

Impact of copper mines and smelter on groundwater quality (Case Study: Rajasthan State in India)

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Abstract: Rajasthan is one of the main mineral potential state of India. During the last 30 years it has witnessed enormous expansion of mining industries, but mining of most of the minor minerals coupled with changing climate has posed serious problems to the environmental fabric in the state, apart from base metal beneficiation plants. Groundwater is also being polluted day-by-day by effluents generated from mineral wastes and beneficiation processes in the vicinity of mining sites such as Khetri. Pollutant concentrations were measured in groundwater at the vicinity of Khetri copper mining project, Rajasthan to investigate the influence of copper mining on environment. Pollutant concentrations in groundwater were investigated. Copper metal concentration in water samples were found above the maximum desirable limit in two sources: G₄ and G₅, due to washing away of mineral with water. Mining industry has deteriorated quality of groundwater resources in the state of Rajasthan, and these industries are becoming centers of pollution sources which need timely actions at government level so that natural resources such as groundwater can be protected.

Keywords: copper mining, India, Rajasthan, smelter, water pollution

INTRODUCTION

Groundwater is an important source of drinking water due to its high-quality, small seasonal variations, storage, easy exploitation, and socioeconomic development. Presently, 85% of the water requirement for domestic use in rural areas, 55% for irrigation, and over 50% for industrial and urban uses are met from groundwater (Ghosh and Sharma, 2006). Due to the rapid growth of population, urbanization, industrialization, and agriculture activities, groundwater resources

are under stress. There is growing concern on the deterioration of groundwater quality due to geogenic and anthropogenic activities (CGWB, 2010). Man has been exploiting natural resources for making his life more comfortable. The natural resources are a part of the ecosystem wherein a mutually balanced relationship exists between living creatures and natural forces. Any exploitation of natural resources means changes within the ecosystem and which spreads its influence to all organism (Maanju and Saha, 2013; Singh, 2013).

Copper is a natural element -a metal that has been one of mankind's most useful and

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valuable materials since time immemorial. It is a vital nutrient which is required by almost all developed life forms. It is an important constituent of nutritional diet which allows the body to metabolize energy and function appropriately (WHO, 2008). Plants and animal health also rely on satisfactory copper intake. The world's two most main food crops -rice and wheat-are both very dependent on appropriate copper in soil. Copper has been key to human growth and development. In fields, extending from energy efficiency to medical equipment, from television to the Internet, and from satellites to jet planes, it is required for well-being of one in daily life (Soetan et al., 2010; Osredkar and Sustar, 2011).

Rajasthan is one of the main mineral potential state of India, and during last 30 years it has witnessed enormous expansion of mining industries (Krishnaswamy and Sinha, 1988; GMRI, 2009). Rajasthan is geologically and minerologically so endowed that it is called museum of minerals. A total of 79 minerals are available in Rajasthan out of which 58 minerals are commercially produced.

Mining of most of the minor minerals coupled with changing climate has posed serious problems to the environmental fabric in the state, apart from base metal beneficiation plants (Younger, 2002). Groundwater is also being polluted day-by-day by effluents generated from mineral wastes and beneficiation processes in the vicinity of mining sites such as: Khetri and Zawar, and so on (Gangal, 2003). The Khetri copper mine is the largest copper producer in Rajasthan. Therefore, an attempt has been made to access the impact of mining on hydrogeochemical status in and around the mines.

Study area

The study area Gothra–Banwas Khetri is located in the Jhunjhunu district of Rajasthan, some 190 km Southwest of Delhi, and 180 km North of Jaipur. It is situated 550 m above mean sea level. Gothra–Banwas Khetri copper mines are located in northern extremity of the Khetri copper belt between lat 28°03'35" to 28°04'45" and long 75°47'40" to 75°46'45" in Jhunjhunu District (Fig. 1).



Fig. 1. Study area

Khetri Copper Complex was established in November 1967. Two mines were functioning in the towns of Singhana and Khetri. It is situated in a cup-shaped valley surrounded by Aravalli hills. In Khetri, the mining of ore (containing 1% copper) is carried out and concentrate is prepared. The concentrate is brought to the smelter plant and subjected to flash furnace. From this step, 95 to 99% pure copper is produced which is then subjected to electrolytic method. Sulfuric and phosphoric acid are produced as by-

products. Most of this part is covered with alluvium soil. The wastewater outleted by the copper plant joins the river Sukh through small water channels. For the assessment of impact of Khetri copper plant on groundwater of nearby area, 19 groundwater sources were selected for study. First three sources are situated along the river Sukh in upstream to Khetri plant. Remaining 14 sources are situated along the river Sukh in the downstream to Khetri plant. Locations and abbreviations of the groundwater sources are given in Table 1.

Table 1. Abbreviations

| S. No. | Particulars | Abbreviation | S. No. | Particulars | Abbreviation |
|--------|-------------------------------------|-----------------|--------|---|-----------------|
| 1 | Ground water source at Gothra | G ₁ | 11 | Ground water source at Devi pura | G ₁₁ |
| 2 | Ground water source at Ban was | G ₂ | 12 | Ground water source at Singhana no. 1 | G ₁₂ |
| 3 | Ground water source at Manota Khurd | G ₃ | 13 | Ground water source at Singhana no. 2 | G ₁₃ |
| 4 | Ground water source at Khetri no. 1 | G ₄ | 14 | Ground water source at Bag Ki Dhani | G ₁₄ |
| 7 | Ground water source at Khetri no. 2 | G ₅ | 15 | Ground water source at Dhani Bhanawalo ki | G ₁₅ |
| 6 | Ground water source at Khetri no. 3 | G ₆ | 16 | Ground water source at Dhani Bala Peer ki | G ₁₆ |
| 5 | Ground water source at Khetri no. 4 | G ₇ | 17 | Ground water source at Dhani Brahmanan | G ₁₇ |
| 8 | Ground water source at Khetri no. 5 | G ₈ | 18 | Ground water source at Bhodan | G ₁₈ |
| 9 | Ground water source at Khetri no. 6 | G ₉ | 19 | Ground water source at Muradpur | G ₁₉ |
| 10 | Ground water source at Khetri no. 7 | G ₁₀ | | | |

MATERIALS & METHODS

Water samples were taken with precleaned plastic polyethylene bottles. Sampling, preservation, and transportation of water samples were as per the standard method (APHA, 2012). Groundwater samples were analyzed for 18 parameters such as hydrogen ion concentration (pH), Electric Conductivity (EC), Total Dissolved Salts (TDS), carbonate (CO₃⁻²), bicarbonate (HCO₃⁻), total hardness (TH), chloride (Cl⁻), calcium (Ca⁺²), magnesium (Mg⁺²), nitrate (NO₃⁻), sulfate (SO₄⁻²), fluoride (F⁻), sodium (Na⁺), potassium (K⁺), Alkalinity, Zinc (Zn), and

Copper (Cu). Water quality parameters, viz, pH, EC, and TDS were measured on the site whereas other parameters were determined in the laboratory. The water samples were preserved by adding 1 ml of nitric acid (Analytical grade) at pH < 2 and stored at 4°C (to minimize deterioration prior to chemical analysis) for the analysis of metal ion concentrations. All the analyses were carried out according to the standards of APHA (2012). Chemicals and standard solutions used in the study were of analytical grade. The analytical precision for the measurements of ions was determined by

calculating the ionic balance error that varies by about 5–10%. TDS/EC ratio was 0.50/1.0 (with excess of anions in water).

RESULTS & DISCUSSION

The physicochemical results of the groundwater are shown in Table 2. The pH of the study area ranges from 7.1 to 7.9 with an average of 7.5. TDS of the study area was below 2,000 mg/L, except two sources (G₄ and G₅). Both minimum (660 mg/L) and maximum (2,380 mg/L) values of TDS was recorded from Khetri town. Such a big variation in TDS of a particular place indicates impact of human or industrial activities. The groundwater sources of the study area were found to have high sulfate and nitrate. Box and Whisker diagram (Fig. 2) represents the minimum and maximum values of major anions and cations with their averages and 25 and 75 percentile.

Sodium is dominant among cations.

Minimum values of these major anions and cations are from source G₈ and G₉ whereas the maximum values of major anions and cations are of source G₅. TDS in most sources of the study area varies between 1,050 and 1,680 mg/L. The ionic constitution diagram (Fig. 3) shows the total ionic concentrations of all sources are nearly equal except source G₄, G₅, G₈, and G₉. The total ionic concentration is high in source G₄ and G₅ and very low in source G₈ and G₉.

Correlation coefficient for major parameters was calculated and shown in Table 3. Most pairs of parameters have correlation coefficient above 0.8. Correlation coefficient above 0.8 is considered as a very good correlation. The good correlation among various set of parameters indicate similar water quality in the area. Such a good correlation among most parameters indicates less or no contamination other than natural.

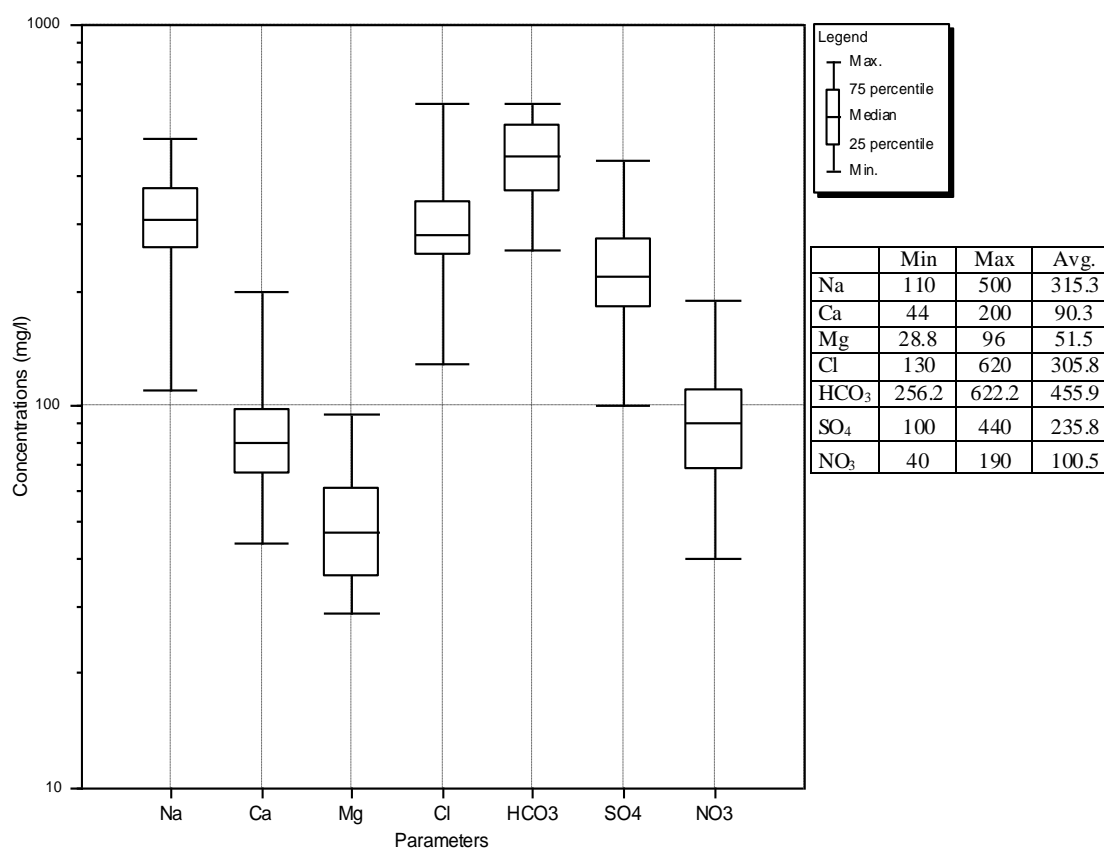


Fig. 2. Box and whisker diagram of study area

Table 2. Physicochemical Results of Groundwater

| S.No. | Parameter | Unit | G ₁ | G ₂ | G ₃ | G ₄ | G ₅ | G ₆ | G ₇ | G ₈ | G ₉ | G ₁₀ | G ₁₁ | G ₁₂ | G ₁₃ | G ₁₄ | G ₁₅ | G ₁₆ | G ₁₇ | G ₁₈ | G ₁₉ |
|-------|------------------------|---------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1 | pH | | 7.4 | 7.5 | 7.3 | 7.8 | 7.5 | 7.9 | 7.1 | 7.4 | 7.8 | 7.1 | 7.6 | 7.5 | 7.4 | 7.3 | 7.4 | 7.8 | 7.7 | 7.6 | 7.2 |
| 2 | Electrical Conductance | µmho/cm | 2484 | 1981 | 2500 | 3366 | 3952 | 2493 | 2381 | 1111 | 1062 | 2413 | 2013 | 2046 | 1774 | 2134 | 2664 | 1843 | 1667 | 2641 | 1642 |
| 3 | Total dissolved Solid | mg/L | 1540 | 1260 | 1520 | 2080 | 2380 | 1540 | 1470 | 700 | 660 | 1520 | 1280 | 1300 | 1120 | 1260 | 1680 | 1120 | 1050 | 1680 | 1050 |
| 4 | Total Hardness | mg/L | 460 | 420 | 480 | 680 | 900 | 430 | 410 | 250 | 310 | 460 | 390 | 340 | 310 | 360 | 560 | 360 | 320 | 550 | 380 |
| 5 | Alkalinity | CaCO ₃ ^{as} | 420 | 410 | 460 | 510 | 510 | 470 | 350 | 220 | 210 | 420 | 360 | 320 | 310 | 380 | 440 | 320 | 260 | 480 | 250 |
| 6 | Bicarbonate | | 512.4 | 500.2 | 561.2 | 622.2 | 622.2 | 573.4 | 427 | 268.4 | 256.2 | 512.4 | 439.2 | 390.4 | 378.2 | 463.6 | 536.8 | 390.4 | 317.2 | 585.6 | 305 |
| 7 | Chloride | | 350 | 270 | 300 | 440 | 620 | 300 | 340 | 150 | 130 | 330 | 270 | 290 | 260 | 250 | 380 | 250 | 250 | 400 | 230 |
| 8 | Sulphate | | 290 | 190 | 300 | 380 | 440 | 270 | 210 | 100 | 120 | 300 | 250 | 220 | 160 | 220 | 200 | 200 | 190 | 260 | 160 |
| 9 | Nitrate | | 70 | 60 | 100 | 180 | 190 | 110 | 170 | 60 | 48 | 90 | 70 | 90 | 110 | 95 | 180 | 70 | 70 | 90 | 65 |
| 10 | Fluoride | mg/L | 0.6 | 1.1 | 0.9 | 0.6 | 0.8 | 1.1 | 1.4 | 0.9 | 1.3 | 0.9 | 0.8 | 1.6 | 1.2 | 1.8 | 1.1 | 0.8 | 1.6 | 2.8 | 2.3 |
| 11 | Calcium | | 92 | 80 | 84 | 144 | 200 | 76 | 104 | 44 | 64 | 84 | 80 | 72 | 76 | 64 | 120 | 68 | 64 | 104 | 96 |
| 12 | Magnesium | | 55.2 | 52.8 | 64.8 | 76.8 | 96 | 57.6 | 36 | 33.6 | 36 | 60 | 45.6 | 38.4 | 28.8 | 48 | 62.4 | 45.6 | 38.4 | 69.6 | 33.6 |
| 13 | Sodium | | 370 | 280 | 360 | 450 | 500 | 380 | 350 | 150 | 110 | 370 | 300 | 310 | 280 | 310 | 360 | 260 | 260 | 380 | 210 |
| 14 | Potassium | | 7 | 6 | 8 | 10 | 14 | 6 | 8 | 6 | 3 | 7 | 12 | 12 | 10 | 4 | 8 | 6 | 2 | 10 | 12 |
| 15 | Copper | | 40 | 87 | 247 | 1348 | 1245 | 420 | 47 | ND | ND | 124 | 14 | 34 | ND | ND | ND | ND | 14 | ND | ND |
| 16 | Zinc | µGm/l | ND | ND | ND | 45 | 427 | ND | 12 | ND | ND | 12 | ND | 10 | ND | ND | 11 | ND | ND | ND | ND |
| 17 | SAR | | 7.529 | 5.964 | 7.174 | 7.53 | 7.271 | 8.001 | 7.537 | 4.142 | 2.726 | 7.531 | 6.629 | 7.336 | 6.936 | 7.133 | 6.638 | 5.982 | 6.343 | 7.073 | 4.698 |
| 18 | RSC | | -0.742 | -0.144 | -0.332 | -3.318 | -7.697 | 0.861 | -1.162 | -0.564 | -1.962 | -0.737 | -0.552 | -0.359 | 0.03 | 0.451 | -2.334 | -0.752 | -1.159 | -1.326 | -2.564 |
| 19 | Kelley Ratio | epm | 0.824 | 0.715 | 0.753 | 0.557 | 0.406 | 0.937 | 0.924 | 0.834 | 0.443 | 0.824 | 0.855 | 1.086 | 1.124 | 0.998 | 0.596 | 0.837 | 0.998 | 0.647 | 0.621 |
| 20 | RSBC | | 3.799 | 4.199 | 4.999 | 2.999 | 0.2 | 5.599 | 1.8 | 2.2 | 1 | 4.199 | 3.199 | 2.799 | 2.399 | 4.399 | 2.799 | 2.999 | 2 | 4.399 | 0.2 |
| 21 | % Na | | 63.33 | 58.91 | 61.67 | 58.7 | 54.37 | 65.54 | 64.54 | 56.05 | 43.41 | 63.34 | 61.83 | 65.62 | 65.47 | 65.03 | 58.01 | 60.76 | 63.83 | 59.65 | 53.72 |

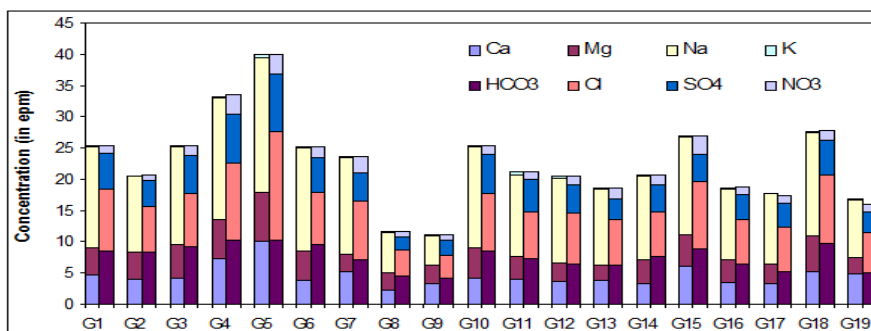


Fig. 3. Ionic Constituent Diagram of Dissolved Ions

Table 3. Correlation Coefficient for Study Area

| | EC | TDS | Na | Ca | Mg | Cl | SO ₄ | HCO ₃ | NO ₃ |
|------------------|------|-------|-------|-------|-------|-------|-----------------|------------------|-----------------|
| EC | 1.00 | 0.999 | 0.967 | 0.888 | 0.822 | 0.971 | 0.942 | 0.903 | 0.798 |
| TDS | | 1.00 | 0.971 | 0.88 | 0.812 | 0.97 | 0.937 | 0.910 | 0.796 |
| Na | | | 1.00 | 0.758 | 0.762 | 0.922 | 0.924 | 0.924 | 0.751 |
| Ca | | | | 1.00 | 0.682 | 0.927 | 0.789 | 0.660 | 0.790 |
| Mg | | | | | 1.00 | 0.752 | 0.850 | 0.849 | 0.511 |
| Cl | | | | | | 1.00 | 0.890 | 0.815 | 0.785 |
| SO ₄ | | | | | | | 1.00 | 0.862 | 0.623 |
| HCO ₃ | | | | | | | | 1.00 | 0.620 |
| NO ₃ | | | | | | | | | 1.00 |

To find out the hydrogeochemical nature of groundwater, Piper diagram was plotted (Fig. 4). The right side triangle diagram represents major anions which do not show dominance of any anion. The left side triangle diagram represents major cations which show all sources except source G₉ are sodium dominant. The

middle diamond-shaped field represents the type of water. Only in one source (G₉) alkaline earth metals exceed alkalizes, and strong acids exceed weak acids. In remaining sources, alkalizes exceed alkaline earth metals. Alkali and strong acids dominate chemical properties of groundwater of these sources.

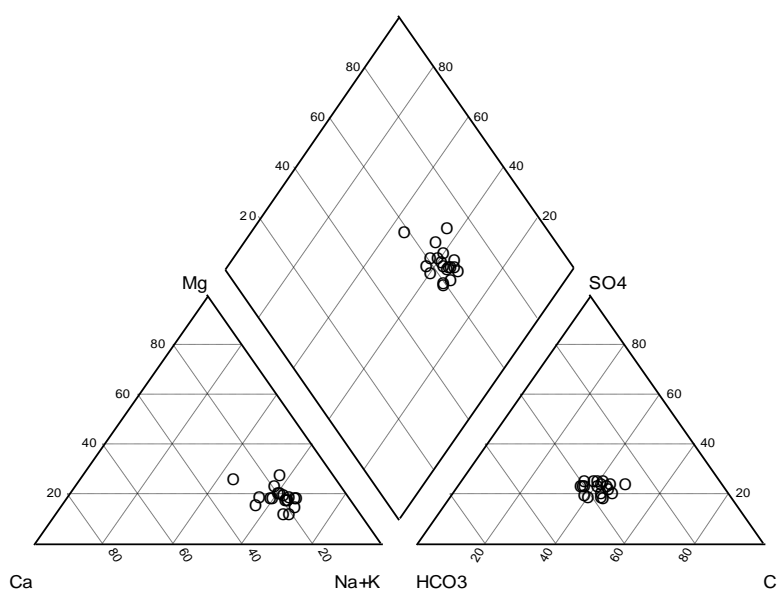


Fig. 4. Piper diagram for study area

There are eight types of groundwater in the study area:

| | |
|---|---|
| Na-Cl-HCO ₃ -SO ₄ | G ₁ and G ₁₀ to G ₁₂ |
| Na-Ca-Cl-HCO ₃ | G ₇ and G ₁₃ , G ₁₅ |
| Na-HCO ₃ -Cl-SO ₄ | G ₆ and G ₁₄ |
| Na-Mg-HCO ₃ -Cl | G ₂ , G ₈ and G ₁₈ |
| Na-Cl-HCO ₃ -SO ₄ | G ₁₇ |
| Na-Ca-Cl-HCO ₃ -SO ₄ | G ₄ , G ₅ and G ₁₉ |
| Na-Mg-Cl-HCO ₃ -SO ₄ | G ₃ and G ₁₆ |
| Na-Ca-Mg-HCO ₃ -Cl-SO ₄ | G ₉ |

Hem (1970) used graphical model for displaying saturation and unsaturation of groundwater with respect to calcite and gypsum.

$$K_{CaCO_3} = \frac{[Ca^{+2}][Ca_3^{-2}]}{[CaCO_3(c)]} \times 10^{-8.3} \quad (1)$$

Dividing equation 1 with 2, we have

$$K_{HCO_3} = \frac{[H^+][Ca_3^{-2}]}{[HCO_3^-]} \times 10^{-10.3} \quad (2)$$

$$\frac{K_{CaCO_3}}{K_{HCO_3}} = \frac{[Ca^{+2}][HCO_3^-]}{[H^+]} \quad (3)$$

$$\text{Log } K_{eq} = \text{Log}[Ca^{+2}] + \text{Log}[HCO_3^{-1}] + \text{pH} \quad (4)$$

The values greater than the equilibrium constant indicate supersaturation. Values of $\log [Ca^{+2}] + \log [HCO_3^{-1}] + \text{pH}$ for different analysis have been plotted in Figure 5. The groundwater of study area is supersaturated with calcite except source G₈ and G₉. These sources are unsaturated and may tend to weathering of rocks. The presence of all sources in the same area shows less or no impact of copper industry on the groundwater.

Suitability of Groundwater for Drinking Purpose

To evaluate the groundwater suitability for drinking purpose Indian standards (IS: 10500, 2012) were used. Table 4 represents

the classification based on the IS: 10500, 2012. In the classification, +, ±, and – signs are used to classify the ground water. The + sign represents that the results are within maximum desirable limit, and the ± sign represents that the results are between maximum desirable limit and maximum permissible limit. The – sign is used to represent the results that are out of maximum permissible limit.

From the table it is clear that the pH in the study area is within the limit. TDS in the study area is above 660 mg/L; hence no source falls in maximum desirable limit. Two sources (G₄ and G₅) have TDS above 2,000 mg/L, hence out of maximum permissible limit. From figure 6 it is clear that the remaining sources are between both limits.

The effect of TDS on human is not studied so far as it has no individual identity. It is contributed by various dissolved ions; hence it is difficult to predict the effect by TDS.

Total hardness of two sources (G₄ and S₅) was found above maximum permissible limit (600 mg/L.) whereas remaining sources was between maximum desirable limit and maximum permissible limit (Fig. 6). The standards are not as per drinking point of view because there is effect on health which is found to be associated with total hardness. However, the use of hard water may cause problems in its domestic use. It may scale in the pipes and obstruct lather with soap during washing. Sawyer classified the water on the basis of hardness. According to this classification, one source (G₈) is hard, while remaining are very hard.

Chloride concentration in the study area is below 1,000 mg/L; hence no source is above maximum permissible limit. Six sources (G₈, G₉, G₁₄, G₁₆, G₁₇, and G₁₉) have chloride concentration below maximum desirable limit as shown in figure 6. Remaining source has chloride concentration between both limits. Chloride toxicity has been observed in

such cases where it is impaired with sodium. When the excess chloride concentration is present with excess sodium concentration, it may cause congestive heart failure (Brooker and

Johnson, 1984; Wesson, 1975), hypertension (WHO, 1978; DNHW, 1978; IOS, 1989), and so on. In the study area, groundwater is sodium dominant; therefore, health concerns may appear.

Table 4. Classification of ground water as per IS: 10500, 2012

| S.No. | | pH | TDS | Total Hardness | Alkalinity | Chloride | Sulphate | Nitrate | Fluoride | Calcium | Magnesium | Copper | Zinc | | | | | | | | | | | | | |
|-------|-----|----|-----|----------------|------------|----------|----------|---------|----------|---------|-----------|--------|------|---------------------------|-----------|------|-----|-----|------|-----|----|-----|-----|-----|-----|----|
| | | | | | | | | | | | | | | Maximum Desirable Limit | 6.5 - 8.5 | 500 | 300 | 200 | 250 | 200 | 45 | 1 | 75 | 30 | 0.5 | 5 |
| | | | | | | | | | | | | | | Maximum Permissible Limit | 6.5 - 8.5 | 2000 | 600 | 600 | 1000 | 400 | - | 1.5 | 200 | 100 | 1.5 | 15 |
| 1 | G1 | + | ± | ± | ± | ± | ± | - | + | ± | ± | + | + | | | | | | | | | | | | | |
| 2 | G2 | + | ± | ± | ± | ± | + | - | ± | ± | ± | + | + | | | | | | | | | | | | | |
| 3 | G3 | + | ± | ± | ± | ± | ± | - | + | ± | ± | + | + | | | | | | | | | | | | | |
| 4 | G4 | + | - | - | ± | ± | ± | - | + | ± | ± | ± | + | | | | | | | | | | | | | |
| 5 | G5 | + | - | - | ± | ± | - | - | + | ± | ± | ± | + | | | | | | | | | | | | | |
| 6 | G6 | + | ± | ± | ± | ± | ± | - | ± | ± | ± | + | + | | | | | | | | | | | | | |
| 7 | G7 | + | ± | ± | ± | ± | ± | - | ± | ± | ± | + | + | | | | | | | | | | | | | |
| 8 | G8 | + | ± | ± | ± | + | + | - | + | + | ± | + | + | | | | | | | | | | | | | |
| 9 | G9 | + | ± | ± | ± | + | + | - | ± | + | ± | + | + | | | | | | | | | | | | | |
| 10 | G10 | + | ± | ± | ± | ± | ± | - | + | ± | ± | + | + | | | | | | | | | | | | | |
| 11 | G11 | + | ± | ± | ± | ± | ± | - | + | ± | ± | + | + | | | | | | | | | | | | | |
| 12 | G12 | + | ± | ± | ± | ± | ± | - | - | + | ± | + | + | | | | | | | | | | | | | |
| 13 | G13 | + | ± | ± | ± | ± | + | - | ± | ± | + | + | + | | | | | | | | | | | | | |
| 14 | G14 | + | ± | ± | ± | + | ± | - | - | + | ± | + | + | | | | | | | | | | | | | |
| 15 | G15 | + | ± | ± | ± | ± | ± | - | ± | ± | ± | + | + | | | | | | | | | | | | | |
| 16 | G16 | + | ± | ± | ± | + | + | - | + | + | ± | + | + | | | | | | | | | | | | | |
| 17 | G17 | + | ± | ± | ± | + | + | - | - | + | ± | + | + | | | | | | | | | | | | | |
| 18 | G18 | + | ± | ± | ± | ± | ± | - | - | ± | ± | + | + | | | | | | | | | | | | | |
| 19 | G19 | + | ± | ± | ± | + | + | - | - | ± | ± | + | + | | | | | | | | | | | | | |

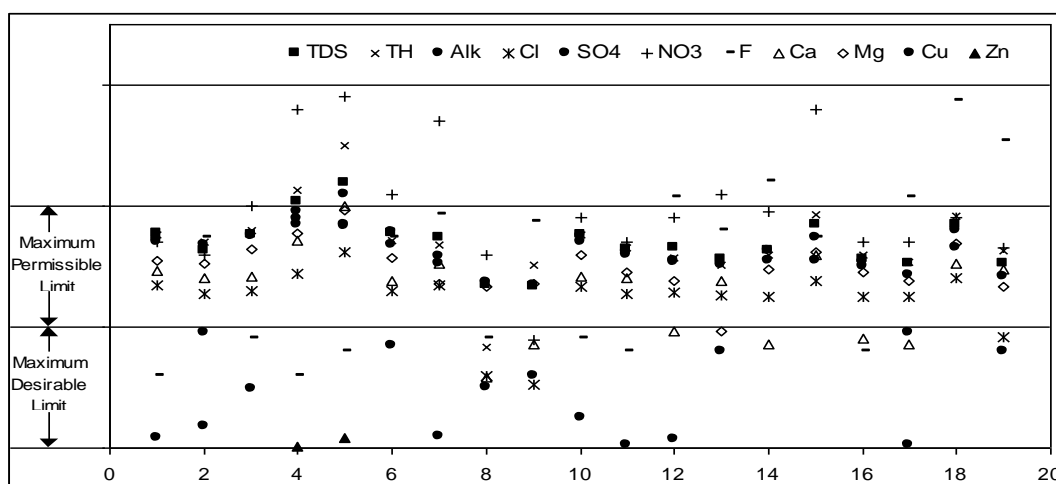


Fig. 6. Classification of ground water as per IS: 10500, 2012

The sulfate concentration in the study area fluctuates in a wide range (100 mg/L to 440 mg/L). Seven sources (**G₂**, **G₈**, **G₉**, **G₁₃**, **G₁₆**, **G₁₇**, and **G₁₉**) have its concentration within maximum desirable limit. One source (**G₅**) has its concentration above maximum permissible limit. Remaining sources are between both limits (figure 6). Fingl (1980), reported dehydration as a common side effect of high-sulfate consumption.

Nitrate concentration in the study area is above 48 mg/L; therefore, all sources are above maximum desirable limit. Nitrate itself does not show toxic effect, but in the human body when it is reduced to nitrite, it creates various serious side effects. Nitrate has been found to react with nitro-stable compounds to form N-nitroso compounds. Most of these compounds have been found to be carcinogenic (NAS, 1981; Speijers, 1989; Challis et al., 1987; Hill et al., 1973). United State National Research Council (USNRC) has found an association between high-nitrate intake and gastric and or esophageal cancer (WHO, 1985). The major biological effect of nitrite in human is its involvement in the oxidation of normal hemoglobin to methemoglobin, which is unable to transport oxygen. When the concentration of methemoglobin reaches 10% of that of hemoglobin; the condition is called methemoglobinemia or blue baby syndrome, which causes cyanosis and at higher concentration asphyxia (Sollman, 1957; Craun et al., 1951).

Fluoride Concentration in five sources (**G₁₂**, **G₁₄**, and **G₁₇** to **G₁₉**) is above maximum permissible limit, while in six sources (**G₂**, **G₆**, **G₇**, **G₉**, **G₁₃**, and **G₁₅**) it is between maximum desirable limit and maximum permissible limit. In remaining sources, it is within maximum desirable limit. Intake of high-fluoride water causes various types of fluorosis states from dental to skeleton. The type of fluorosis depends not only on fluoride concentration but also on environmental conditions and

consumers' diet (Hussain et al., 2004, 2010; Arif et al., 2012, 2013a, b and 2014). Long term use of groundwater of 11 sources may cause teeth fluorosis.

A 0.05 mg/L concentration of copper is maximum desirable limit, while 1.5 mg/L concentration is maximum permissible limit in Bureau of Indian Standard (BIS), absence of another, source. In the study area, two sources (**G₄** and **G₅**) have copper concentration between maximum desirable limit and maximum permissible limit as shown in 10500; 2012 (figure 6). Prolonged use of such ground water may cause "Wilson diseases" (Linder and Munro, 1975; Salonen, 1991). However, zinc was found in three sources, but its concentration is below maximum desirable limit.

Suitability of Groundwater for Irrigation Purpose

To find out the suitability of groundwater for irrigation purposes, various factors have been used. Most classifications are based on EC, Na⁺, Ca⁺², Mg⁺², and HCO₃⁻. On the basis of these parameters, the groundwater of the study area was classified using following classifications:

1. Sodium Adsorption Ratio (SAR)
2. Electrical Conductance (EC)
3. Residual sodium carbonate (RSC)
4. Residual sodium bicarbonate (RSBC)
5. Kelley Ratio
6. SAR and EC classification
7. % Na and EC classification

Sodium Adsorption Ratio (SAR)

On the basis of SAR values, irrigation water is classified into four sodium hazard classes from low-sodium hazard to very high-sodium hazard. SAR in the study area is below 10; hence it belongs to low-sodium hazard quality.

Electrical Conductance (EC)

United State Salinity Laboratory (USSL), 1954 proposed a classification based on EC value. They classified water into four classes as shown in Table 5. From the table

it is clear that no source has EC below 750 $\mu\text{mho/cm}$. Ten groundwater of the study area have EC between 750 and 2250 $\mu\text{mho/cm}$ hence these source may create medium salinity hazard. Such water can be

used if a moderate amount of leaching occurs. Plant with moderate salt tolerance can be grown in most cases without most special practices for salinity control.

Table 5. Classification based on electrical conductance (USSL, 1954)

| S.No | Class | Type of Salinity hazard | EC ($\mu\text{mho/cm}$) | No. of samples | Detail of samples |
|------|----------------|-------------------------|---------------------------|----------------|---|
| 1 | C ₁ | Low | < 750 | - | - |
| 2 | C ₂ | Medium | 750 - 2250 | 10 | G ₂ , G ₈ , G ₉ , G ₁₁ to G ₁₄ , G ₁₆ , G ₁₇ and G ₁₉ |
| 3 | C ₃ | High | 2250 - 5000 | 9 | G ₁ , G ₃ to G ₇ , G ₁₀ , G ₁₅ , and G ₁₈ |
| 4 | C ₄ | Very high | > 5000 | - | - |

Nine groundwater sources have EC above 2,250 $\mu\text{mho/cm}$ and may cause high-salinity hazard if used for irrigation. Such water cannot be used on soils with restricted drainage. Even with adequate drainage, special management for salinity control may be required and plants with good salt tolerance should be selected.

Residual Sodium Carbonate (RSC)

Eaton (1950) introduced the concept of RSC. He calculated excess carbonate and bicarbonate concentration to calcium and magnesium concentration. The excess carbonate and bicarbonate concentration tends to precipitate as calcium carbonate (CaCO_3) producing a white layer of CaCO_3 on the soil surface. Such layer reduces permeability of soil resulting in the reduction in the yield of crop. According to this classification, irrigation water may be classified into three classes from safe to unsafe. The RSC value for the study area is below 1.25; hence it is safe for irrigation purpose.

Residual Sodium Bicarbonate (RSBC)

The groundwater contains a very low- or nil-carbonate concentration and precipitates with only calcium. Hence, a new hypothesis based on only bicarbonate and sodium concentration was introduced which is called Residual Sodium Bicarbonate (RSBC). It is calculated as

excessive carbonate concentration to calcium concentration. The RSBC values classify water into three classes, viz, safe, marginal, and unsafe. In the area, only one source (G₆) is in marginal class with RSBC value between 5 and 10 epm. Remaining sources are safe for irrigation purposes.

Classification Based on Kelley ratio

Kelley (1940), proposed a ratio of sodium concentration against calcium and magnesium concentration. He also considered the excess sodium concentration than calcium and magnesium. He suggested that the ratio should be below 1.0 for safe irrigation. The Kelley ratio was calculated by using following formula.

$$\text{Kelley's Ratio} = \text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+})$$

In the study area, two sources (G₁₂ and G₁₃) have Kelley ratio above one, hence unsuitable for irrigation purpose. The use of water having Kelley ratio more than one may produce sodium hazard. Out of 19 sources classified as low sodium hazard in SAR classification only two sources are suitable for irrigation purpose as per Kelley's classification. Remaining 17 sources are suitable for irrigation purposes.

SAR and EC Classification

SAR and EC both represent sodium and salinity hazard, respectively. Considering both type of hazard, United State Salinity

Laboratory (USSL) proposed a classification combined both hazard to determine the integrated effect on quality. For the classification, graph was plotted as shown in Figure 7. The curves were given a negative slope to take into account the dependence of the sodium hazard on the total salt concentration. In the curve, the sodium class changes with a change in the EC of water.

Although this classification classifies water into 16 classes, but the ground water of study area belongs to two classes as shown in Table 6. From the table it is clear that two sources (**G₈** and **G₉**) of the area belong to **C₃S₁** (high-salinity low-sodium hazard) class, while eight sources belong to **C₃S₂** (high-salinity and medium sodium

hazard) class, and nine sources belong to **C₄S₂** (very high salinity and medium sodium hazard).

Percentage Sodium and EC

Percentage sodium is the percentage of sodium concentration against all cationic concentration related to sodium hazard. Therefore, Wilcox (1948) used a classification based on these two factors. For the purpose, the percentage sodium (%Na) against EC was plotted as shown in Figure 8. This classification demarcates irrigation water into five classes, but the ground water of study area belongs to four classes as shown in Table 7. No source in the study area belongs to excellent to good class, while three sources (**G₁** to **G₃**)

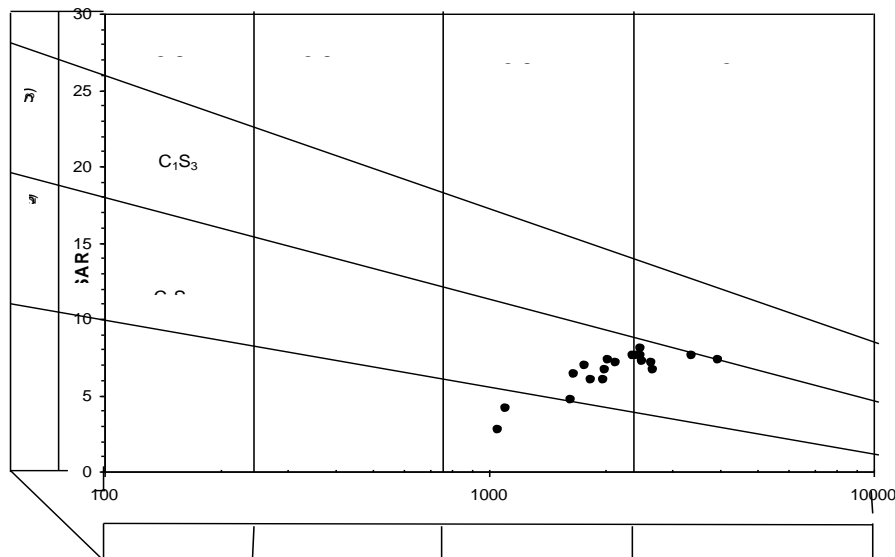


Fig. 7. Salinity and sodium hazard relation for irrigation water

Table 6. Classification based on SAR and EC curve (USSL, 1954)

| S. No | Category | Type of Water | No. of samples | Detail of samples |
|-------|-------------------------------|--------------------------------------|----------------|---|
| 1 | C ₃ S ₁ | High salinity and low sodium | 2 | G ₈ and G ₉ |
| 2 | C ₃ S ₂ | High salinity and medium sodium | 8 | G ₂ , G ₁₁ to G ₁₄ , G ₁₆ , G ₁₇ and G ₁₉ |
| 3 | C ₄ S ₂ | Very high salinity and medium sodium | 9 | G ₁ , G ₃ to G ₇ , G ₁₀ , G ₁₅ and G ₁₈ |

Table 7. Classification based on % Sodium and EC (Wilcox)

| S. No | Class | No. of samples | Detail of samples |
|-------|-------------------------|----------------|--|
| 1 | Excellent to good | - | - |
| 2 | Good to Permissible | 2 | G ₈ and G ₉ |
| 3 | Permissible to Doubtful | 5 | G ₂ , G ₁₃ , G ₁₆ , G ₁₇ and G ₁₉ |
| 4 | Doubtful to Unsuitable | 10 | G ₁ , G ₃ , G ₆ , G ₇ G ₁₀ to G ₁₂ , G ₁₄ , G ₁₅ and G ₁₈ |
| 5 | Unsuitable | 2 | G ₄ and G ₅ |

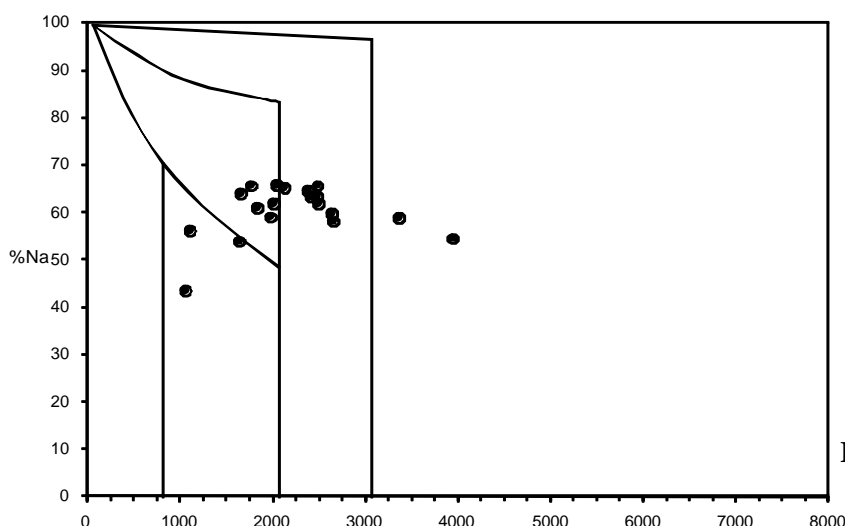


Fig. 8. Water classification in relation to %Sodium and EC

belong to good to permissible class. Remaining eight sources of the study area are permissible to doubtful.

CONCLUSION

Environmental pollution control measures have been adopted at Khetri Copper Complex. Rajasthan Pollution Control Board had set a time-bound program for pollution control in Khetri Copper Complex. KCC has completed, as per the time-table, work on the desulfurization scheme by setting up a Fluorine Scrubbing System in the smelter plant and an effluent treatment plant. With the setting up of the effluent treatment plant, the discharge from the plant has been brought down to the zero level. There is no pollution from liquid effluents which are treated and recovered, water is recycled. KCC has made an investment of around Rs. 10 crore on various pollution control-related measures. KCC is also working on certain long-term plans at an outlay of Rs. 38 crore. The long-term plans include the setting up of another sulfuric acid plant at the cost of Rs. 22 crore, establishment of a gas cleaning plant, and an alkali scrubbing plant. No groundwater sources were found to have slight impact of copper smelter plant. From geochemical studies it is clear that the groundwater of the study area have nearly same quality.

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