

## Research Article

# Evaluating Geochemistry by Multivariate Analysis of Groundwater in DCM Industrial Area Kota, Rajasthan (India)

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## Abstract

Monsoon Ground water samples of DCM Industrial area locations and adjoining areas were analysed by multivariate studies for quality assessment by estimating physico-chemical parameters, major cations and anions, irrigation quality parameters like SAR & % Na. The studies indicate that alkaline earth elements exceeded alkalis concentration while weak acids exceeded strong acid element. It was found that  $\text{HCO}_3^-$  was predominant among anions, while Ca-Mg dominated cations. Classification based on SAR and Salinity Hazard revealed that samples by Wilcox analysis diagram were under excellent (S1, 60 %), good (S2, 33.33 %), (C2, 33.33%) and doubtful (S3, 6.66 %), (C3, 66.66%) categories respectively. Cluster analysis show sampling station S6 & S7 in Group C alone which formed a group with highest Euclidian distance compared to other cluster group's noticeable spatial variation in the physicochemical parameters.

**Keywords:** Ground water, Geochemistry, Piper diagram, Wilcox analysis, Cluster analysis



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## Introduction

Being an important constituent of environment, water is base material for sustaining life on the earth. Water also plays significant role in photosynthesis and therefore, is of prime importance for production of crops. Obviously, optimum agricultural production largely depends on water as well as soil quality [1].

Water resources have played critical role in the economic growth of contemporary societies. In societies like those in India with developing economics, optimum development, efficient utilization and effective management of water resources is quite crucial. But unscientific management and exploitation of water resources invariably has created undesirable problems in the form of water logging, salinity and pollution levels of alarming limits as a result of mining, industries and municipal use.

India with agricultural based economy uses water for irrigation abundantly and its quality depends upon type and quantity of dissolved salts. Salts present in water used for irrigation are in relatively small but significant amounts, usually originated from dissolution or weathering of the rocks and soil, including dissolution of lime, gypsum and other soil minerals. These salts either remain behind in the soil or are used by the crop. In irrigated agriculture, the hazard of salty water is a constant threat. Poor quality of water used for irrigation is of much more concern in arid climatic conditions. Besides affecting crop yield and soil's physical conditions, water used for irrigation quality affects fertility needs, irrigation system performance and longevity [2]. The suitability of groundwater for agricultural, municipal, industrial and domestic water supplies can be determined by evaluating

physico-chemical parameters along with some calculated hydro geochemical/hydro chemical parameters and graphical representations [3]. Thus, a study on related areas appears to be the need of hour.

Keeping these factors in consideration, Kota situated on the banks of Chambal river was identified as an area in which millet, wheat, rice, pulses, coriander and oilseeds are grown and has industries like cotton and oilseed milling, textile weaving, distilling, dairying, manufacture of metal handicrafts, fertilizers, chemicals and engineering equipment etc. Hence, the present study aimed at understanding the prevailing groundwater quality in the DCM Industrial area during the monsoon season of the July, 2014 by employing multivariate statistical analysis. From studies carried, an attempt has been made to assess suitability of groundwater for drinking and agricultural purposes.

## Experimental

### *Study Area*

Kota is located along eastern bank of Chambal River in Rajasthan, India. The cartographic coordinates are 25°11'N 75°50'E/ 25.18°N 75.83°E. It covers an area of 318 km<sup>2</sup> (3.63 per cent of the Rajasthan State). It has an average elevation of 271 meters (889 ft). The district is bound on the North and North West by Sawai Madhopur, Tonk and Bundi districts. The Chambal River separates these districts from Kota district, forming the natural boundary.

DCM industrial area and its adjoining areas have been chosen as area of study. Total covered area under study is 10 sq. Kms. (**Table 1, Figure 1**).

### *Materials and Reagents*

A total of 15 samples of groundwater used for drinking purpose were collected from different sources like hand pumps or open wells at different spots spread over DCM Industrial area during monsoon season in the month of July, 2014. These spots were specifically identified on the basis of frequent use and probability of contamination and were mapped. The season was selected because contamination often increases due to starting of rain and tends to the accumulation of ions. Before sampling, the water was left to run from the source for five minutes [in case of hand pumps] while water was taken out from a depth of 03 meters of available water [in case of wells]. The water samples were collected in pre cleaned, sterilized polyethylene bottles of 1 L capacity. All water samples were analyzed within 12 to 24 hrs after collection.

The samples were analyzed using standard methods of analyses to assess various physicochemical parameters according to APHA & WHO norms. Some parameters like temperature, color, and pH were measured on site. Water sample were analyzed by standard methods [4] for physicochemical parameters like water temperature(°C), TDS, conductivity, turbidity, odor, nitrate, sulphate, phosphate, Dissolved Oxygen, hardness, chlorides, fluorides, nitrate, sodium, potassium and Chemical Oxygen Demand(COD), Biological Oxygen Demand(BOD), alkalinity, free NH<sub>4</sub>, Coli form Organism, heavy metals like Fe<sup>+2</sup>, As, Cu, Zn. The physico-chemical analysis of groundwater samples were carried out by instrumental and non-instrumental methods. Temperature, pH, conductivity and TDS were determined by using water analysis Kit. Hardness, DO, chloride, CO<sub>2</sub> and all such parameters were analyzed by standard procedure mentioned in APHA [5]. The elemental analysis was carried out by digital Flame Photometer. All the reagents used for the analysis were AR grade. Double distilled water was used for preparation of solutions.

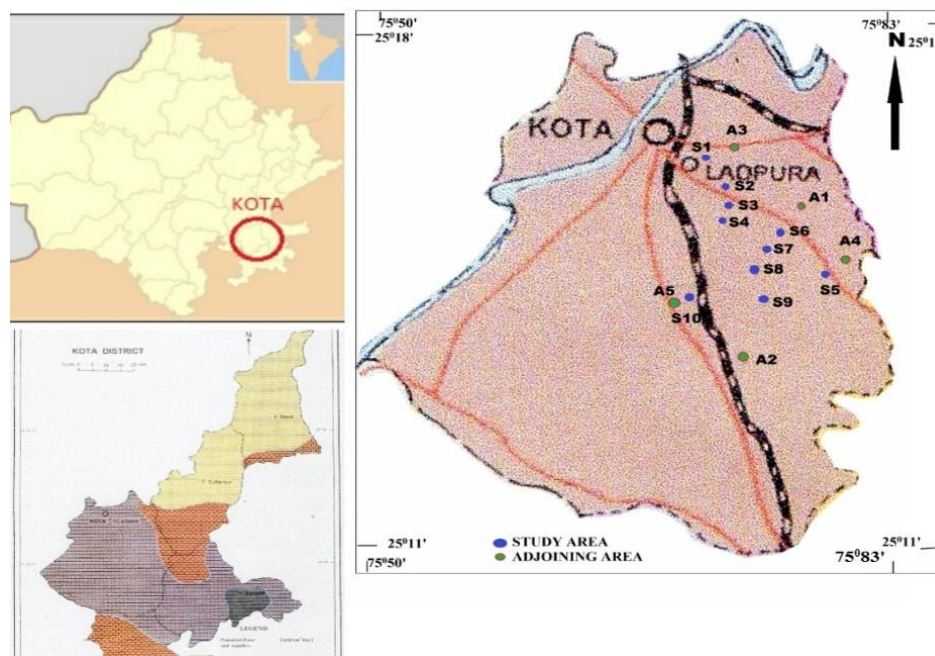
## Results and Discussion

The physicochemical parameters were analysed in monsoon season (July, 2014) and results so obtained were compared to the adjoining regions of study area are presented in **Table 2**.

The findings and their comparison with WHO health based drinking water guide lines [6] revealed considerable variations in the water samples with respect to their pollutants. The results indicate that the quality of water varies considerably from location to location. The pH concentration varied from 7.3 to 8.9. The lowest pH value of 7.3 was noticed in sample number S10 (Near Dakniya Station) and maximum pH value of 8.9 was noticed in sample number A4 (Dhakerkhari).

**Table 1** Description of spots

| Spot No. | Name of the spot                                                   | Source type | ~ Distance between spots [In ms.] | Area [~1 sq. km.] Spot population |
|----------|--------------------------------------------------------------------|-------------|-----------------------------------|-----------------------------------|
| S1       | Near Govt. Girls Senior Secondary School, Bombay Yogena, Kansua    | Tube Well   | 500m                              | 5000                              |
| S2       | Near Bombay Yogena Colony, Kansua                                  | Hand Pump   | 550 m                             | 5000                              |
| S3       | Near Samudayik Bhawan, Near Maszid, Kansua                         | Hand Pump   | 500m                              | 2000                              |
| S4       | Near Shiv Mandir, Kansua                                           | Hand Pump   | 750 m                             | 3000                              |
| S5       | Near Govt. Senior Secondary , Ram Nagar                            | Hand Pump   | 1000 m                            | 4000                              |
| S6       | Near Govt. Senior Secondary School, Indra Colony, DCM              | Hand Pump   | 750 m                             | 2000                              |
| S7       | Shri Ram Fertilizer Gate , Near Fly Over, Prem Nagar               | Hand Pump   | 500 m                             | 2000                              |
| S8       | Samudayik Bhawan Ke Paas Prem Nagar III                            | Tube Well   | 450 m                             | 3000                              |
| S9       | Papaji Ke Bhatte Ke Paas, Rayans Industry Boundary, Prem Nagar III | Tube Well   | 500 m                             | 2000                              |
| S10      | Industrial Area, Near Dakaniya Station, Sanjay Nagar               | Hand Pump   | 1000 m                            | 1000                              |
| A1       | Raipura                                                            | Dug Well    | 1000 m                            | 3000                              |
| A2       | Daddevi                                                            | Dug Well    | 1000 m                            | 500                               |
| A3       | Soorsagar                                                          | Pizometer   | 1000 m                            | 1000                              |
| A4       | Dhakerkhari                                                        | Dug Well    | 850 m                             | 1000                              |
| A5       | Dakniya talav                                                      | Hand pump   | 1000 m                            | 2000                              |

**Figure 1** Map of Kota district and DCM industrial area, Kota

Many samples were observed to give electrical conductivity value high and the value vary from 580 to 1099  $\mu\text{S}/\text{cm}$  and the value of conductivity of all samples [Sample S1 to A5] was higher than the acceptable limits.

The WHO acceptable limit for alkalinity in drinking water is 200 -500 Mg/L and values of all the samples were in acceptable limit that is 140 to 280 mg/L.

**Table 2** Analytical results of ground water sample in the DCM Industrial Area, Kota (Monsoon July 2014)

| Sample ID | General parameters |      |        |        |        |        |                  |            |                                   |      |      |       |
|-----------|--------------------|------|--------|--------|--------|--------|------------------|------------|-----------------------------------|------|------|-------|
|           | EC                 | pH   | TDS    | TA     | TH     | Ca H   | Fe <sup>2+</sup> | Total Coli | Free NH <sub>4</sub> <sup>+</sup> | DO   | BOD  | COD   |
| S1        | 591.00             | 7.80 | 550.00 | 180.00 | 240.00 | 180.00 | 0.00             | 100.00     | 1.90                              | 4.50 | 1.40 | 6.00  |
| S2        | 595.00             | 7.80 | 545.00 | 190.00 | 320.00 | 270.00 | 0.10             | 120.00     | 1.80                              | 4.30 | 1.30 | 5.00  |
| S3        | 907.00             | 7.50 | 765.00 | 180.00 | 330.00 | 200.00 | 0.10             | 280.00     | 0.50                              | 4.20 | 1.50 | 3.00  |
| S4        | 915.00             | 7.50 | 675.00 | 185.00 | 360.00 | 230.00 | 0.25             | 250.00     | 1.50                              | 3.70 | 1.00 | 5.00  |
| S5        | 1057.00            | 7.60 | 870.00 | 280.00 | 420.00 | 320.00 | 1.20             | 160.00     | 0.20                              | 4.40 | 1.30 | 7.00  |
| S6        | 1099.00            | 7.40 | 890.00 | 250.00 | 500.00 | 300.00 | 1.40             | 190.00     | 0.60                              | 4.30 | 1.50 | 10.00 |
| S7        | 1017.00            | 7.50 | 880.00 | 180.00 | 420.00 | 160.00 | 0.50             | 100.00     | 0.40                              | 3.80 | 1.80 | 4.00  |
| S8        | 1044.00            | 7.30 | 910.00 | 140.00 | 440.00 | 320.00 | 1.20             | 100.00     | 0.50                              | 4.00 | 1.20 | 4.00  |
| S9        | 985.00             | 7.40 | 620.00 | 220.00 | 340.00 | 230.00 | 0.50             | 80.00      | 0.30                              | 4.60 | 1.90 | 5.00  |
| S10       | 782.00             | 7.30 | 630.00 | 250.00 | 300.00 | 250.00 | 0.70             | 250.00     | 2.50                              | 5.00 | 1.20 | 10.00 |
| A1        | 580.00             | 8.50 | 380.00 | 180.00 | 195.00 | 150.00 | 1.50             | 130.00     | 1.20                              | 4.50 | 0.50 | 6.00  |
| A2        | 710.00             | 8.30 | 487.00 | 150.00 | 230.00 | 180.00 | 1.60             | 235.00     | 0.80                              | 3.20 | 1.50 | 5.00  |
| A3        | 850.00             | 8.80 | 560.00 | 200.00 | 180.00 | 110.00 | 0.60             | 145.00     | 1.45                              | 4.00 | 1.60 | 8.00  |
| A4        | 680.00             | 8.90 | 380.00 | 240.00 | 240.00 | 160.00 | 1.40             | 70.00      | 1.30                              | 4.50 | 1.00 | 7.00  |
| A5        | 780.00             | 7.40 | 620.00 | 250.00 | 310.00 | 250.00 | 0.70             | 250.00     | 2.50                              | 5.00 | 1.30 | 10.00 |

Total dissolved solids comprised mainly of carbonates, bicarbonates, chlorides, phosphates and nitrates of calcium, magnesium, sodium, potassium, manganese, organic matter salt and other particles. In present findings TDS value varied from 380 mg/L to 910 mg/L. Minimum TDS value was recorded in sample number A1 (Raipura), while minimum TDS was recorded in sample number S8 (Prem Nagar III). TDS values are much higher in the study area in comparison to the other adjoining regions.

Except for some spots, the calcium hardness in water samples was present in higher proportions than the acceptable limit that is 110 to 120 mg/L. Also the magnesium hardness was lower than the calcium levels in water samples with lower and higher values being 45 and 260 mg/L respectively. Total hardness was found to be in the category of “very hard” for the samples of all the locations that is in the range of 180 to 500 mg/L with a minimum value of 180 mg/L, noticed in sample number A3 (Soorsagar) and the maximum value of 500 mg/L in sample number S6 (Indra Colony) [6].

Iron as Fe<sup>2+</sup> concentration in the present study area varied from 0.0 to 1.60 mg/L. However, 11 samples with exceeded iron concentration above the permissible limit of 0.3 mg/L are indicative of soil nature.

The Total Coli form Organism varied from 70 to 280 MPN/100 ml and it was found that all the samples were in permissible limit of <500 MPN/100 ml.

### **Cation chemistry**

Calcium (as Ca<sup>2+</sup>) and magnesium (as Mg<sup>2+</sup>) ranged from 44.05 to 128.13 mg/L and 10.94 to 63.37 mg/L and it was found that all the samples showed calcium and magnesium concentration within the permissible limit of 200 and 100 mg/L (BIS, 1991) respectively. Sodium values ranged from 25.10 to 110.60 mg/L, while potassium values ranged from 1.25 to 8.15 mg/L [6]. Out of 15 samples, 01 sample showed sodium concentration, exceeding the permissible limit of 100 mg/L, while none of the samples showed potassium concentration exceeding the permissible limit of 10 mg/L [7] (**Table 3**).

**Table 3** Major Cations & Anions result of ground water sample in the DCM Industrial Area,( July 2014)

| Sample ID | Major Cations    |                  |                 |                | Major Anions                  |                               |                 |                |                               |                              |                               |
|-----------|------------------|------------------|-----------------|----------------|-------------------------------|-------------------------------|-----------------|----------------|-------------------------------|------------------------------|-------------------------------|
|           | Ca <sup>2+</sup> | Mg <sup>2+</sup> | Na <sup>+</sup> | K <sup>+</sup> | CO <sub>3</sub> <sup>2-</sup> | HCO <sub>3</sub> <sup>-</sup> | Cl <sup>-</sup> | F <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> | NO <sub>3</sub> <sup>-</sup> | PO <sub>4</sub> <sup>3-</sup> |
| S1        | 72.08            | 14.59            | 58.3            | 1.25           | 180                           | 60                            | 60              | 0.1            | 45                            | 15                           | 2                             |
| S2        | 108.11           | 12.13            | 64.1            | 2.48           | 190                           | 130                           | 90              | 0.7            | 50                            | 25                           | 2                             |
| S3        | 80.08            | 31.66            | 25.1            | 2.14           | 180                           | 150                           | 120             | 0.14           | 69                            | 55                           | 1.5                           |
| S4        | 92.1             | 31.65            | 59.7            | 6.14           | 185                           | 175                           | 140             | 0.2            | 72                            | 63                           | 1.5                           |
| S5        | 128.13           | 24.31            | 45.65           | 5.75           | 280                           | 140                           | 145             | 0.25           | 75                            | 20                           | 1.2                           |
| S6        | 120.13           | 48.7             | 31.45           | 3.14           | 250                           | 250                           | 145             | 0.2            | 74                            | 55                           | 1.5                           |
| S7        | 64.07            | 63.37            | 47.15           | 2.94           | 180                           | 240                           | 130             | 0.3            | 110                           | 48                           | 0.5                           |
| S8        | 128.13           | 29.19            | 87.47           | 8.15           | 140                           | 300                           | 100             | 0.35           | 78                            | 50                           | 1.24                          |
| S9        | 92.1             | 26.77            | 43.16           | 4.15           | 220                           | 120                           | 110             | 0.15           | 80                            | 65                           | 2.18                          |
| S10       | 100.1            | 12.13            | 94.15           | 2.13           | 250                           | 50                            | 120             | 0.2            | 39                            | 15                           | 1.4                           |
| A1        | 60.06            | 10.94            | 61.3            | 3.2            | 180                           | 15                            | 50              | 0.14           | 50.03                         | 65.07                        | 1.5                           |
| A2        | 72.08            | 12.15            | 98.8            | 3.8            | 150                           | 80                            | 75              | 0.24           | 80.85                         | 67.65                        | 1.2                           |
| A3        | 44.05            | 17.05            | 110.6           | 1.8            | 180                           | 0                             | 110.5           | 1.5            | 40.35                         | 82.12                        | 0.8                           |
| A4        | 64.07            | 19.47            | 68.5            | 4.1            | 240                           | 0                             | 75.5            | 1.3            | 21.12                         | 22.19                        | 1.23                          |
| A5        | 100.1            | 14.57            | 98.45           | 2.13           | 250                           | 60                            | 125             | 0.2            | 35                            | 15                           | 1.4                           |

### Anion chemistry

The concentration of fluoride ranged between 0.10 and 1.5 mg/L and all samples showed fluoride concentration within the permissible limit of 1.5 mg/L [6]. The nitrate values ranged from 15 and 82.12 mg/L, lowest level being recorded in sample number S1 (Bombay Yogena Area) and the highest concentration was noticed in sample number A3 (Soorsagar). Out of 15 samples, 07 samples showed nitrate concentration, exceeding the permissible limit of 45 mg/L. The sulphate values in the sampling sites ranged between 21 and 110 mg/L and all the samples showed sulphate concentration within the permissible limit of 400 mg/L [7]. The lowest value of 21 mg/L was found in the sample number A4. (Dhakerkhari) and highest sulphate concentration of 110 mg/L has been observed in sample number S7 (Near Fly Over Prem Nagar). Chloride contents were found to be varying from 50 to 145 mg/L and all the samples showed chloride values within the permissible limit of 1000 mg/L. Phosphate values varied from 0.50 to 2.18 mg/L and all the samples were having phosphate value out of the limit of 0.3 mg/L. (Table 3)

### Hydro chemical facies

To know the hydro chemical regime of the study area, the analytical values obtained from the water samples are plotted on Piper (1994) trilinear diagram. 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. The diamond shape field of Piper diagram can be further classified into

- I. Ca<sup>2+</sup>-Mg<sup>2+</sup>-Cl<sup>-</sup>-SO<sub>4</sub><sup>2-</sup>,
- II. Na<sup>+</sup>-K<sup>+</sup>-Cl<sup>-</sup>-SO<sub>4</sub><sup>2-</sup>,
- III. Na<sup>+</sup>-K<sup>+</sup>-HCO<sub>3</sub><sup>-</sup> and
- IV. Ca<sup>2+</sup>-Mg<sup>2+</sup>-HCO<sub>3</sub><sup>-</sup>.

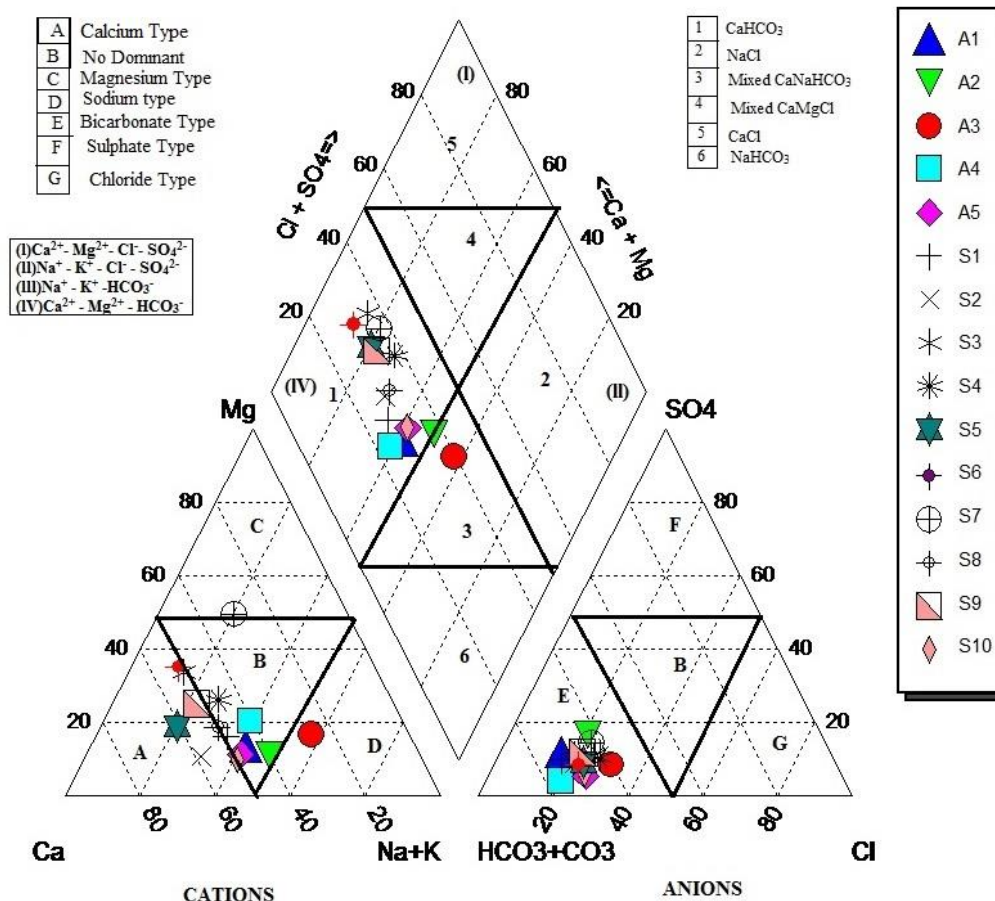


Figure 2 Piper trilinear diagram.

These tri-linear diagrams are useful in bringing out chemical relationships among water samples in more definite terms rather than with other possible plotting methods. Hydro chemical facies are distinct zones that possess cations and anions concentration categories and this concept helps to understand and identify the water composition in different classes [8].

Majority of the samples belong to Ca<sup>2+</sup>-Mg<sup>2+</sup>-HCO<sub>3</sub><sup>-</sup> type followed by Ca<sup>2+</sup>-Mg<sup>2+</sup>-Cl<sup>-</sup>-SO<sub>4</sub><sup>2-</sup> in the study area (Figure 2). It clearly explains the variations and domination of cation and anion concentrations in studied ground water samples. Calcium type of water predominated in all samples while in anion concentration, bicarbonate type of water predominated. It shows that samples collecting places are probably having the rock types with mixed CaMgHCO<sub>3</sub> and Ca Mg Cl compositions.

### Irrigational Quality Parameters

Irrigation water quality parameters of water samples collected in the DCM Industrial area during monsoon season (July, 2014) are summarized in Table 4.

### Total Hardness (TH)

In determining the suitability of water for domestic and industrial purposes, hardness is also an important parameter as it is responsible for making the water hard for these purposes. With this in consideration, classification of water of the study area based on hardness has been carried out and is presented in Table 5 [9–10]. Accordingly all samples collected during monsoon season of the year 2014 fall under very hard category and are an area of concern.

**Table 4** Irrigational water quality parameters of water samples from DCM Industrial Area, Kota

| Sample ID | Irrigation quality parameters |           |           |
|-----------|-------------------------------|-----------|-----------|
|           | Na%                           | RSC(mg/L) | SAR(mg/L) |
| S1        | 39.87                         | 153.34    | 8.86      |
| S2        | 34.31                         | 199.76    | 8.27      |
| S3        | 18.06                         | 218.26    | 3.36      |
| S4        | 31.49                         | 236.26    | 7.59      |
| S5        | 22.39                         | 267.56    | 5.23      |
| S6        | 15.46                         | 331.17    | 3.42      |
| S7        | 26.56                         | 292.56    | 5.91      |
| S8        | 34.58                         | 282.68    | 9.86      |
| S9        | 25.97                         | 221.13    | 5.6       |
| S10       | 45.15                         | 187.76    | 12.57     |
| A1        | 45.24                         | 124.00    | 10.29     |
| A2        | 52.88                         | 145.78    | 15.22     |
| A3        | 63.75                         | 118.91    | 20.01     |
| A4        | 43.87                         | 156.46    | 10.60     |
| A5        | 45.74                         | 195.32    | 13.00     |

**Table 5** Durfor and Becker's Classification of the water samples based on total hardness

| S.No. | Water classes   | Hardness (Mg/L) | Range(Number of samples) | %   |
|-------|-----------------|-----------------|--------------------------|-----|
| 1     | Soft            | 0 – 60          | –                        | 0   |
| 2     | Moderately Hard | 61 – 120        | –                        | 0   |
| 3     | Hard            | 121 – 180       | –                        | 0   |
| 4     | Very Hard       | >180            | 180-500 (1to 15)         | 100 |

### Sodium Absorption Ratio (SAR)

Sodium absorption ratio (SAR) is considered as a better measure of sodium (alkali) hazard in irrigation as SAR of water is directly related to the adsorption of sodium by soil and is a valuable criterion for determining the suitability of the water for irrigation. Excessive sodium content relative to the calcium and magnesium may deteriorate the soil characteristics, thereby reduces the soil permeability and inhibits the supply of water needed for the crops. The SAR measures the relative proportion of sodium ions in a water sample to those of calcium and magnesium. The SAR is used to predict the sodium hazard of high carbonate waters especially if they contain no residual alkali. The excess sodium or limited calcium and magnesium are evaluated by SAR [11] which is computed as

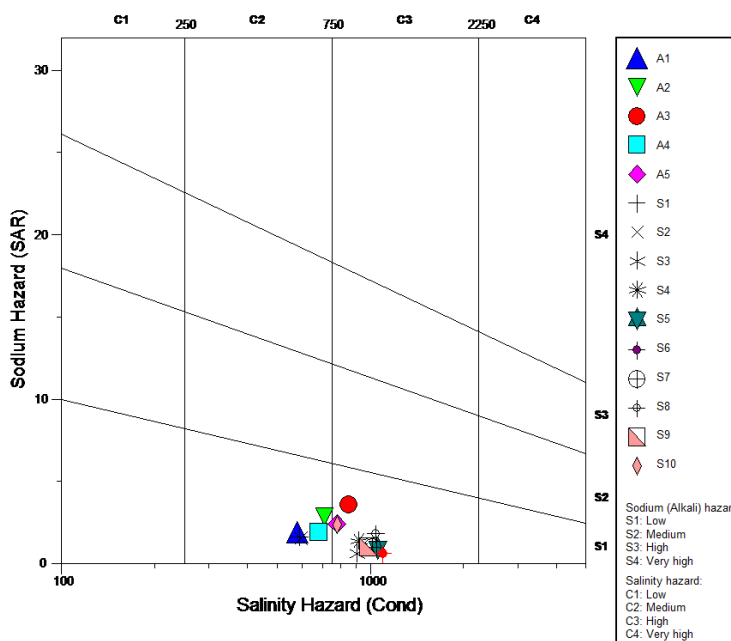
$$SAR = \frac{Na^+}{(\sqrt{Ca^{2+} + Mg^{2+}})/2}$$

According to the classification of water samples (**Table 6**) from the study area with respect to SAR majority of the samples (60 %) were under excellent category [12].

The studies were also done on the basis of Wilcox – diagram. Wilcox- diagram was (**Figure3**) obtained by plotting of SAR and electrical conductivity and illustrates that the ten ground water samples fall in the field of C3S1, indicating high salinity and low Na water while remaining five samples fall in the field C2S1 indicating medium salinity and low Na which can be used for irrigation[13, 14]. (**Table7**).

**Table 6** Todd (1959) Classification of the water samples based on SAR values

| Water classes | SAR values | Sodium hazard class | Range(Number of Samples) | %     |
|---------------|------------|---------------------|--------------------------|-------|
| Excellent     | <10        | S1                  | 3.36-9.86(9)             | 60    |
| Good          | 10-18      | S2                  | 10.29-15.22(5)           | 33.33 |
| Doubtful      | 19-26      | S3                  | 20.01(1)                 | 6.66  |
| Unsuitable    | >26        | S4 & S5             | -                        | -     |



**Figure 3** Wilcox diagram

**Table 7** Salinity hazard Class

| Salinity hazard Class | EC in $\mu\text{S/cm}$ | Remark on Quality | Range(No. of Samples) |
|-----------------------|------------------------|-------------------|-----------------------|
| C1                    | 100-250                | Excellent         | -                     |
| C2                    | 250-750                | Good              | 580-710(05)           |
| C3                    | 750-2250               | Doubtful          | 780-1099(10)          |
| C4 & C5               | >2250                  | Unsuitable        | -                     |

**Percent sodium (% Na)**

Methods of Wilcox and Richards [14] have been used to classify and understand the basic character of the chemical composition of water, since, the suitability of the water for irrigation depends on the mineralization of water and its effect on plants and soil [15-16]. Percent sodium can be determined using the following formula:

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

Based on the classification of water samples with respect to percent sodium (**Table 8**), maximum samples belong to good category.



**Table 8** Classification of the water samples based on Na%

| S.No. | Water classes | Wilcox Na% | Range(No. of Samples) |
|-------|---------------|------------|-----------------------|
| 1     | Excellent     | <20        | 15.46-18.06(2)        |
| 2     | Good          | 20-40      | 22.39-39.87(7)        |
| 3     | Permissible   | 40-60      | 43.87-(5)             |
| 4     | Doubtful      | 60-80      | 63.75-52.88(1)        |
| 5     | Unsuitable    | >80        | -                     |

**Table 9** Pearson's Correlation matrix of analyzed groundwater quality parameter

|                                   | pH      | EC     | TDS    | TA    | TH     | Ca H  | Mg H   | Cl <sup>-</sup> | FreeNH <sub>4</sub> <sup>+</sup> | Total Coli | Iron  |
|-----------------------------------|---------|--------|--------|-------|--------|-------|--------|-----------------|----------------------------------|------------|-------|
| pH                                | 1.000   |        |        |       |        |       |        |                 |                                  |            |       |
| EC                                | -.548*  | 1.000  |        |       |        |       |        |                 |                                  |            |       |
| TDS                               | -.732** | .879** | 1.000  |       |        |       |        |                 |                                  |            |       |
| TA                                | -.119   | .210   | .092   | 1.000 |        |       |        |                 |                                  |            |       |
| TH                                | -.756** | .811** | .899** | .206  | 1.000  |       |        |                 |                                  |            |       |
| Ca H                              | -.716** | .483   | .618*  | .320  | .765** | 1.000 |        |                 |                                  |            |       |
| Mg H                              | -.411   | .741** | .734** | -.021 | .735** | .125  | 1.000  |                 |                                  |            |       |
| Cl <sup>-</sup>                   | -.605*  | .812** | .759** | .480  | .718** | .492  | .586*  | 1.000           |                                  |            |       |
| Free NH <sub>4</sub> <sup>+</sup> | .084    | -.640* | -.498  | .172  | -.476  | -.142 | -.583* | -.209           | 1.000                            |            |       |
| Total Coli                        | -.312   | .080   | .130   | .109  | .039   | .147  | -.0950 | .418            | .275                             | 1.000      |       |
| Iron                              | .351    | .098   | -.089  | .139  | .026   | .095  | -.060  | -.163           | -.294                            | -.090      | 1.000 |

\* Correlation is significant at the 0.05 level, \*\* Correlation is significant at the 0.01 level.

## Statistical analysis

### Correlation matrix

The correlation matrix to find the relationships between two or more variables was carried out using SPSS 16.0 as it describes the interrelationship among various variables. The correlation matrix of analyzed groundwater quality parameters are presented in **Table 9** and it was found that samples showed negative correlations in 21 cases. Some of the highly significant correlations were discernible between conductivity with TDS, hardness, Mg H, chloride, free NH<sub>4</sub><sup>+</sup>, and TDS with hardness, Ca H, Mg H, chloride, and hardness with Ca H, Mg H, and chloride. Poor positive correlation was found between pH with free NH<sub>4</sub><sup>+</sup>, conductivity with coliform, iron, TDS & alkalinity, alkalinity & Mg H, Mg H & Coli form.

### Cluster analysis (CA)

Cluster analysis (CA) is a multivariate technique, whose primary purpose is to classify the objects of the system into categories or clusters based on their similarities, and the objective is to find an optimal grouping for which the observations or objects within each cluster are similar, but the clusters are dissimilar to each other. CA was applied to water quality data using a single linkage method, wherein the distances or similarities between two clusters A and B are defined as the minimum distance between a point in A and a point in B:

$$D(A, B) = \min \{d(x_i, x_j), \text{for } x_i \text{ in } A \text{ and } x_j \text{ in } B\}$$

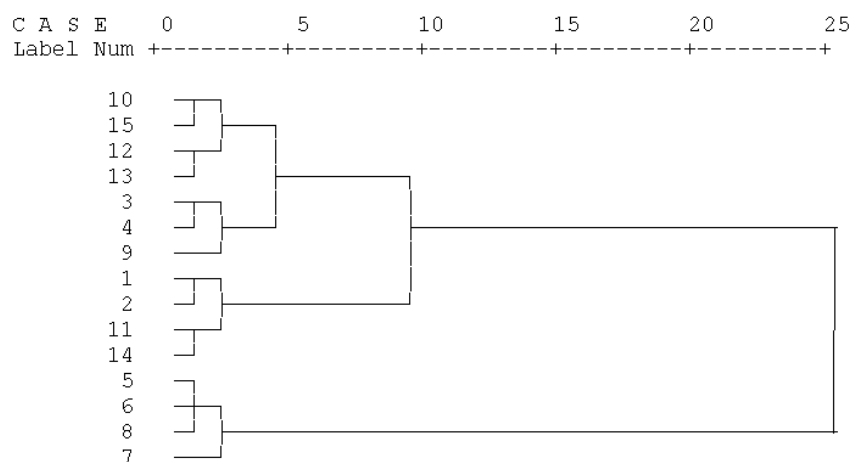
Where,  $d(x_i, x_j)$  is the Euclidean distance in Equation . At each step the distance is found for every pair of clusters and the two clusters with smallest distance (largest similarity) are merged. After two clusters are merged the procedure is repeated for the next step: the distances between all pairs of clusters are calculated again, and the pair with minimum distance is merged into a single cluster. Eventually as the similarity decreases, all subgroups are

merged into a single cluster [17]. The Euclidean distance usually gives the similarity between two samples, and a distance can be represented by the difference between transformed values of the samples [18]. The result of a hierarchical clustering procedure can be displayed graphically using a tree diagram, also known as a dendrogram [19].

In the present study, hierarchical CA was performed on the standardized data using single linkage method (linkage between groups) with Euclidean distances as a measure of similarity and was amalgamated into dendrogram plot. All the physico-chemical characteristics were used as variables to show the spatial heterogeneity among the stations as a result of sequence in their relationship and the degree of contamination. Accordingly, dendrogram classified 15 monitoring sites in the DCM Industrial Area into four groups (Group A, Group B, Group C, and Group D) based on similarities of water quality characteristics (**Table 10, Figure 4**). The group classifications varied with significance level, because the sites in these groups had similar features and natural backgrounds that were affected by similar sources. It is evident from the Figure 4 that sampling stations in Group A were free from major point and non-point pollution sources, could be categorized as less polluted and less noticeable spatial variation. The sampling stations in Groups B even though appears to have less noticeable spatial variation, they formed different cluster. The sampling stations in Groups C even though appears to have noticeable spatial variation, they formed different cluster. It is also apparent from the Spatial-CA as enunciated by Euclidian distance that, sampling station, S6 & S7 in Group C alone formed a group with highest Euclidian distance compared to other cluster groups reflecting noticeable spatial variation in the physicochemical parameters and appears to be highly polluted, marginally free from major point and nonpoint pollution sources [20].

**Table 10** Group of clustered stations during monsoon season

| Group | Sampling stations |
|-------|-------------------|
| A     | S10,A15,A12,A13   |
| B     | S3,S4,S9          |
| C     | S1,S2,A11,A14     |
| D     | S5,S6,S7          |



**Figure 4** Dendrogram Showing clustering of sample sites in the DCM Industrial Area

## Conclusions

The suitability of groundwater for irrigation evaluated on the basis of irrigation quality parameters like SAR & % Na point out that majority of the samples were in safer limits and can be presumed to be excellent for irrigation purposes. TDS value indicates that the water samples are fresh to slightly saline in nature. On the basis of hydro geochemical facies study, majority of the samples belong to  $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$  type followed by  $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^-\text{-SO}_4^{2-}$  in the study

area. Wilcox diagram studies too indicate that the most of the groundwater samples are suitable for irrigation purposes under normal condition but there are bottlenecks and require further investigations. However, it is revealed that groundwater in the region can be classified as of very hard category based on hardness. In general, it can be concluded that overall quality of ground water is controlled by lithology apart from other local environmental conditions and anthropogenic activities.

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