	25
W16	-1.1	0.6	1.1	-0.94	-0.84	-6.4	0.25	0.09	1.6	24.3
W17	-1.02	0.7	1.3	-0.96	-0.82	-6.4	0.3	0.1	1.5	24.4

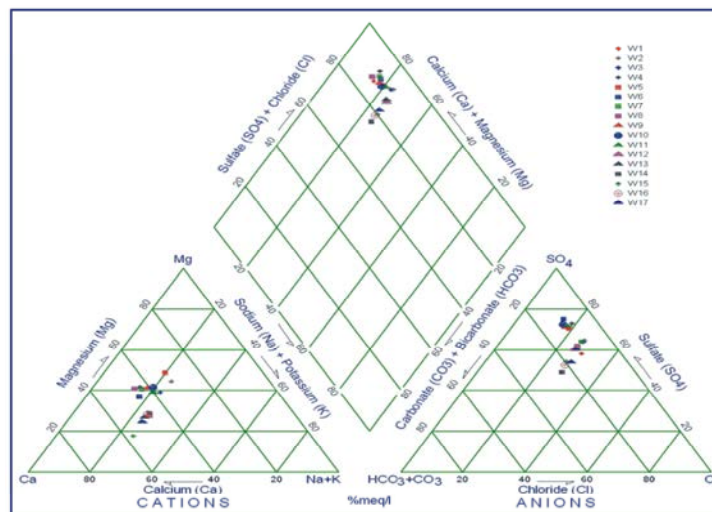


Fig. 2: Chemical analyses of the studied wells on a Piper diagram (1944).

purposes, because it coagulates soap lather [14]. All of the studied samples belong to very hard water type [15] and falls beyond the maximum permissible limit of TH of the [16] international standard, so that water softening processes for removal of hardness are needed. Fluoride is one of the main trace elements in groundwater, which generally occurs as a natural constituent. Bedrock containing fluoride minerals is generally responsible for high concentration of this ion in groundwater [13, 17, 18].

The fluoride content in the groundwater shows a range of 0.68-1.8 with an average 1.38. Nine samples exceed the maximum permissible allowable limit of [16] of fluoride (1.5 mg/l) suggested for drinking, which had resulted in skeletal fluorosis and enamel fluorosis.

### Hydrochemical Classification and Relationships:

The major ion composition from studied wells is shown in the Piper diagram, where the relative content of a cation or an anion is defined as the percentage or the milliequivalent per liter (meq/l) respectively, of the total cations or anions. States of hydrochemical facies are product of solution kinetics, flow patterns and lithology of aquifer [19, 20]. Based on these and other parameters, two distinct Hydrochemical facies can accordingly be used to describe groundwater in the study area. In this regard, the two groundwater facies of the study area can be seen to move from earth alkaline type water (Ca + Mg) in the first nine wells (W1 to W9) to that of increased portion of alkalis (Na, K) in the other wells.

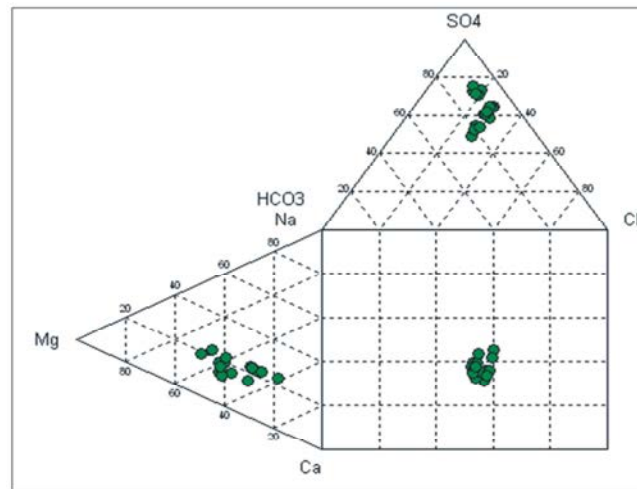


Fig. 3: Durov diagram of groundwater samples in the study area.

In two groundwater facies  $\text{SO}_4 + \text{Cl}$  are the dominant anion (Fig. 2). These groundwater types in the study area is predominately indicative of the lithology of aquifer and the role of evaporation in the water composition as the loss by evaporation results in the transfer of salts from soil water to the soils [21-23]. The structure geology of the study area belongs to Hadhramout Group Jeza Formation strata. Gypsum beds in the Jeza Formation are the probable cause of elevated groundwater mineralization [11] and the study area lies in the semi-arid climate, which leads to a high rate of evaporation especially during summer. The major ion concentrations of groundwater samples are also plotted on Durov diagram using “Aquachem” software. This diagram has advantages over Piper diagram because it reveals some geochemical processes that could affect groundwater genesis. Figure 3 reveals that all samples plot in field of the dissolution or mixing line based on the classification of [24]. This trend suggests the hydraulic connection between the different aquifers in the study area.

**Ion-Exchange Processes:** Control on the dissolution of undesirable constituents in water is impossible during the subsurface runoff but it is essential to know the various changes undergone by waters during their travel [14, 25-27]. According to [28], the ion exchange between the groundwater and its environment during residence or travel can be understood by studying the chloride-alkaline indices, i.e. CA-I  $((\text{Cl} - \text{Na} + \text{K})/\text{Cl})$  and CA-II  $((\text{Cl} - \text{Na} - \text{K}) / (\text{SO}_4 + \text{HCO}_3 + \text{CO}_3 + \text{NO}_3))$ . Na and K ions in water are exchanged with Mg and Ca ions, if the indices value is positive, it indicates base-exchange reaction whereas negative values indicate chloro-alkaline disequilibrium.

The reaction is known as a cation-anion exchange reaction. During this process the host rocks are the primary sources of dissolved solids in the water [28]. Indices values of the groundwater samples of the study area are presented in Table 1 that reveal a base - exchange reaction exist all over the area. Groundwater with a base - exchange reaction in which alkaline earths have been exchanged for Na ions ( $\text{HCO}_3 > \text{Ca} + \text{Mg}$ ) may be referred to a base – exchange – softened water and those in which the Na ions have been exchange for the alkaline earths ( $\text{Ca} + \text{Mg} > \text{HCO}_3$ ) may be referred to as base – exchange- hardened water [17]. In the study area the alkaline earths have higher concentrations than  $\text{HCO}_3$ , which indicates the exchange of Na ions for alkaline earths and the water as base – exchange – hardened water.

**Dissolution and Precipitation:** Mineral equilibrium calculations for groundwater are useful in predicting the presence of reactive minerals in the groundwater system and estimating mineral reactivity [29]. If certain minerals, such as calcite and dolomite are commonly found in equilibrium with groundwater, it is then reasonable to assume that these minerals are reactive in typical groundwater environments and that they can control solution concentration. By using the saturation index (SI) approach, it is possible to predict the reactive mineralogy of the subsurface from groundwater data without collecting the samples of the solid phase and analyzing the mineralogy [29]. In the present study, to determine the chemical equilibrium between minerals and water, SI of gypsum, anhydrite, halite, calcite, dolomite and fluorite were studied to interpret the hydrochemical properties of the groundwater in the study area.

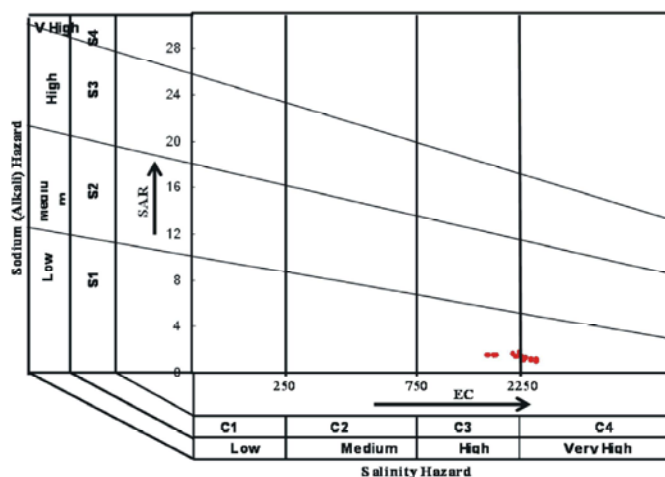


Fig. 4: Sodium adsorption ratio (SAR) and salinity hazard.

When the SI value equals zero then the water is in equilibrium with respect to a particular mineral. But if the SI is over zero (positive value) then the water is over-saturated with respect to the concerned mineral and that mineral tends towards precipitation, while if the SI is less than zero (negative value) then the water is under-saturated and that mineral tends towards dissolution from the rock matrix. The PHREEQC 2.8 [9] was used to calculate SI and is listed in Table . Minerals such as calcite and dolomite are unlikely to undergo precipitation even under super-saturation conditions [30, 31]. Therefore, SI equilibrium theory is most advantageous in the identification of dissolution process. The calculated values of SI for the studied samples show that groundwater within the study area is under-saturated with respect to all considered minerals with different under-saturation degrees except for dolomite and to a lesser extent calcite. The over-saturated state in calcite and dolomite is due to highly evaporation condition in the area and the dissolution of gypsum [32-34].

**Irrigation Water Quality:** The suitability of groundwater for irrigation is contingent on the effect of the mineral constituents of the water on both plant and soil. Salts may harm plant growth physically by limiting the uptake of water through modification of osmotic processes, or chemically by metabolic reaction such as those caused by toxic constituents [35]. The electrical conductivity is a good measure of salinity hazard to crop as it reflects the TDS of the water. Excess salinity reduces the osmotic activity of plants and thus interferes with the absorption of water and nutrients from the soils [36]. Eleven samples out of the studied seventeen belong to doubtful water class whereas the rest samples are permissible for

irrigation purposes [37]. The irrigation water containing a high proportion of Na will increase the exchange of Na content of the soil, affecting the soil permeability and the texture makes the soil hard to plough and unsuitable for seedling emergence [38]. If the percentage of Na+K with respect to (Ca + Mg + Na + K) is above 50% in irrigation water, Ca and Mg exchange with Na, thus causing deflocculation and impairment of the tilth and permeability of the soils [22]. A Na level of more than 60% is considered unsafe for irrigation. The values for the percent Na in the study area range from 14-25%. It indicates that the groundwater in the study area is excellent to good for irrigation purposes. A more detailed analysis with respect to the suitability of groundwater for irrigation purposes was made by plotting the Na adsorption ratio (SAR) and EC in the US salinity diagram where SAR values are taken as a Na hazard (S) and EC values salinity hazard (C). According to this classification groundwater of the study area falls into two categories C3S1 and C4S. C3S1 field indicating high salinity and low Na water, which can be used for irrigation on almost all types of soil with little danger of exchangeable Na. C4S1 indicating very high salinity and low alkalinity hazard (Fig. 4). This can be suitable for plants having good salt tolerance and also restricts their suitability for irrigation, especially in soils with restricted drainage [39].

## CONCLUSIONS

The hydrochemical investigation reveals that groundwater in the study area is brackish, very hard. Generally, groundwater is alkaline in nature ( $\text{pH} > 7$ ), with  $\text{EC} > 1600 \mu\text{S/cm}$ . the sequence of abundance of the major ions is in the following order:  $\text{Ca} > \text{Mg} > \text{Na} \geq \text{K}$  and

$\text{SO}_4 > \text{Cl} > \text{HCO}_3 > \text{NO}_3$ . The Piper trilinear diagram (Piper, 1944) shows that, the study area is characterized by two water types' earth alkaline and earth alkaline water with increased portions of alkalis with prevailing  $\text{SO}_4$  and Cl. The groundwater quality of the study area has a problem of salinity, hardness and somewhat high fluoride concentration. The Groundwater studied samples of the study area exceeded the recommended limits of TDS and TH and more than a half of them has fluoride concentration also exceeded the maximum permissible limits for drinking purposes. The Schoeller indices values are positive showing a base – exchange reaction. Graphical representation shows that the study area has high to very high salinity with low Na water types, which need adequate drainage to overcome salinity problems for irrigation purposes.

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