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Hydrochemical and Physicochemical Monitoring of Ground water in North-West Region of Punjab, India- A Study Involving Analysis of Major Ions ,Heavy Metal Ions and Other Related Parameters

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ABSTRACT

The district of Tarntaran is situated in Punjab State of Northwestern part of Punjab, India covering 5059 Sq. Km area, located 45 km from Amritsar its geographical coordinates are 31^0 16' 51" north and 74^0 51' 25" East longitudes. Water samples are collected from 100 locations in 20 villages on the Patti –Khem Karan highway with 5 samples from each village, and were subjected to analysis for chemical characteristics. The type of water that predominates in the study area is Ca-Mg-HCO_3 type, based on hydro-chemical analysis. Besides, suitability of water for irrigation is evaluated based on sodium adsorption ratio (SAR), residual sodium carbonate, sodium percent and salinity hazard. Other physicochemical parameters such as pH, TDS, conductance etc were also determined using water analysis kit. Analysis of water samples for heavy metal analysis was also carried out in the present study.

Keywords: Groundwater, chemical classification, SAR, RSC, USSL diagram

INTRODUCTION

Monitoring the quality of water is one of the most important aspects in groundwater studies. The suitability of water for drinking, agriculture and industrial purposes is assessed by hydro chemical studies. Any natural or anthropogenic effect on water quality can also be studied if regular monitoring of water samples is carried out in a specified region. The most important one is hydrochemical study which determines the presence of ion such as Ca^{+2}, Mg^{+2}, Cl^{-1}, HCO_3^{-1} Na^{+1}, K^{+1}, and SO_4^{-2} in groundwater. Different criterion has been studied for deciding the suitability of water for various purposes. It was observed that the criteria used in the classification of waters for a particular purpose considering the

individual concentration may not find its suitability for other purposes and better results can be obtained only by considering the combined chemistry of all the ions rather than individual or paired ionic characters[1-5].

Classification of water based on these parameters is a big challenge as it requires the determination of concentration of various ions present in water and their interrelationships. In order to decide the quality of water that is suitable for a particular purpose, it important to evaluate and interpret its physical and chemical parameters. A number of techniques and methods have been developed to interpret the chemical data. Presentation of chemical data in graphical form makes understanding of complex groundwater system. Methods of representing the chemistry of water like Collin's bar diagram[6], radiating vectors of Maucha[7], and parallel and horizontal axes of Stiff[8], have been used in many parts of the world to show the proportion of ionic concentration in individual water samples.[9] Numerous methods have been developed by Subramanian to interpret the chemistry of ground water in coastal southern parts of India. The objective of the present work is to monitor the major ions present in underground water and to evaluate the ground water quality in north-west region of Punjab, India. In this case study the methods proposed by Back[10] and Hanshaw, Wilcox, Eaton, Todd[10] and USSL (US Salinity Laboratory) classification have been used. Moreover other parameter such as TDS, pH, DO etc have also been studied to assess the overall quality of water and its suitability for drinking and irrigation purposes.[11-12]

Study Area

The district of Tarntaran is situated in northwest region of Punjab, India covering 5059 Sq Km Area.. It is surrounded by district Amritsar in the north, Kapurthala in the east, Ferozepur in the South and Pakistan in the West. Patti town is a municipal council of the Tarntaran district, located 45 km from Amritsar with geographical coordinates 31^0 16' 51" north and 74^0 51' 25" east. Even though only limited region experience temperature below 0 ^{0}C, ground frost is commonly found in majority of the areas in winter season. The temperature rises gradually with high presence of moisture and overcast sky. However, the rise in temperature is steep when sky is clear and moisture content is very less, falling within the semiarid region and frequently facing water scarcity as well as quality problems, so assessment of water quality becomes an important research concern.

Methodology

Sampling, storage and preservation

Field visits were carried out to collect water samples from hundred locations in twenty villages

Fig. 1: location map Sample collection sites

on the Patti –Khem Karan highway with five samples from each village, and were subjected to analysis for chemical characteristics. These samples were collected in duplicates randomly from water sources (Hand-pumps/submersible pumps/public and private Tube wells) of the selected sites. The collected water samples were transferred into pre-cleaned polythene bottles for analysis of chemical characteristics.

Hydrochemical analysis of water samples

Chemical analyses was carried out for the major ion concentrations in water samples collected from different locations using the standard procedures recommended by APHA-1994[13]. The analytical data can be used for the classification of water for utilitarian purposes and for ascertaining various factors on which the chemical characteristics of water depend. Cations like calcium and magnesium were analyzed using volumetric method while sodium and potassium were analyzed by flame photometer, whereas anions like chloride and bicarbonate were analyzed by volumetric method while sulphate was analyzed by spectrometric method.

Physicochemical analysis of water samples

The onsite analysis of various physicochemical parameters (such as pH, TDS, DO, Electrical conductance and salinity) was carried out using water analysis kit. The conductance and pH measurements were done using microprocessor based conductivity meter and pH meter (Systronics, India). The analysis of other parameters such as TDS, pH, DO etc was carried out for the classification of water for purposes other than agricultural use and also for ascertaining various factors on which the chemical characteristics of water depends[14-17].

Analysis of water samples for Heavy metal ions

The analysis of heavy metal was carried out by emission spectrometer, ICAP 6300 (Thermo Electron Corporation)[18-26]. ICAP 6300 allows for simultaneous analysis of all elements from sub ppb to percentage level. The instrument is calibrated by using stock solutions of known concentration of heavy metals ions and various dilutions of stock solution. Analysis of a solution of known concentration is required to check the performance of the instrument.

RESULTS AND DISCUSSIONS

Hydro-Chemistry

The assessment of hydro chemistry of ground water is important for its irrigational and domestic usage. Maximum and minimum

Table 1: Hydro-chemical analysis of ground water

Village	Na^{+1}	K^{+1}	Ca^{+2}	Mg^{+2}	HCO_3^{-1}	CO_3^{-2}	Cl^{-1}	SO_4^{-2}	Total Hardness
Patti	61.9	14.2	56	24	314	34	534	162	856
Patti Rural	68.1	13.8	76	34	354	35	587	154	912
Kulla	149.8	27.3	84	46	298	27	486	134	798
Chuslewar	171.5	14.2	118	56	346	36	438	102	976
ThakarPura	178.9	19.2	128	43	178	25	432	121	768
Asal	143.8	10.1	114	34	179	29	398	125	698
Boparai	71.8	17.2	134	47	278	28	476	89	854
Dhaliwal	165.2	16.9	69	36	179	27	498	144	916
ParagPura	176.2	27.2	158	47	197	29	578	121	924
Thatha	156.4	21.9	76	34	243	29	459	140	912
Dhagana	146.1	19.8	112	29	198	26	528	145	871
Gharyala	112.4	23.3	115	31	178	27	473	136	824
Punian	168.8	18.1	164	37	199	31	472	117	874
Maan	164.2	23.8	119	39	187	36	481	148	891
Varnala	145.6	17.4	167	43	204	33	477	143	901
Valtoha	114.2	19.3	185	26	213	29	397	98	746
Khern Karan	87.4	26.6	180	43	243	25	295	129	721
Asaluttar	137.6	25.5	143	48	196	26	574	151	970
Mashika	76.5	22.7	104	37	231	33	538	141	995
Khem Karan	89..7	16.3	97	41	195	34	412	135	859

concentration of major ions present in the groundwater from the study area is presented in Table 1.

Cations

Cation concentration (Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}) in the groundwater samples come out to be much below the WHO limits (WHO 2011). Presence of calcium (Ca^{+2}) and magnesium (Mg^{+2}) ions in water is largely due to leaching of limestone, dolomites, gypsum and anhydrites. The concentration of Ca^{+2} is varied from 56.0 mg/l to 180.0 mg/l. (WHO limit 100 mg/l; WHO 2011). The concentration of Mg^{+2} ion varied from 24 mg/l to 56 mg/l. (WHO limit 30 mg/l; WHO 2011) similarly, the concentration of Na^{+} ion varied from 61.9 mg/l to 178.9 mg/l. (WHO limit 175 mg/l; WHO 2011). The concentration of K^{+} ion varied from 13.8 mg/l to 27.2 mg/l. (WHO limit 25 mg/l; WHO 2011)

Anions

The concentration of Chloride ion varied from 397 mg/l to 587 mg/l. (WHO limit 600 mg/l; WHO 2011). The bicarbonate ion concentration varied from 178 mg/l to 354 mg/l. The Sulphate ion concentration varied from 98 mg/l to 162 mg/l. (WHO limit 250 mg/l; WHO 2011). A number of correlation studies between various major cations and anions present in water were carried out to know the extent of availability of one type of ion in reference to other.

Piper Tri linear diagram

The Piper-Hill diagram[13] is used to infer

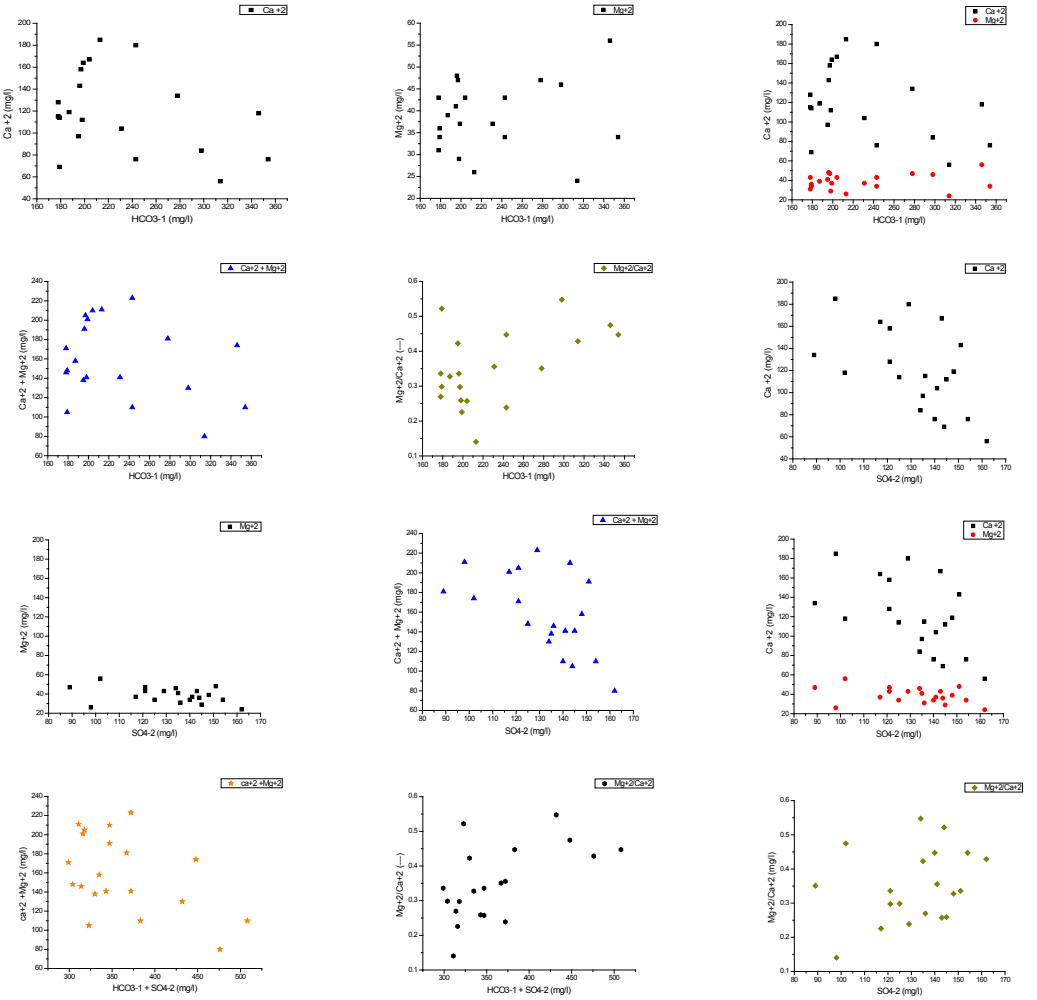

Fig. 2: Variation and correlations of various ions in water samples

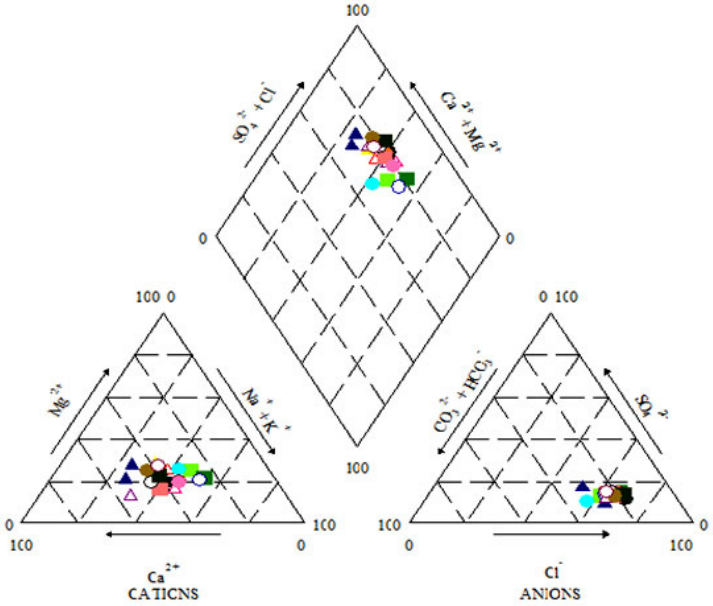

Fig. 3: Piper-Hill Trilinear diagram of analyzed water samples

Table 2: Physico-chemical analysis of ground water

S No.	Village	Temp	TDS	EC	pH	Salinity(ppt)	DO
1	Patti	32	256	687	7.31	0.001	2.4
2	Patti Rural	29	912	780	7.93	0.003	2.9
3	Kulla	28	798	1431	7.12	0.001	2.6
4	Chuslewar	27	976	1122	8.40	0.002	2.5
5	ThakarPura	26	768	2130	8.32	0.002	2.5
6	Asal	30	598	1243	8.14	0.003	2.8
7	Boparai	31	854	1187	7.75	0.001	2.7
8	Dhaliwal	32	816	3212	7.71	0.001	2.3
9	ParagPura	30	924	1232	7.24	0.001	2.3
10	Thatha	32	412	879	8.63	0.002	2.4
11	Dhagana	32	871	978	8.91	0.002	2.3
12	Gharyala	30	824	971	7.01	0.001	2.6
13	Punian	29	1096	1134	6.97	0.001	2.5
14	Maan	28	891	1287	7.91	0.001	2.4
15	Varnala	27	901	1553	7.17	0.002	2.4
16	Valtoha	25	746	876	7.20	0.001	3.2
17	Khern Karan	29	721	710	7.34	0.002	2.5
18	Asaluttar	32	470	3090	7.21	0.001	2.3
19	Mashika	30	995	680	7.43	0.003	2.5
20	Khem Karan	31	859	554	7.11	0.001	2.5

hydro-geochemical facies. These plots include two triangles, one for plotting cations and the other for plotting anions. The cation and anion fields are combined to show a single point in a diamond-shaped field, from which inference is drawn on the basis of hydro-geochemical facies concept. This tri-linear diagram is useful in bringing out chemical relationships among groundwater samples in more definite terms rather than with other possible plotting methods.

Chadha's diagram

The difference in milli equivalent percentage between alkaline earth metal ions (Ca^{+2} and Mg^{+2})and alkali metal ions ($Na^{+}$and K^{+}) expressed as percentage is plotted on the X- axis and difference in milli equivalent percentage between weak acidic anions($CO_3^{-2}$and HCO_3^{-1})and strong acidic anions ($Cl^{-1}$and SO_4^{-2})expressed as percentage is plotted on the y axis

Table 3: Concentrations of heavy metals (mg/l) in ground wayer samples

Village	Arsenic	Cadmium	Chromium	Copper	Iron	Nickel	Manganese	Lead	Zinc
Patti	0.005	0.0012	0.001	0.004	0.053	0.001	0.114	0.005	0.037
Patti Rural	0.003	0.0010	0.000	0.003	0.033	0.001	0.001	0.006	0.064
Kulla	0.000	0.0010	0.000	0.000	0.003	0.002	0.005	0.003	0.012
Chuslewar	0.002	0.0011	0.000	0.001	0.006	0.002	0.007	0.003	0.013
ThakarPura	0.004	0.0012	0.000	0.000	0.010	0.001	0.001	0.001	0.012
Asal	0.001	0.0010	0.001	0.000	0.001	0.001	0.001	0.001	0.020
Boparai	0.001	0.0012	0.000	0.002	0.001	0.002	0.001	0.007	0.012
Dhaliwal	0.001	0.0011	0.001	0.000	0.001	0.003	0.013	0.004	0.010
ParagPura	0.001	0.0011	0.001	0.000	0.002	0.001	0.017	0.004	0.010
Thatha	0.002	0.0010	0.000	0.001	0.010	0.001	0.001	0.001	0.009
Dhagana	0.001	0.0010	0.000	0.000	0.001	0.004	0.001	0.001	0.009
Gharyala	0.001	0.0010	0.000	0.000	0.002	0.001	0.010	0.003	0.070
Punian	0.005	0.0011	0.001	0.000	0.002	0.004	0.001	0.001	0.012
Maan	0.001	0.0012	0.001	0.001	0.000	0.004	0.009	0.002	0.078
Varnala	0.001	0.0010	0.000	0.001	0.000	0.004	0.003	0.007	0.024
Valtoha	0.001	0.0010	0.000	0.000	0.000	0.001	0.007	0.002	0.012
Khern Karan	0.002	0.0010	0.000	0.000	0.020	0.001	0.001	0.001	0.012
Asaluttar	0.002	0.0012	0.001	0.000	0.034	0.002	0.010	0.001	0.012
Mashika	0.001	0.0011	0.001	0.001	0.032	0.001	0.001	0.002	0.010
Khem Karan	0.004	0.0010	0.001	0.001	0.047	0.001	0.001	0.002	0.031

Table 4: Safe limits of heavy bmetals in the water as prescribed by various agencies

Heavy metal	Safe Limit(WHO standards)	Safe Limit(Indian standards)	Safe Limit(European standards)
Arsenic(As)	0.01 mg/l (ppm)	0.05 mg/l (ppm)	0.01 mg/l (ppm)
Cadmium(Cd)	0.003 mg/l (ppm)	0.01 mg/l (ppm)	0.005 mg/l (ppm)
Chromium(Cr)	0.05 mg/l (ppm)	0.05 mg/l (ppm)	0.05 mg/l (ppm)
Copper(Cu)	1.5 mg/l (ppm)	1.5 mg/l (ppm)	2.0 mg/l (ppm)
Iron(Fe)	—-	1.0 mg/l (ppm)	0.2mg/l (ppm)
Nickel(Ni)	0.02 mg/l (ppm)	3.0 mg/l (ppm)	0.02 mg/l (ppm)
Manganese(Mn)	0.5 mg/l (ppm)	0.5 mg/l (ppm)	0.05 mg/l (ppm)
Lead(Pb)	0.01 mg/l (ppm)	0.1 mg/l (ppm)	0.01 mg/l (ppm)
Zinc(Zn)	3.0 mg/l (ppm)	10.0 mg/l (ppm)	——

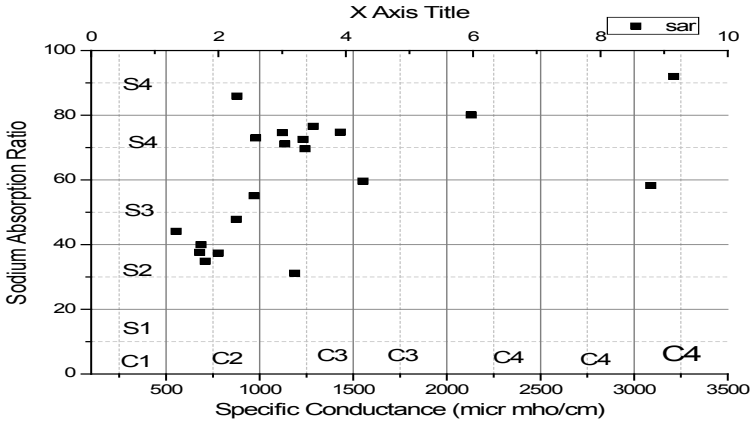

Fig. 5: USSL Classification of Water in the study area

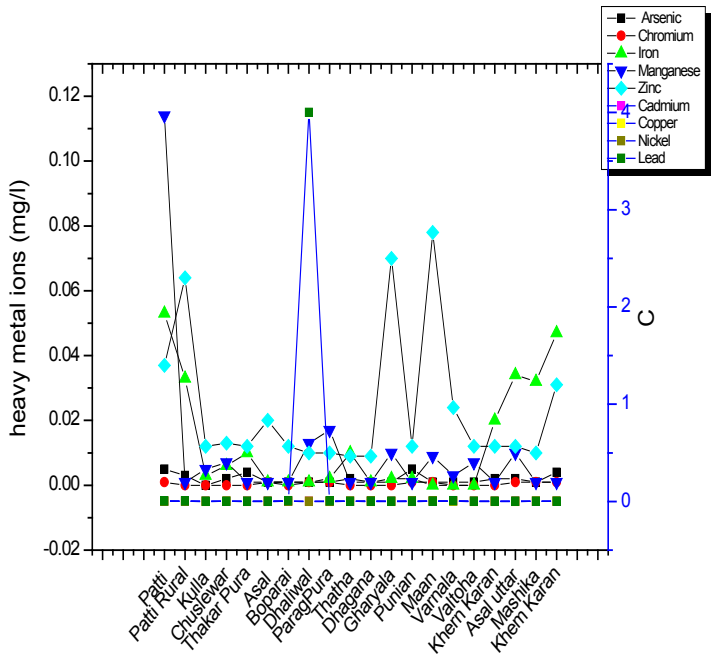

Fig. 6: Variation of heavy metal ions

Table 5: Distribution of physicochemical parameters in the water samples (statistical analysis)

S. No.	Parameter	N	Mean ± S.D.	Max.	Min.	Median	WHO
1.	Temp	100	29.5±1.8	32	26	30	—
2.	TDS	100	784.4±0.8	1096	256	839	—
3.	EC	100	1286.8±14	3212	554	1128	—
4.	pH	100	7.64±0.20	9.1	7.2	7.385	6.5-8.5
5.	salinity	100	0.0016±0.001	0.003	0.001	0.001	—
6.	DO	100	2.53±0.2	3.2	2.3	2.5	—

Sodium Adsorption Ratio (SAR)

It is a measure of the suitability of water for use in agriculture and given by the relation:

$$\frac{Na^{+1}}{\sqrt{\frac{Ca^{+2}+Mg^{+2}}{2}}}$$

Based on SAR values water samples are classified as excellent (SAR<10), good (10-20), doubtful (20-30) and unsuitable (>30). The SAR value is associated with alkalinity hazard in ground water used for irrigation. In the present study of ground water samples SAR value varied from 5.85 to 13.83.

Residual Sodium carbonate (RSC)

The hazardous effects of carbonate and bicarbonate in ground water used for irrigation are best explained in terms of residual sodium carbonate (RSC) which is calculated as follows

$$RSC = (HCO3^{-1} + CO3^{-2}) - (Ca^{+2} + Mg^{+2})$$

Based on RSC water has been classified as safe (RSC<1.25), marginal (RSC=1.25-2.50) and unsuitable (RSC>2.50). In the present study of ground water samples RSC value varied from -5.85 to 1.48.

Magnesium Ratio

The quality of water is greatly affected by magnesium, because large amount of magnesium in water makes the soil alkaline which leads to a decrease in crop yield. The amount of magnesium in water is best expressed as the magnesium ratio which is calculated as follows

$$Magnesium\ Ratio = \left[\frac{Mg^{+2}}{(Ca^{+2} + Mg^{+2})}\right] \times 100$$

Water has been classified as good (Mg ratio<20), suitable (Mg ratio=20-50) and poisonous (Mg ratio>50) for plants. In the present study of ground water samples RSC value varied from 27.3 to 47.7.

Permeability Index (PI)

Permeability index (PI) is used to measure the suitability of ground water for irrigation purpose. With the consistent use of water the levels of sodium potassium magnesium and bicarbonates change in the soil so that permeability index changes. Permeability index is given by the equation

$$Permeabilty\ Index(PI) = \left[\frac{Na^{+1} + 0.5(HCO_3^{-1})}{(Ca^{+2} + Mg^{+2} + Na^{+1})}\right] \times 100$$

Based on PI water has been classified as good (Mg ratio<20), suitable (Mg ratio=20-50) and poisonous (Mg ratio>50) for plants. In the present study RSC value varied from 27.3 to 47.7.

USSL classification

For the use of water in irrigation purpose it useful to interpret the water quality by USSL diagram which tells us about the alkali hazard of the groundwater samples for the study area. (Todd 1980). In this diagram the sodium adsorption ratio is plotted against specific conductance. The

Table 6: Distribution of heavy metal ions in the water samples (statistical analysis)

S. No.	Heavy Metal ion	N	Mean	Max.	Min.	Median	WHO
1.	Arsenic	100	0.00195	0.005	0.000	0.001	0.01
2.	Cadmium	100	0.001075	0.0012	0.0010	0.00105	0.003
3.	Chromium	100	0.00045	0.001	0.000	0.000	0.05
4.	Copper	100	0.00075	0.004	0.000	0.000	1.5
5.	Iron	100	0.0129	0.053	0.000	0.0025	—-
6.	Nickel	100	0.0019	0.004	0.001	0.001	0.02
7.	Manganese	100	0.01025	0.114	0.001	0.002	0.5
8.	Lead	100	0.00285	0.007	0.001	0.002	0.01
9.	Zinc	100	0.02345	0.070	0.010	0.012	3.0

sixteen classes in the diagram indicate the extent that waters can affect the soil in terms of salinity hazard as low(C1),Medium(C2), high(C3), and very high(C4)and similarly sodium hazard as low(S1), medium(S2), High(S3) and very high(S4). Most of the sample of the analyzed data fall in the region C3S4.This category is predominant in the study area and it is suit-able for irrigations purposes as shown in Fig. 5.

Physicochemical Characteristics

The assessment of Physicochemical characteristic of ground water is carried out on site using the water testing kit. The value of various parameters collected from the study area is presented in Table 2

pH measurements

The pH of groundwater in the study area varied from 7.1 to 9.2, indicating its alkaline nature. (WHO limit 6.5 to 8.5; WHO 1993), only two samples exceed the limit of 8.5.

Electrical Conductivity (EC)

Conductivity of the groundwater in the study area varied from 554 to 3212 µS/cm. (WHO limit 1500 µS/cm ; WHO 1993). Measurement of conductivity is important as it provides an insight to concentrations and type of ions present in ground water. A high conduction is generally an indication of high chloride ion concentration in ground water. Water is regarded as excellent (conductivity less than 500 µS/cm), good (500-1250 µS/cm), permissible (1250-2500 µS/cm), bad (2500-5000 µS/cm) and unsuitable for irrigation (above 5000 µS/cm).

Total dissolved solids (TDS)

Cations including (Na^+, K^+, Ca^{+2} and Mg^{+2}) and anions including (HCO_3^{-1}, CO_3^{-2},Cl^{-1}, SO_4^{-2}, NO_3^{-1}) are the major contributors toward TDS .The TDS of ground water in the study area varies from 256 to 1096 mg/l. Water is regarded as excellent with TDS less than 150 ppm, with 150-400 good, with 400-1500 permissible and above 1500 ppm it becomes unsuitable for irrigation.

Dissolved Oxygen (DO)

DO content varied from a minimum value of 2.3 mg/l to 3.g mg/l. It showed a typical relationship with temperature as the temperature rises the DO content falls.

Heavy metal ion

The ground water samples were also analyzed for metal concentrations (Tables 3) it was found that the metal ion concentration was well within the safer limits as given by WHO. The recommendation for safe limits of metal ions in drinking water is given in Table 4 .Maximum arsenic concentration was found in Patti town (0.005mg/l) and it varied from 0.001 mg/l to 0.005 mg/l in the entire study area. These values of As are well within the permissible limits recommended by USEPA[32]. Hence the water of the study area is suitable for human consumption and domestic usage.

Statistical analysis

The data were subjected to normal distribution analysis and Pearson correlation using Microsoft Excel 2007 and origin pro 8.5.Normal distribution analysis (involved mean, median, standard deviation, skewness and kurtosis) analysis is an important statistical tool for identifying the distribution patterns of the different water quality parameters in groundwater samples.[35-41] . Pearsons correlation coefficient is usually signified by σ(rho), and can take on the values from -1.0 to 1.0. Where -1.0 is a perfect negative inverse) correlation, 0.0 is no correlation and 1.0 is a perfect positive correlation. The variables having coefficient value (r) > 0.5 or < -0.5 are considered significant.

CONCLUSIONS

1. The type of water that predominates in the study area is Ca-Mg-HCO_3 type during based on hydro-chemical analysis.
2. The suitability of water for irrigation is determined based on SAR, %Na, RSC and salinity hazard, it is only an empirical conclusion. Other factors like soil type, type of crop, frequency and pattern of crop, rain fall and its frequency, climate, etc. all are important in deciding the suitability of water. Most of the samples in the study area fall in the suitable range for irrigation purpose either from SAR, % Na or RSC values.
3. Physicochemical characteristic of water were determined in order to assess the overall quality of water.
4. The concentrations of heavy metal ions in water samples were well below the

permissible limits indicating their suitability for drinking and irrigation purposes

5. The correlation coefficient values for the water samples show a perfect positive correlation
6. Most of the samples in study area fall in the suitable range for irrigation and drinking purpose as recommended by WHO 2011.

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