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Understanding the Hydrochemistry of Groundwater and its Suitability for Drinking and Irrigation in Ellenabad Area of Haryana (India)

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Abstract

The present study deals with the evaluation of groundwater quality of some villages near Ellenabad city of Haryana state (India). For this, 40 representative groundwater samples were collected in the pre-monsoon period of 2017. The samples were analyzed for various physicochemical parameters like pH, TDS, EC, Ca, Mg, Na, K, sulfate, nitrate, chloride, fluoride, carbonate and bicarbonate ions. The drinking water quality has been assessed by the comparison of the results by WHO and BIS standards. Water Quality Index (WQI) has been calculated to assess groundwater quality. A number of parameters such as %Na, sodium absorption ratio, residual sodium carbonate, Kelly Index, soluble sodium percentage, base exchange, and meteoric genesis have been calculated to assess the suitability for irrigation. Pearson's correlation matrix has been used to study the relationship between variables.

Keywords: Ellenabad; Groundwater quality; Haryana; Irrigation water quality; Water quality index

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Introduction

The population explosion is continuously increasing stress on natural resources like air, water, food, land, etc. For the survival of life on this blue planet, fresh and clean water is of prime importance. To meet the agricultural, domestic and industrial needs, careful management of water is therefore required. Degradation in groundwater quality may lead to serious problems for biotic life, soil quality and for human health [1]. The surface water cannot meet all the requirements due to its limited availability. Under this situation, the dependency on groundwater keeps on increasing. The suitability of groundwater largely depends upon the water chemistry, which is controlled by a number of factors like lithology, soil quality, infiltration process, human activities and recharge [2,3].

The quality of groundwater for drinking and irrigation depends upon the concentration of salts, major ions and their interactions with host rocks [4]. The alteration in the physicochemical parameters of water is usually caused by urbanization, climate conditions, human activities like unplanned use of chemicals in agriculture and untreated sewage discharge may cause very serious environmental problems. Keeping this in view, the hydro-geochemical study of the groundwater of Ellenabad city and its nearby village of Sirsa district of Haryana State (India) was undertaken where the groundwater is the major source for drinking and irrigation. The statistical-WQI hybrid model was used for the assessment of groundwater quality for drinking and rrigation purposes **(Figure 1)**.

Study Area

Aim and scope of the work

The economy of the study area is agriculture based on some small agricultural industries. In Ellenabad block, availability of net annual groundwater is 14285 Ham. For irrigation, the groundwater requirement is 21223 Ham and for industrial activities, the groundwater requirement is 155 Ham. So the present study area falls under over exploited category. The present study was carried out to assess the quality of ground water in the study area and to assess its suitability for both drinking and irrigation. At present no awareness programs have been running in the study area by any NGO or any governmental agency related to groundwater quality for public awareness. The findings of the study might be helpful for the public and the policymakers for future groundwater quality management.

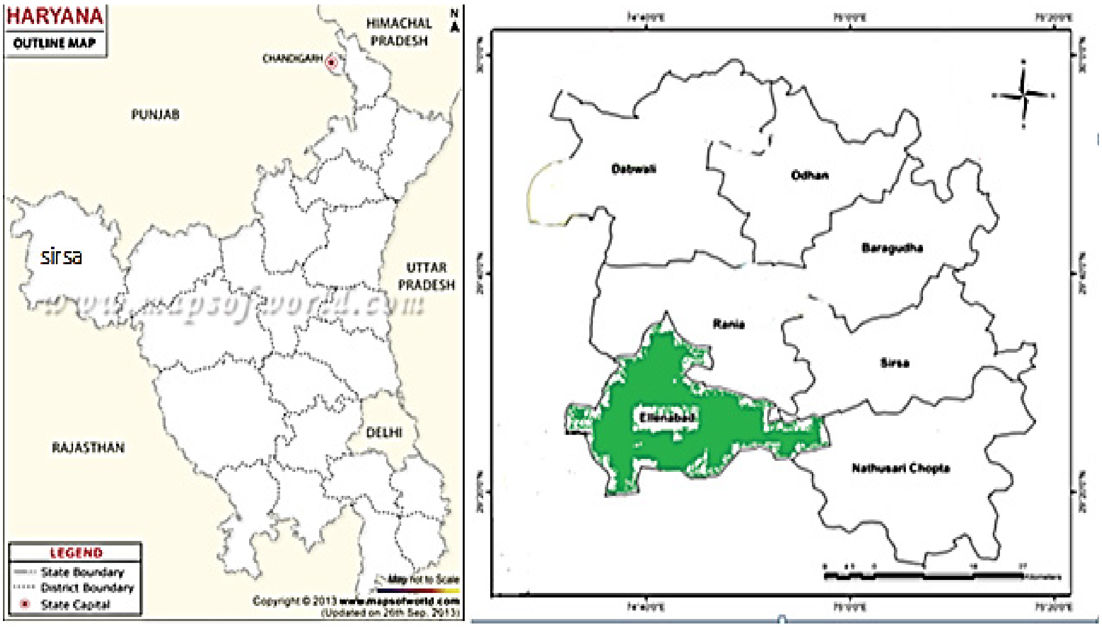

Figure 1 Assesment of groundwater quality for drinking and irrigation purposes in the nearby village of Sirsa district of Haryana State.

Physiography and climate

Ellenabad, situated in this Sirsa district of Haryana state has coordinate 29.45°N and 74.65°E as shown in **Figure 1**. The elevation of the study area is 189 m from sea level. Its location is in the north of the Ghaggar-Hakra River and it is a port of entry into Haryana state. Largely, Ellenabad's climate is a desert with very less annual rainfall. The average temperature of the study area is 25.1°C with an annual rainfall of 280 mm. The lowest rainfall will be observed in the month of April (2 mm) and highest in the month of July (89 mm). June is the hottest month and January is the coldest one.

Population of the study area

As per the report of Census 2011, the total population of Ellenabad Municipal Committee was 36623 out of which the male population was 19441 and that of the females were reported as 17182. The population of children with age group 0-6 years was reported to be 4478. The literacy rate in the study area was found to be 75.19% which was lower than the state average of 75.55%.

Materials and Methods

A total of 40 samples were collected from different locations of Ellenabad city and its nearby villages in pre-cleaned PET bottles. The samples were collected after running the tube well for 30 minutes. pH and EC were measured at the site. Na^+, K^+, $Ca^{2+,}$ and Mg^{2+} were measured using ICP-MS in the Central University of Punjab, Bathinda. SPSS 16.0 was used for statistical analysis and correlations matrix. All the reagents used were of A.R. Grade and double distilled water was used for the preparation of solutions.

Results and Discussion

The groundwater quality plays an important role to determine the suitability of water for different purposes. The statistical analysis such as maximum, minimum and standard deviation are given in **Table 1**. pH, EC, TDS, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO, F^-, NO_3^-, carbonate and bicarbonate ions were selected to determine the groundwater quality.

pH

The pH scale varies from 0 to 14. If the pH of water is below 7, it is acidic and if the pH is above 7 it is basic water. For the pure water, pH is 7. Lesser is the pH, more is the acidic character of water whereas higher is the pH more is the basic character of water. In our study area, water is off slightly acidic and slightly basic nature. If the pH is not within the permissible limit it might be harmful to human beings. It may damage the mucous membrane.

Total hardness (TH)

The hardness of water is caused by the presence of carbonates, sulfates, and bicarbonates of calcium and magnesium. Hard water is unable to form lather with soap. For the use of water in domestic purpose, TH is a very important parameter to determine.

As mentioned in **Table 2**, the acceptable limit for TH in domestic use is 75 mg/l. Hardness in the range of 150-300 mg/l and above may lead to kidney stone formation [5].

In the present study, 5% samples were soft, 27.5% samples are moderately hand, 25% samples in hard and 42.5% samples fell in the very hard category.

Total dissolved solids (TDS)

The irrigation water quality depends upon the type and amount of salts present in water. These salts move with water as it is used for irrigation and get accumulated by the soil when water gets

Table 1 Table showing the descriptive statistics of quality parameters.

	Unit	Minimum	Maximum	Std. Deviation	BIS acceptable	WHO Standards
TDS	mg/l	366	5200	1080.69173	500	500
EC	µS/cm	575	8125	1688.42991	300	-
TH	mg/l	68	1850	363.47935	200	500
TA	mg/l	58	2050	442.39007	200	-
Ca	mg/l	4.8	400	88.70359	75	75
Mg	mg/l	14	570	124.2695	30	150
Carbonate	mg/l	0	92	28.11778	-	-
Bicarbonate	mg/l	62	2500	494.76157	-	-
Chloride	mg/l	45	1100	230.40052	200	500
Fluoride	mg/l	0.1	7.4	2.17363	1	1.5
pH	-	6.5	8.5	0.6479	6.5-9.2	6.5-9.2
Nitrate	mg/l	0	78	17.59544	-	
Na	mg/l	92	2386	597.99684	-	200
K	mg/l	3	29	5.98155	-	-
Sulfate	mg/l	25	1250	368.51197	200	-

Table 2 Hardness Classification of water [6].

Hardness (mg/l) as $CaCO_3$	Class of water	Sample number
0-75	Soft	21, 23
75-150	Moderately hard	7, 11, 13, 16, 17, 18, 19, 26, 25, 26, 38
150-300	Hard	8, 9, 22, 29, 30, 31, 32, 33, 34, 37
Over 300	Very hard	1, 2, 3, 4, 5, 6, 10, 12, 14, 15 20, 28, 35, 36, 39, 40

Table 3 Classification of hardness on the basis of TDS.

TDS Range	Type of water	Number of samples
<1000	Freshwater	10, 11, 16, 20, 27, 29, 30, 31, 32, 37, 38
1000-3000	Slightly saline	2, 3, 4, 5, 6, 7, 8, 9, 13, 14, 15, 17, 21, 22, 23, 24, 26, 28, 33, 34, 35, 36, 40
3000-10000	Moderately saline	1, 18, 19, 25, 39
10000-35000	Highly saline	Nil

evaporates. Such type of water creates salinity problem in the soil which is further taken up by the roots of the plants and this decreases the overall crop yield. In our study, 27.5% of samples are found to be fresh, 57.5% as slightly saline and 12.5% as moderately saline.

Table 3 gives us the maximum desirable limit for TDS is 500 mg/l, Water with TDS in the range of 500-1000 mg/l is permissible to use in drinking and up to 3000 mg/l can be used for irrigation. Water with TDS>3000 is unsuitable for drinking and irrigation [7,8].

Calcium (Ca^{2+}) and Magnesium (Mg^{2+})

The TH, Ca^{2+}, and Mg^{2+} are interrelated with each other. More magnesium content in groundwater makes the soil more alkaline and this will adversely affect the crop yield. The permissible limit for magnesium in groundwater to use for drinking is 30 mg/l [9]. In our study the magnesium content in sample numbers 1, 2, 3, 4, 5, 6, 8, 9, 10, 12, 14, 15, 20, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40 shows that the groundwater of these areas are not suitable for drinking and irrigation purpose. Although magnesium ions play an important role in many enzyme activations, in its higher concentration it acts as a laxative agent and its deficiency may lead to the functional and structural changes in the human body [10].

Calcium (Ca^{2+}) is essential for proper bone growth and it is commonly found in the groundwater due to its abundance and its solubility.

The desirable limit for calcium ion in drinking water is 75 mg/l [11]. In the present study area the sample number 1, 3, 6, 15, 25, 35, 36, 39, 40 are found to have high concentration of calcium ions and therefore the water from these study areas are not found to be suitable for drinking.

Sodium (Na^+)

Sodium is a very important parameter to decide the irrigation water quality. It reacts with soil and reduces its permeability. Therefore, assessing the sodium concentration in water is very important to decide its suitability for irrigation. The suitability for irrigation can be decided by sodium percentage [12].

$$\%Na = \left(\frac{Na^+ + K^+}{Na^+ + K^+ + Ca^{2+} + Mg^{+2}} \right) \times 100$$

Sodium on reaction with chloride forms saline soils while on reaction with carbonate forms alkaline soils. In our study, sodium percentage varies from 35.5 to 93%. **Table 4** helps us to understand the classification of hardness on the basis of Na%.

The higher concentration of Na in irrigation water displaces Ca and Mg ions from the clay and hence reduces the soil permeability. Such types of soils are usually hard under dry conditions [14].

For drinking purpose, the concentration of Na ions more than 50 mg/l is unsuitable and it may cause hypertension and it may cause risk to those persons suffering from renal, circulatory and cardiac diseases [15,16].

Table 4 Classification of hardness on the basis of Na% [13].

Na%	Type of water	Sample Number
<20	Excellent	Nil
20-40	Good	20
40-60	Permissible	1, 3, 5, 6, 10, 12, 14, 15, 23, 25, 27, 28, 35, 37
60-80	Doubtful	3, 4, 8, 9, 11, 16, 17, 24, 26, 29, 30, 31, 32, 33, 34, 36, 39, 40
>80	Unsuitable	2, 7, 13, 18, 19, 21, 22, 38

Potassium (K^+)

Potassium behaves similarly to that of Sodium in water. The permissible value of potassium is 10 mg/l [9]. In the higher concentration, Potassium may cause digestive and nervous disorder [17]. The sample stations 18, 19, 26, 33, 34, 35, 36, 37, 38, 39, 40 have concentration of potassium higher than 10 mg/l. The domestic sewage and excessive use of fertilizer is responsible for the higher concentration in these areas.

Sulphate (SO_4^{2-})

The permissible value of sulfate is 400 mg/l [9]. In concentration higher than 150 mg/l, sulfate causes dehydration, gastrointestinal irritation in human beings. The sample stations 1, 3, 4, 13, 18, 19, 22, 24, 25, 36, 37, 38, 39, 40 have sulphate concentration more than 400 mg/l. This higher concentration of sulfate may be due to the contribution of Industrial process biochemical and agricultural process.

Chloride (Cl^-)

In potable water, the desired concentration of chloride ion is 250 mg/l with the permissible value of 1000 mg/l [9]. The sample numbers 1, 2, 3, 4, 13, 15, 18, 19, 22, 28, 32, 33, 36, 37, 39 have concentration of chloride ions above 250 mg/l. The higher concentration of chloride in groundwater is found in those areas where the temperature is high and rainfall is less. Most commonly, chloride is present as sodium chloride in groundwater. In the higher concentration, it causes risk for stroke, hypertension renal stones, and asthma in human beings [18]. The higher concentration of chloride in groundwater is due to the soil porosity and soil permeability. Dry climate and leaching of the upper layers of soil by domestic and industrial activities may also lead to higher chloride concentration.

Fluoride (F^-)

In the present study, the fluoride concentration varies from 0.1 to 7.40 mg/l. The sample stations 1, 3, 5, 6, 12, 16, 24, 25, 28, 34, 35, 37 have fluoride concentration between 1.0 to 1.5 mg/l which is the desired limit for fluoride and the sample stations 4, 9, 14, 17, 19, 23, 33, 38, 40 have fluoride concentration above 1.5 mg/l which is the permissible value for fluoride in drinking water.

Nitrate (NO_3^-)

Nitrate is one of the major contaminants of water. The permissible limit for NO_3^- is 45 mg/l for drinking water. The sample stations 39 and 40 have high nitrate concentration. Excessive nitrate in drinking water cause Methemoglobinemia (MetHb) in the infants and also been reported for cancer [19].

Irrigation Water Quality

The irrigation water quality is not only essential for good crop yield but it is also essential to maintain soil quality and environmental protection. The irrigation water quality has been derived by calculating Sodium percentage (Na%), Electrical Conductivity (EC), SAR, RSC, SSP and KR [20,21].

Sodium Adsorption Ratio (SAR)

High sodium content in water reduces the soil permeability. So, to assess the groundwater quality for irrigation, the assessment of sodium concentration is very important. SAR is an important parameter to express the relative activity of sodium ion is an exchange reaction with soil. The SAR can be calculated by the equation

$$SAR = \frac{Na}{\sqrt{Ca + Mg / 2}}$$

All the concentrations have been expressed in mEq/l [22].

Residual Sodium Carbonate (RSC)

The increase in the relative proportion of sodium in the form of sodium carbonate (Na_2CO_3) is called as the Residual Sodium Carbonate (RSC). It is calculated by the equation RSC=(CO_2^{3-} +HCO_3^-)-(Ca^{2+}+Mg^{2+}) [23,24]. If the amount of carbonate and bicarbonate is more than that of the calcium and magnesium the precipitation of calcium and magnesium may take place [25]. This may diminish the irrigation water quality and on prolonged irrigation with such type of water, the land becomes infertile.

In our study, as in **Table 5** the RSC varies from –57.26 to 39.0. The sample numbers 2, 5, 6, 7, 8, 11, 12, 13, 14, 16, 17, 18, 19, 20, 21, 22, 23, 24 are found to have RSC>2.5. The sample station 22 has the highest RSC with the value 39.0. The water from these seventeen locations cannot be considered suitable for irrigation.

Soluble Sodium Percentage (SSP)

The excess of sodium ions (Na^+) ion water tends to absorb by clay and disperses the calcium and magnesium ions. This exchange of Na^+ with Ca^{2+} and Mg^{2+} results in the reduction of soil permeability. Classification of hardness on the basis of SSP is being shown in **Table 6** [25]. The SSP is calculated by the equation:-

$$SSP = \left(\frac{Na^+ + K^+}{Na^+ + K^+ + Ca^{2+} + Mg^{2+}}\right) \times 100$$

All concentrations are in mEq/l

Kelly's Ratio (Kl)

The Kl was calculated by the equation as under and the Classification of hardness on the basis of Kl as shown in **Table 7** [26] is as under:

Table 5 Classification of hardness on the basis of RSC [21].

RSC (EPM)	Water type	Number of samples
<1.25	Safe	22
1.25-2.5	Marginally Suitable	1
>2.5	Unsuitable	17

Table 6 Classification of hardness on the basis of SSP.

SSP	Water type	Sample number
<20	Excellent	Nil
20-40	Good	2
40-60	Permissible	13
60-80	Doubt full	17
>80	Unsuitable	80

Table 7 Classification of hardness on the basis of KI.

KI	Water type	Sample number
≤ 1	Suitable	7
>1	Unsuitable	13

$$KI = \frac{Na}{Ca + Mg}.$$

Soltan classification

Soltan classified the groundwater into two classes on the basis of Base Exchange (B.E.) and Meteoric Genesis (Met. gen.) [27] as shown in **Table 8**.

$$B.E = \frac{Na^{+} - Cl^{-}}{SO_4^{2-}},\ Met.Gen. = \frac{\left(Na^{+} + K^{+}\right) - Cl^{-}}{SO_4^{2-}}$$

All the concentrations are in mEq./l.

If B.E.<1 and met.gen.<1, the major sources of groundwater are

Table 8 Groundwater type on the basis of Soltan classification.

Sample No.	Name of the sample station	B.E.	Water type	Met. gen.	Water type
1	Kashi ka baas	0.54	Na^+ - SO_4^{2-}	0.55	Deep meteoric
2	Kashi ka baas	3.42	Na^+ - HCO_3^-	3.45	Shallow meteoric
3	Kashi ka baas	0.91	Na^+ - SO_4^{2-}	0.92	Deep meteoric
4	Kashi ka baas	0.8	Na^+ - SO_4^{2-}	0.82	Deep meteoric
5	Sirsa road	0.99	Na^+ - SO_4^{2-}	1.06	Shallow meteoric
6	Sirsa road	1.2	Na^+ - HCO_3^-	1.3	Shallow meteoric
7	Near Tehsil	5.61	Na^+ - HCO_3^-	5.7	Shallow meteoric
8	Near Honda showroom	1.45	Na^+ - HCO_3^-	1.47	Shallow meteoric
9	Mameran road	0.94	Na^+ - SO_4^{2-}	1.34	Shallow meteoric
10	Near Tehsil	0.54	Na^+ - SO_4^{2-}	0.58	Deep meteoric
11	Sirsa road	0.89	Na^+ - SO_4^{2-}	0.91	Deep meteoric
12	Nohar road	1.1	Na^+ - HCO_3^-	1.22	Shallow meteoric
13	Nohar road	0.47	Na^+ - SO_4^{2-}	0.49	Deep meteoric
14	Nohar road	1.79	Na^+ - HCO_3^-	1.85	Shallow meteoric
15	Talwara road	1.43	Na^+ - HCO_3^-	1.47	Shallow meteoric
16	Near grain market	1.88	Na^+ - HCO_3^-	1.92	Shallow meteoric
17	Mameran road	0.39	Na^+ - SO_4^{2-}	0.45	Deep meteoric
18	Waterworks tubewell near Devi LalChowk	-0.14	Na^+ - SO_4^{2-}	-0.11	Deep meteoric
19	Talwara road	0.24	Na^+ - SO_4^{2-}	0.27	Deep meteoric
20	Talwara road	-0.24	Na^+ - SO_4^{2-}	-0.22	Deep meteoric
21	Near Govt. Girls School	1.93	Na^+ - HCO_3^-	1.96	Shallow meteoric
22	Near HUDA colony	0.99	Na^+ - SO_4^{2-}	1.01	Shallow meteoric
23	Grain market	-0.24	Na^+ - SO_4^{2-}	-0.22	Deep meteoric
24	Kashi Ka baas	1.14	Na^+ - HCO_3^-	1.16	Shallow meteoric
25	Hanumangarh road	0.8	Na^+ - SO_4^{2-}	0.81	Deep meteoric
26	Hanumangarh road	2.66	Na^+ - HCO_3^-	2.72	Shallow meteoric
27	Mirjapur	-0.12	Na^+ - SO_4^{2-}	-0.06	Deep meteoric
28	Thobrian	0.7	Na^+ - SO_4^{2-}	0.76	Deep meteoric
29	Mirjapur	7.09	Na^+ - HCO_3^-	7.38	Shallow meteoric
30	Amritsar Kalan	0.9	Na^+ - SO_4^{2-}	0.93	Deep meteoric
31	Thobrian	2.08	Na^+ - HCO_3^-	2.12	Shallow meteoric
32	Amritsar Khurd	6.05	Na^+ - HCO_3^-	5.26	Shallow meteoric
33	Talwara Khurd	2.94	Na^+ - HCO_3^-	3.09	Shallow meteoric
34	Talwara Khurd	5.53	Na^+ - HCO_3^-	5.69	Shallow meteoric
35	Bhuratwala	3.13	Na^+ - HCO_3^-	3.16	Shallow meteoric
36	Kashi Ka baas	3	Na^+ - HCO_3^-	3.03	Shallow meteoric
37	Mehna Khera	0.05	Na^+ - SO_4^{2-}	0.06	Deep meteoric
38	Poharka	8.65	Na^+ - HCO_3^-	8.68	Shallow meteoric

39	Nimla	3.14	Na^+ - HCO_3^-	3.16	Shallow meteoric
40	Mithi sureran	2.04	Na^+ - HCO_3^-	2.05	Shallow meteoric

If B.E.>1 and the met.gen.>1, the main sources of groundwater are Na^+ and HCO_3^- and water is shallow meteoric type respectively.

Water Quality Index (WQI): WQI is a single number that provides the overall quality of water based upon many parameters. Based on the groundwater chemistry, the drinking and irrigation water qualities can be discriminated [28]. In order to assess the suitability of water for drinking purpose, WQI is a very important parameter [29]. Based on some very important water quality parameters, the WQI provide an indicator of water quality as in **Table 9**. The parameters considered to calculate the WQI are pH, EC, TDS, Bicarbonate, Chloride, Sulphate, Nitrate, Calcium, Magnesium, Sodium and Potassium as in **Table 10**. EC is in µS/cm whereas all other parameters except pH are in mg/l. The quality rating (q_n) was calculated using the equation:-

$$q_n = \left(\frac{V_n - V_i}{S_n - V_i}\right) \times 100;$$

where 'q_n' is the quality rating corresponding to the n^{th} parameter

V_n=Calculated value of the nth parameter for the sample

S_n=Standard value for an nth parameter as per WHO standards

V_i=Ideal value for an nth parameter in pure water

V_i=0 for each parameter except the pH where it is 7.0

The relative weight for the quality parameters was assigned based on the relative importance of each parameter for drinking purpose. The relative weight for each parameter is given in **Table 11**.

In our study 2.5% samples showed excellent water quality, 17.5% samples showed good water quality, 47.5% samples fell under poor water quality, 20% samples showed very poor water quality and 12.5% samples were found to be unsuitable for drinking. **Table 12** gives us the description of sample stations on the basis of the Water Quality Index (WQI).

Table 9 The classification of water quality based on WQI.

WQI	Class of water	Number of samples
<50	Excellent water	1
50-100	Good water	7
100-200	Poor water	19
200-300	Very poor water	8
>300	Unsuitable for drinking purpose	5

Table 10 Table showing the calculation of the Water Quality Index (WQI).

	S_n	V_i	V_n	Q_n	W_nq_n	
pH (on scale)	7.5	7	6.8	40	4.56	$\Sigma\omega\nu\theta\nu = 294.59$
EC (µs/cm)	500	0	4765	953	108.64	$\Sigma\omega l = 0.998$
TDS (Mg/l)	500	0	3050	610	86.62	$WQI = \frac{\sum w_n q_n}{\sum w_i}$
HCO_3^- (Mg/l)	500	0	500	100	8.6	$= \frac{294.59}{0.998}$
Cl^- (Mg/l)	250	0	560	224	19.26	= 295.18
SO_4^{2-} (Mg/l)	250	0	590	236	26.9	
NO_3^-(Mg/l)	45	0	7.5	16.6	2.36	
Ca^{2+} (Mg/l)	75	0	128	170.6	9.72	
Mg^{2+} (Mg/l)	50	0	225	450	13.05	
Na^+ (Mg/l)	200	0	576	258	14.71	
K^+ (Mg/l)	200	0	6	3	0.17	

Table 11 Table showing the relative weight of the quality parameters.

S.No.	Chemical Parameters	WHO standards	Relative weight (Wi)	$W_i = \sum_{i=1}^{n} w_1 = 0 \cdot 998$
1	pH	6.5-8.5	0.114	
2	EC	500	0.114	
3	HCO_3^-	500	0.086	
4	Cl^-	250	0.086	
5	TDS	500	0.142	
6	NO_3^-	45	0.142	
7	SO_4^{2-}	250	0.114	
8	Ca^{2+}	75	0.057	
9	Mg^{2+}	50	0.029	
10	Na^+	200	0.057	
11	K^+	200	0.057	

Factors Responsible for Controlling the Hydrochemistry of Groundwater

Gibbs diagrams

The plots of Gibbs ratio 1 (cations) and Gibbs ratio 2 (anions) v/s TDS are used to assess the dominance of three natural mechanisms which are responsible to control the hydrochemistry of groundwater **(Figure 2)**. These are rock dominance, precipitation dominance, and evaporation dominance. The Gibbs ratios were calculated using the equations [30]:

Gibbs ratio 1 = $(Na^+ + K^+)/(Na^+ + K^+ + Ca^{2+})$

Gibbs ratio 2 = $(Cl^-)/(Cl^- + HCO_3)$

Generally, water with TDS more than 1000 mg/l is influenced by evaporation dominance. In the present study, none of the samples was found to belong to precipitation dominant. 11 out of 40 samples were found to belong to rock dominant and the rest to evaporation dominant categories.

Chloro-alkaline Indices

It is very important to understand the dissolution of some undesirable components in groundwater during its flow along the sub-surface. Scholar proposed chloro-alkaline indices that indicate the ion exchange relationship between groundwater and its host environment [31,32]. The negative values of these indices indicate the exchange of Ca and Mg ions from the water with the Na and K ions from the rock and the positive values indicate the reverse ion exchange. These indices were calculated as:

Chloro-alkaline Index 1 = Cl^- - $(Na^+ + K^+)/Cl^-$

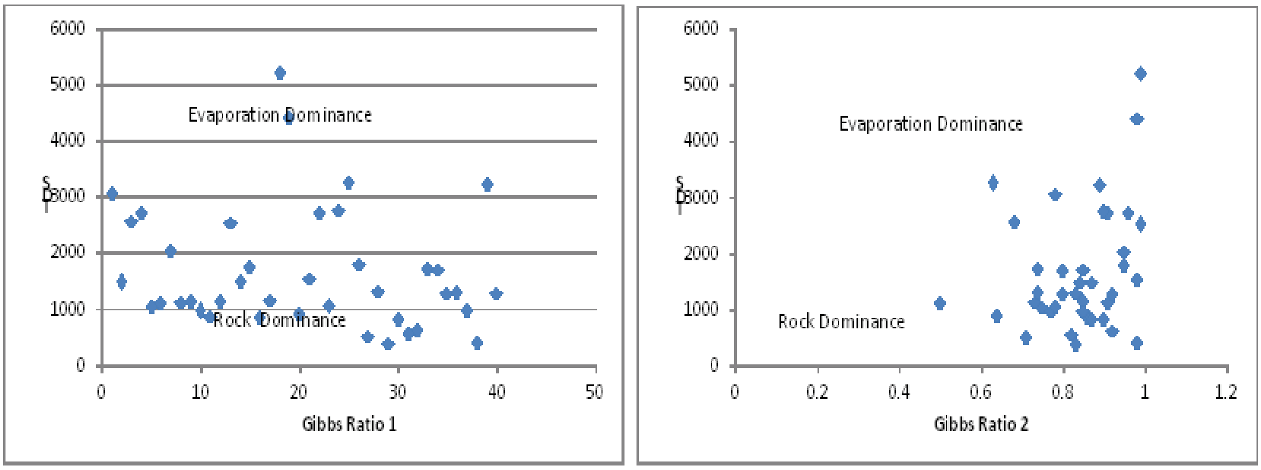

Figure 2 Plots of Gibbs Ratio 1 (Cations) and Gibbs Ratio 2 (Anions) v/s TDS.

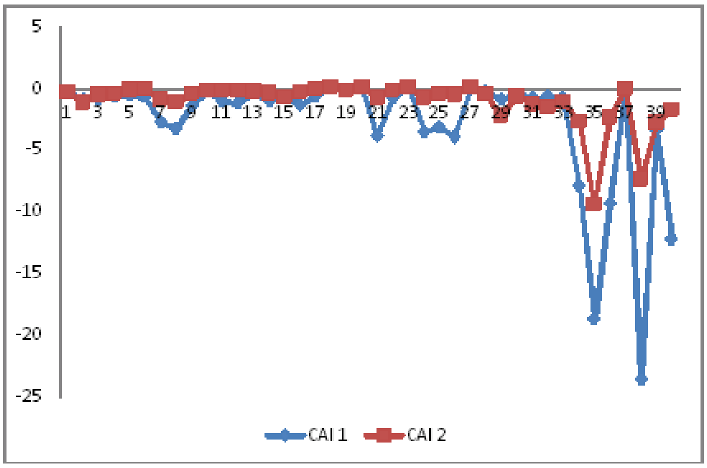

Figure 3 Chloro alkaline indices CAI (1 and 2).

Table 12 Description of sample stations on the basis of WQI.

S.No.	WQI	Sample stations
1	294.59	Kashi ka baas
2	298.24	Kashi ka baas
3	337.8	Kashi ka baas
4	265.98	Kashi ka baas
5	113.86	Sirsa road
6	125.19	Sirsa road
7	181.08	Near Tehsil
8	104.32	Near Honda showroom
9	105	Mameran road
10	68.38	Near Tehsil
11	81.49	Sirsa road
12	131	Nohar road
13	239.81	Nohar road
14	158.82	Nohar road
15	173.85	Talwara road
16	92.45	Near grain market
17	129.74	Mameran road
18	448.77	Waterworks tubewell near Devi LalChowk
19	378.36	Talwara road
20	102	Talwara road
21	142.62	Near Govt. Girls School
22	280.9	Near HUDA colony
23	114.5	grain market
24	170	Kashi ka baas
25	303.46	Hanumangarh road
26	177.33	Hanumangarh road
27	75.47	Mirjapur
28	145.32	Thorian
29	49.24	Mirjapur
30	93.03	Amritsar kalan
31	74.24	Thobrian
32	91.06	Amritsar khurd
33	190.82	Talwara khurd
34	174	Talwara khurd
35	250.3	Bhuratwala
36	292.44	Kashi ka baas
37	194.08	Mehna khera
38	155.44	Poharka
39	461.49	Nimla
40	251.42	Mithi sureran

Chloro-alkaline Index 2 = $Cl^{-} - (Na^{+} + K^{+})/(CO_3^{2-} + HCO_3^{-} + NO_3^{-} + SO_4^{2-})$

In the present investigation, 4 out of 40 samples were found to have a positive value and remaining samples were found to have a negative value of chloro-alkaline indices. Therefore, the majority of the samples belonged to the exchange of Ca and Mg ions from water with the Na and K ions from the rock **(Figure 3)**.

Pearson's correlation matrix was made to study the relationship among variables **(Table 13)**. A strong positive correlation significant at 0.01 level was observed between EC-TDS (r=1), Mg-TH (r=0.802), Mg-Ca (r=0.837), Cl-TDS and Cl-EC (r=0.781), Na-Mg (r=0.795), K-Na (r=0.724). A moderate correlation significant at 0.01 level was observed between Ca-TH (r=0.644), CO_3^{2-} with TDS and EC (r=0.594), HCO_3^{-}-TA (r=0.665), NO_3^{-}-TH (r=0.549), Na-TH (r=0.520), Na-Ca (r=0.630), K-Ca (r=0.556), K-Mg (r=0.609), SO_4^{2-} with TDS and EC (r=0.530), SO_4^{2-}-Cl (r=0.568), SO_4^{2-}-Na (r=0.574) and SO_4^{2-} K (r=0.596). A weak correlation significant at 0.01 level

Table 13 Pearson correlation matrix for the quality parameters. (**Correlation is significant at the 0.01 level: 2-tailed; *Correlation is significant at the 0.05 level: 2-tailed).

	TDS	EC	TH	TA	Ca	Mg	CO_3^{2-}	HCO_3^-	Cl^-	F^-	pH	NO_3^-	Na	K	SO_4^{2-}
TDS	1														
EC	1.00**	1													
TH	0.163	0.163	1												
TA	0.364*	0.363*	-0.151	1											
Ca	0.108	0.108	0.644**	-0.245	1										
Mg	0.099	0.099	0.802**	-0.199	0.837**	1									
CO_3^{2-}	0.594**	0.594**	0.003	0.304	0.168	0.102	1								
HCO_3^-	0.079	0.079	-0.18	0.665**	-0.171	-0.217	0.247	1							
Cl^-	0.781**	0.781**	0.364*	0.24	0.084	0.261	0.347*	-0.089	1						
F^-	0.108	0.108	-0.117	-0.116	-0.204	-0.115	0.082	0.074	0.061	1					
pH	-0.239	-0.239	0.312*	-0.497**	0.335*	0.459**	-0.227	-0.559**	0.001	-0.163	1				
NO_3^-	0.075	0.075	0.549**	-0.181	0.312	0.463**	-0.005	-0.27	0.146	0.011	0.497**	1			
Na	0.171	0.171	0.520**	-0.137	0.630**	0.795**	0.121	-0.24	0.276	-0.113	0.492**	0.352*	1		
K	0.384*	0.384*	0.237	-0.036	0.556**	0.609**	0.318*	-0.152	0.393*	-0.008	0.449**	0.274	0.724**	1	
SO_4^{2-}	0.530**	0.530**	0.318*	-0.013	0.303	0.435**	0.358*	-0.155	0.568**	-0.008	0.237	0.289	0.574**	0.596**	1

was observed between pH-Mg (r=0.459), NO_3^--Mg (r=0.463), NO_3^- pH (r=0.497), Na-pH (r=0.492), K-pH (r=0.449), SO_4^{2-}-Mg (r=0.435), SO_4^{2-}-CO_3^{2-} (r=0.358). A negative correlation significant at 0.01 level was also observed between pH-TA (r=-0.497) and pH-HCO_3^- (r=-0.559). On the basis of the correlation matrix, it can be said that the role of pH to control the groundwater chemistry is not much significant. A strong correlation between Mg-TH and Ca-Mg shows that the hardness of water is of the permanent type.

Conclusion

The results of the study showed that most of the samples were found to be hard and very hard. On the basis of TDS, most of the samples belonged to slightly saline to moderately saline. %Na showed that water from most of the stations was found to be permissible and doubtful for irrigation. Some of the stations have higher fluoride concentration than the standards. The values of WQI revealed that water from most of the stations was found to be poor, very poor and even unsuitable for drinking. Therefore, prior treatment of water is necessary before use.

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