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Research Paper

Analysis of Groundwater Quality Using Statistical Techniques: A Case Study of Dholpur District, Rajasthan (INDIA)

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Abstract: *The study was conducted to evaluate the groundwater quality of Dholpur district, Rajasthan, (India). Groundwater samples were collected from 40 different locations in summer, winter and rainy seasons during the year of 2014 to 2015 and analyzed the water quality parameters. The variability of physicochemical parameters in groundwater can be measured with high coefficient of variance. The correlation between dependent and independent variables was determined using statistical analysis. It was observed from correlation analysis that moderate correlations exist between EC and TDS also between TDS and total hardness. In 100% of the samples, alkalinity concentration recorded higher than maximum permissible limit prescribed by BIS: IS: 10500: 2012. The concentration of electrical conductivity (EC), total dissolved solids (TDS), nitrate (NO_3^-), Iron (Fe) and Lead (Pb) were also found above the standard limits prescribed by BIS. This reveals deterioration of water quality. It is therefore, suggested to take up regular monitoring of groundwater in areas of Dholpur district.*

Keywords: Contamination, physicochemical characteristic, correlation coefficients etc.

Introduction

The quality of water is of vital concern to the humankind as it is directly linked with human welfare[1]. The assessment of groundwater is very important before it's used for drinking, domestic, industrial or agricultural purpose. Groundwater is an important source of fresh water having a balanced concentration of minerals. Human activities such as overpopulation, urbanization, industrialization, agricultural activities, and mining have greatly affected this balance[2]. The need of water are more complex due to population growth, urbanization and industrialization. Water is believed to be elixir of life. Although it is plentiful in nature, occupying 71% of the earth's surface, only 1% is accessible for human consumption. Thus, the quality of this 1% drinking-water is a powerful environmental determinant of health, as it has an important impact on health of people. Humanity highly depends on water and its proper utilization and management[3].

Unavailability of good quality drinking water is wide spread and this has serious health implications. In developing nations of the world, 80% of all diseases and over 30% of deaths are related to drinking water [4].

Material and Methods

In the present study, forty water samples were collected in summer, rainy and winter seasons during the year of 2014 to 2015. The samples were collected as per the standard methods prescribed for sampling. Plastic bottles of 1.5 liter capacity with stopper were used for water sampling. Each bottle was washed with 2% Nitric acid and then rinsed three times with distilled water. Samples were analyzed as per the standard methods described by American Public Health Association (APHA 2005).

Table 1: Water quality parameters and their used methods

S. No.	Parameters	Method Used
1	pH	Digital pH meter
2	Electrical conductivity (EC) and TDS	Digital EC-TDS analyzer (model No: CM 183)
3	Turbidity	Nephalometer (model No: 2100 Q-01 make: Hach USA)
4	Iron (Fe)	UV-Vis laboratory spectrophotometer
5	Nitrate, Sulphate and Fluoride	UV-Vis laboratory spectrophotometer
6	Calcium and Magnesium	UV-Vis laboratory spectrophotometer
7	Cu, Zn and Pb	UV-Vis laboratory spectrophotometer

Results and Discussion

General Chemistry

Temperature: Temperature is an important parameter which affects dissolved oxygen, rate of photosynthesis and distribution of biota. The average temperature values were obtained 28.45, 27.05 and 28.46^{0}C in rainy, winter and summer seasons, respectively. During present investigation the temperature was found to be significantly lower in the winter season than the summer and rainy season. This might be the temperature of water changes with respect to season and environmental conditions[5]. During winter, the temperature remains low due to cold low ambient temperature and shorter photo period [6].

pH: The average pH values were found 7.607, 6.837 and 8.077 in rainy, winter and summer seasons respectively. The pH value was found higher in summer season as compare to rainy and winter season. This implied because during winter and rainy season, rainfall combines with carbon dioxide, can influence the water toward acidity. The study was also shown that water samples are slightly alkaline in nature. The groundwater samples were shown the pH within the standard limit prescribed by BIS and WHO (6.5 to 8.5 and 6.9-8.5 respectively). Most of the similar study suggested that water samples are slightly alkaline due to presence of carbonates and bicarbonates [6-8].

Turbidity: The turbidity is a measure of the extent to which light is either absorbed or scattered by suspended material in water. The average turbidity values were found 2.770, 2.717and 2.693 NTU in rainy, winter and summer seasons, respectively. The highest value of turbidity is 5.00 NTU. The present finding coincides that the turbidity of groundwater was found to be higher in winter and rainy than summer due to the presence of dissolved clay and mud materials in groundwater[9]. Also water becomes turbid mainly due to the presence of colloidal and extremely fine dispersion[8].

Electrical Conductivity: Electrical Conductivity of water is a good indicator of pollution as most of the soluble pollutants exist as ions in water. The average electrical conductivity values were found 3015, 2286 and 2858 µS/cm in rainy, winter and summer seasons, respectively. In contrast to previous studies, the higher value of electrical conductivity in rainy season due to flood containing high electrolyte in water, the electrolytes of water sample increases drastically[10]. According to range of EC in Table 2, it was found doubtful in Dholpur district.

Table 2: The range of electrical conductivity for water class given by APHA

S. No.	Electrical Conductivity (µS/cm) range	Water Class
1	0 – 250	Excellent
2	250 – 750	Good
3	750 – 2250	Moderate
4	2250 – 4000	Doubtful
5	> 4000	Not-suitable

Total Alkalinity: The average total alkalinity values were obtained 541.087 mg/L in rainy, 526.477 mg/L in winter and 514.790 mg/L in summer seasons. It was observed that the 100% of samples were found above the standard limits prescribed by of BIS (200 mg/L) and WHO (300 mg/L) also the higher value of total alkalinity was observed during the month of rainy season as compare to winter and summer. These results were coincides with the study of Singh and Saha (1987) according to them the value of total alkalinity was found to be higher during summer. Similarly, the total alkalinity had higher values in summer season followed by steep fall in monsoon due to dilution of water[11] and the excess of alkalinity could be due to dissolved mineral compounds in mineral rich soil [12].

Total Dissolved Solids (TDS): Total dissolved solids include salt and variety of organic substances, which readily dissolve in water and often impart a degree of hardness. The average value of TDS found 1300.893, 1264.220 and 1277.620 mg/L in rainy, winter and summer seasons, respectively. TDS value observed high in rainy season than winter and summer. The values found to be significant higher than permissible limits prescribed by BIS and WHO. The present findings were matched with the observation reported by Trivedi et al., (1984)[13]. The presence of total dissolved solids in groundwater may be due to ground water pollution. The groundwater becomes polluted by discharge of waste water from both residential and commercial areas. They were migrated into pits, ponds in ground surface, down to the water table[14].

Total Hardness: The water hardness is usually due to the multivariate metal ions which come from minerals dissolved in the water. The average value of values of total hardness was obtained 537.233, 474.593 and 448.420 mg/L in rainy, winter and summer seasons, respectively. The observation found to be significant higher value of total hardness in rainy season than winter and summer. These value much higher than those in groundwater of Angul Talcher region in Orissa[15].

Table 3: The range of total hardness as per APHA standard

S. No.	Total hardness (mg/l) range	Water Class
1	0 – 30	Soft
2	30 – 60	Moderate soft
3	60 – 120	Moderate hard
4	120 – 180	Hard
5	> 180	Very hard

Calcium: The mean value of calcium hardness was found 64.050, 53.653 and 51.525 mg/L in rainy, winter and summer seasons, respectively. The value of Ca-hardness found within the permissible limit (75 mg/L and 75-200 mg/L) prescribed by BIS and WHO. The values of Ca-hardness were significantly higher in rainy, moderate in winter and lower in summer. It might be due to run off municipal sewage, domestic waste and plant nutrients from surrounding of the ponds[13]. The organic substance and agricultural waste increase calcium hardness[16].

Table 4: The ideal range of Ca^{2+} hardness as per APHA standard

S. No.	Ca^{2+}- hardness (mg/l) range	Water Class
1	0 – 20	Soft
2	20 – 40	Moderate soft
3	40 – 80	Moderate hard
4	80 – 120	Hard
5	> 120	Very hard

Magnesium: The average values of magnesium were obtained 78.993 mg/L, 71.920 mg/L and 70.353 mg/L in rainy, winter and summer seasons respectively. These values were significant to be higher (30 mg/L) prescribed by BIS but under the limit of WHO (30-150 mg/L) standard.

Nitrate: The mean nitrate in groundwater was found 71.303, 66.587 and 56.730 mg/L in rainy, summer and winter seasons, respectively. It was observed that the concentration of nitrate ions were higher in rainy season as compare to winter and summer. It was significantly higher compared to BIS value (45 mg/L) and WHO Value (40-50 mg/L).The highest nitrate concentrations were observed in groundwater where water circulation occurs close to surface.

Sulphate: The present investigation found the average values of sulphate 58.550 mg/L, 58.893 mg/L and 66.353 mg/L in rainy winter and summer seasons respectively. The values were found within the standard limits (200 mg/L and 200-250 mg/L) prescribed by BIS and WHO respectively. The observation showed the higher value of sulphate in summer than winter and rainy seasons. The results of present study were also agreement with Angadi et al., (2005)[17] who revealed that the sulphate is produced by biological oxidation of sulphur content of organic matter and had minimum concentration in winter and maximum in summer.

Fluorides: The fluoride average values were obtained 1.003, 0.060 and 0.853 mg/L in rainy, winter and summer seasons, respectively. The study showed the higher value in rainy season than winter and summer, found above (in rainy season) the standard limit (1.0 mg/L) prescribed by BIS but within the limit (1.0-1.5 mg/L) prescribed by WHO. The higher concentration in rainy season which may be attributed to surface run off, infiltration and leaching of Fluoride from the ground layers[18].

Total Organic Nitrogen: The average value of total nitrogen content were found 5.960, 5.747 and 5.527 mg/Lin rainy, winter and summer season respectively. The nutrient nitrogen commonly present naturally in ground water but high concentration of nitrate in shallow groundwater might be associated with animal or human waste, septic or sewage releases as well as lawn and garden fertilization[19].

Table 5: The ideal range of dissolved oxygen as per BIS standard

S. No.	Dissolved Oxygen (mg/l) range	Water Class
1	6.5	Non/ slightly polluted
2	4.5 – 6.5	Lightly polluted
3	2.0 – 4.5	Mostly polluted
4	< 2.0	Severely polluted

Dissolved Oxygen (DO): The average value of dissolved oxygen has been found 4.743, 5.560 and 5.033 mg/L in rainy, winter and summer seasons, respectively. The good quality of water has solubility of oxygen 7.0 to 7.6 mg/L at 30-35^{0}C and 14.6 mg/L in fresh water. The present finding showed the higher level of Dissolve Oxygen in winter, moderate in summer and lower in rainy season due to high value of conductivity of water.

Table 6: Parameters exceeding the permissible limit

S. No.	Parameter	Permissible limit as per BIS IS:10500:2012	Permissible limits as per WHO drinking water standards	Average results of samples		
				Seasonal		
				Rainy	Winter	Summer
1	Temperature in ^{0}C	-	30-40	28.450	27.057	28.460
2	pH	6.5-8.5	6.9-8.5	7.607	6.837	8.077
3	TDS in mg/L	500.00	500-1500	1300.893	1277.620	1264.220
4	EC in mmohs/cm	1500.00	300	3015	2286	2858
5	Turbidity in NTU	1.00	No guideline	2.770	2.717	2.693
6	Iron in mg/L	0.3	2.0	0.470	0.550	0.647
7	Nitrate (mg/L)	45.00	40-50	66.587	71.303	56.730
8	Sulphate (mg/L)	200.0	200-250	66.353	58.893	58.550
9	Fluorides (mg/L)	1.0	1.0-1.5	1.003	0.060	0.853
10	Total Alkalinity (mg/L)	200.00	300.00	514.790	526.477	541.087
11	Total Hardness (mg/L)	200.00	100-500	537.233	474.593	448.420
12	Calcium(mg/L)	75.00	75-200	53.653	64.050	51.525
13	Magnesium (mg/L)	30.00	30-150	78.993	71.920	70.353
14	Copper (mg/L)	0.05	1.5	0.503	0.590	0.670
15	Zinc (mg/L)	5.00	15.0	2.217	2.273	2.277
16	Nitrogen (mg/L)	No guideline	-	5.960	5.747	5.527
17	Lead (mg/L)	0.01	-	0.020	0.023	0.019
18	Dissolved Oxygen (mg/L)	No guideline	6.0	5.560	4.743	5.033
19	COD (mg/L)	No guideline	-	5.287	4.330	4.717

Note: Electrical conductivity in different seasons in (µS/cm)

Chemical Oxygen Demand: The chemical oxygen demand indicates the extent of chemical pollution mainly from industrial effluent. The average value of chemical oxygen demand found 5.287 mg/L, 4.330 mg/L and 4.717 mg/L in rainy, winter and summer seasons respectively. The present study showed higher value in rainy season than winter and summer. This may be due to introduction of chemical waste minerals in surface water and infiltration into the groundwater during rainfall.

Iron: The average value of iron in groundwater was obtained 0.470 mg/L, 0.550 mg/L and 0.647 mg/L in rainy, winter and summer seasons respectively. The values were found above the standard limit (0.30 mg/L) prescribed by BIS.

Copper: The average level of copper was found 0.503 mg/L, 0.590 mg/L and 0.670 mg/L in rainy, winter and summer seasons respectively. It was observed that the level of copper was to be significantly higher beyond the limit (0.05 mg/L) prescribed by BIS.

Zinc: The average level of zinc was found 2.217 mg/L, 2.273 mg/L and 2.277 mg/L in rainy, winter and summer seasons respectively. It was observed that the level of zinc was to be significantly within the limit (5.0 mg/L) prescribed by BIS. Zinc compounds are astringent, corrosive to skin, eye and mucus membrane. They cause special type of dermatitis known as ‘Zinc pox’.

Lead: Lead is highly toxic metals and should normally be present only in traces. In the present study, the average levels of lead was found to be maximum in winter (0.023, mg/L) and rainy (0.020 mg/L) seasons than summer (0.019 mg/L).

Statistical Analysis

The statistical analysis of the obtained data was conducted and performed using SPSS-PASW 18.0 trial version and MS-excel 2000. This analysis was carried out to establish the relationship between dependent and independent variables.

Correlation Analysis

Correlation is the mutual relationship between two variables. Direct correlation exists when increase or decrease in the value of one parameter is associated with a corresponding increase or decrease in the value of other parameter[20]. The relationship between two variables is the correlation coefficient (r) which shows how one variable predicts the other. It is the percentage of variance in the dependent variable explained by the independent variables. A high correlation coefficient (r) nearly 1 or -1 means good relationship between two variables. A correlation coefficient r=0, means there is no relationship between two variables. The positive sign or values indicate the positive correlation and negative values indicates the negative correlation between two variables. The correlation and regression analysis is useful technique for interpretation of quality data of groundwater and relate them to specific hydro geological processes. [21] These tools are quite useful for identification of the distribution patterns of different water quality parameters in groundwater samples. The correlation for different water quality parameters has shown in Table 7. It has shown the correlation between dependent and independent water quality parameters. If the P<0.05, then r value found to be significant. On the other hand if P>0.05, then r value found to be non-significant.

Table 7: Correlation between dependent and independent variables

Correlations					
S. No.	**Parameters**		**pH**	**Electrical Conductivity**	**Temperature**
1	Total Alkalinity	r value	0.019	-0.090	0.071
		P value	0.714	0.088	0.179
2	Total Hardness	r value	-0.065	-0.160	-0.167
		P value	0.221	0.002	0.001
3	TDS	r value	0.045	0.138	-0.016
		P value	0.396	0.009	0.758
4	Turbidity	r value	0.103	0.071	-0.040
		P value	0.051	0.177	0.448
5	Calcium	r value	-0.020	0.042	-0.039
		P value	0.701	0.422	0.463
6	Magnesium	r value	-0.005	0.007	-0.057
		P value	0.918	0.900	0.280
7	Nitrate	r value	-0.115	-0.031	-0.129
		P value	0.029	0.552	0.014
8	Fluoride	r value	0.228	0.332	0.409
		P value	0.000	0.000	0.000
9	Sulphate	r value	-0.128	-0.098	0.121
		P value	0.015	0.063	0.021
10	DO	r value	0.007	0.124	-0.102
		P value	0.892	0.018	0.053
11	COD	r value	0.107	0.220	0.138
		P value	0.043	0.000	0.009
12	Nitrogen	r value	-0.049	0.004	-0.124
		P value	0.357	0.935	0.018
13	Iron	r value	0.007	-0.167	0.032
		P value	0.891	0.002	0.550
14	Lead	r value	-0.074	-0.039	-0.116
		P value	0.162	0.460	0.027
15	Zinc	r value	-0.082	0.086	-0.018
		P value	0.119	0.103	0.737
16	Copper	r value	0.065	-0.161	0.088
		P value	0.218	0.002	0.097

Total no. of observation (N) = 360 and Correlation is significant at the 0.05 level (2-tailed).

r value- Correlation coefficient P value- Level of significance

The independent variable, pH has shown the positive correlation with turbidity (r = 0.103), fluoride ions (r = 0.228) and COD (r = 0.107) variables. It showed the moderate relationship with them. Similarly, pH shown the negative correlation with NO_3^- (r = -0.115) and SO_4^{2-} (r = -0.128) variables and showed the moderate correlation. i.e. P < 0.05 as shown in Table 8. As the pH value increases, the value of turbidity, fluoride ions and COD were also increased likewise on increasing the pH value, the concentration of nitrate and sulphate were decreased.

Table 8: Correlation of independent variable (pH) with other dependent variables

S. No.	Positive (+ve) Correlation	Negative (-ve) Correlation
1	Turbidity (r = 0.103)	Nitrate, NO_3^- (-0.115)
2	Fluoride ions (r = 0.228)	Sulphate, SO_4^{2-} (r = -0.128)
3	COD (r =0.107)	

The electrical conductivity (EC, independent variable) has shown the positive correlation with TDS (r=0.138), COD (r=0.220), DO (r =0.124) and fluoride (r=0.332) and were found to be significant i.e. $P < 0.05$ as shown in Table 8. On the other hand, EC has shown the negative correlation with Cu(r=-0.161), Fe(r=-0.167) and total hardness (r=-0.160). It has shown the moderate significant with all these dependent variables as presented in Table 9.

Table 9: Correlation of independent variable (EC) with other dependent variables

S. No.	Positive (+ve) Correlation	Negative (-ve) Correlation
1	TDS (r = 0.138)	Total hardness (r=-0.160)
2	Fluoride (r = 0.332)	Iron (r = -0.167)
3	DO (r = 0.124)	Copper (r = -0.161)
4	COD (r = 0.220)	

Table 10: Correlation of independent variable (T) with other dependent variables

S. No.	Positive (+ve) Correlation	Negative (-ve) Correlation
1	Fluoride (r = 0.409)	Total hardness (r = -0.167)
2	Sulphate (r = 0.121)	Nitrate (r = -0.129)
3	COD (r = 0.138)	Nitrogen (r =-0.124)
4	-	Lead (r = -0.116)
5	-	DO (r = -0.102)

The temperature (independent variable) has shown the strong positive correlation fluoride (r=0.409), moderate correlation with sulphate (r=0.121) and COD (r=0.138) as shown in Table 10 which were found to be significant i.e. $P<0.05$. On the other hand, temperature has shown the negative correlation with total hardness (r=-0.167), DO (r=-0.102), NO_3^- (r=-0.129), Nitrogen (r=-0.124) and Pb (r=-0.116). It has also been moderately associated or significant with all these dependent variables as presented in Table 9. The inverse relationship between T and DO is a natural process because warmer water becomes more easily saturated with O_2 and holds less[22].

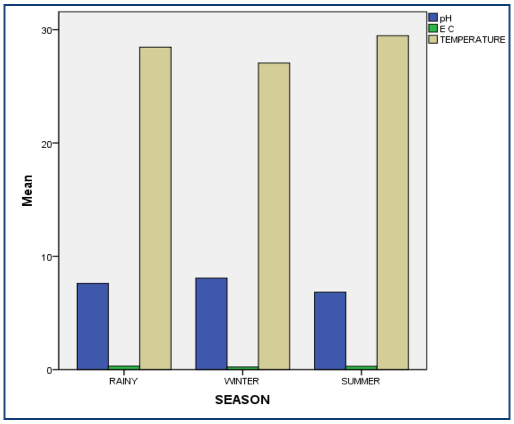

Figure 1 (a)

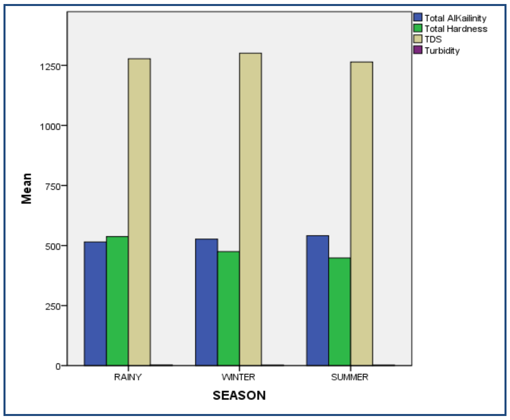

Figure 1 (b)

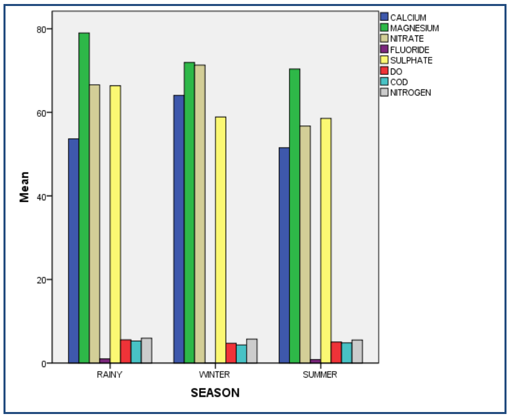

Figure 1 (c)

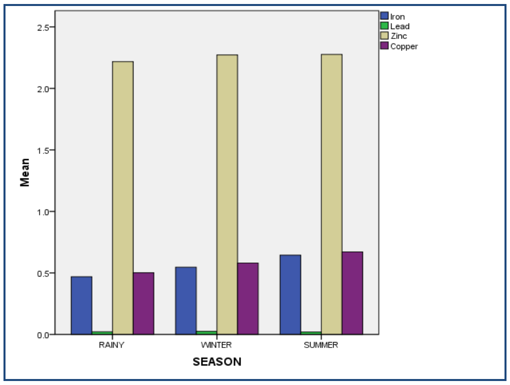

Figure 1 (d)

Figure 1: Graph showing the variation between seasons and means of some parameters

Conclusion

On the basis of current investigation, it was concluded that the water quality in the investigated area is found to be suitable for drinking only in few locations. Most of the water quality parameters showed beyond the permissible limits of BIS and WHO like nitrate, total hardness, TDS, EC and Fe and some parameters achieving near permissible limits. The Ca^{2+} and Mg^{2+} ion and total hardness values were high in most of the places, becomes very hard to groundwater. A proper planning and implementation is required to mitigate the problem of drinking water contamination in the study area.

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