Hydrogeochemical assessment of groundwater of Raipur city industrial area Chhattisgarh, India

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Abstract. The present study aims to assess the hydrogeochemistry of groundwater of the industrial area of Raipur. During the investigation, groundwater is found to be neutral to slightly alkaline, and it is suitable for drinking and domestic purposes. Calculation of various quality parameters such as soluble sodium percentage (SSP), sodium adsorption ratio (SAR), residual sodium carbonate (RSC), percentage of sodium (%Na) and Permeability Index (PI) reveals that this groundwater can also be used for irrigation as well. Similarly industrial parameters i.e., Corrosivity Ratio (CR), Ryznar Stability Index (RSI), and Langelier Saturation Index (LSI) are calculated, which indicates the non-corrosive nature of the groundwater in most of the study area.

1. Introduction
Raipur is one of the most developed industrial areas in the Chhattisgarh state of India. This area's main industrial activities include steel and power plant, plastic industries, chemical industries, rice mills, and other small scale industries. The effluents discharge by these industries may directly or indirectly reach both surface water body and groundwater and affect its quality.

The Raipur city is situated on the Proterozoic Chandi formation belonging to the Raipur Group of Chhattisgarh supergroup and comprises limestone, shale, and sandstone dolerite intrusion at places. The Chandi formation consists of horizontally bedded to gently dipping and structurally non-deformed rocks. The Karst development is irregular, and features observed in the area are sinkholes or dolines, microkarren and karrrens, and solution channels or cavities. Shales are thinly laminated with varying thickness. The shale is non-calcareous and impervious. The sandstones are highly brittle, silicified, ferruginous, glauconite, and ortho-quartzite in nature and thinly bedded to laminated, covering mostly the area's elevated parts [1].

The subsurface geology observed from groundwater exploration indicates that the Chandi limestones are intercalated with purple to grey calcareous shale spaces [2]. The Chandi formation comprising sandstone, shale, and limestone forms groundwater's main repository in the area. In general, the dug
wells in the area tap the upper part of the shale or limestone, whereas the bore wells tap mostly the limestone aquifer.

Present work focuses on the study of groundwater quality of Raipur industrial cluster with reference to various parameters such as pH, electrical conductivity, alkalinity, chloride, sulfate, fluoride, calcium, magnesium, total hardness, sodium, potassium, and heavy metals iron, lead, manganese, copper, zinc, and chromium. The samples were collected in and around the industrial complex in the pre-monsoon period. The collected samples were analyzed by the standard method given in the American public health association (APHA). The obtained results get the overall existing groundwater hydrochemistry scenario and with respect to their application for drinking/domestic agriculture and industrial purpose (CGWB[3]).

2. Location of the study area
Raipur, the capital city of Chhattisgarh, along with its outgrowths, lies between 21° 10’ and 21° 21’ N latitudes and 81° 32’ to 81° 44’ E longitudes and falls under Survey of India toposheets no. 64G/11 & 64G/12. Geographically study area displays a gently undulating topography with a general slope towards the north. The elevation varies from 268 to 304 m in a MSL. On the West, it is surrounded by Kharun River and on the South by Chhokra Nala. These two are the main drainage of the city, along with their distributaries. The average annual rainfall in the Raipur area is about 1200 mm. The temperature ranges from 9°C in winter to 46°C in summer. The sample locations of the study area are presented in Figure 1.

![Location Map of the Study Area](image)

**Figure 1.** Locations map along with Groundwater sampling points of Raipur industrial area
3. Materials and Methods

3.1 Collection of groundwater samples
Twenty water samples (n=20) were collected in good quality, cleaned, and well-washed polyethylene bottles. It is soaked with nitric acid, and the samples were filtered at the site before filling in the sample bottles [4]. The water samples were divided into two portions of one liter for basic parameters and 500 ml of the bottle for heavy metal analysis with necessary precautions. The 1st portion was used for the measurement of physical parameters, cations, and anions. The second portion was acidified with a few drops of ultra-pure acid (E. Merck) for the analysis of metals [5]. These bottles were labeled with respect to collecting points, dates, and time to avoid any error between collection and analysis. The collected samples were brought to CGWB, NCCR Chemical laboratory, to analyze both physical and chemical parameters by the standard methods [4].

3.2 Laboratory analysis of groundwater samples
All the chemicals were used AR grade of pure quality. Extra pure deionized water was used for the preparation of all the reagents and standard solutions. The pH was measured by using WTW digital pH meter, and Electrical Conductivity was measured by a digital Conductivity meter.

Total hardness, calcium were measured by Ethylene diamine tetraacetic acid (EDTA) complexometric titration method, and magnesium was calculated by the difference of Total hardness and calcium (TH- Ca). The Flame photometer determined the sodium and potassium. Total alkalinity was measured by titrimetric analysis method. Chloride was measured volumetrically by silver nitrate and lead. Fluoride is determined by the ion-selective electrode using the TISAB solution. The ECIL Atomic absorption spectrophotometer (model 4141) was employed for analysis of heavy metals i.e. manganese, iron, zinc, copper, chromium, and lead.

4. Results and Discussion
In the study area, twenty water samples (N=20) were collected from different locations and various sources to analyze for the physicochemical parameters and for major cations calcium, magnesium, sodium, and potassium (Ca, Mg, Na & K) and major anions carbonate, bicarbonate, chloride, sulfate and fluoride (CO3, HCO3, Cl, SO4 & F) by using the standard method given in APHA. The obtained chemical analysis result and the Bureau of Indian Standard [6] limit for drinking water were summarised in Table-1 and 2.

| S. No. | Location | Sample location code | Source | pH | EC at 25°C (µS/cm) | TDS (mg/l) | TH | TA |
|-------|----------|----------------------|--------|----|-------------------|------------|----|----|
| 1     | Atari    | S-1                  | BW     | 7.7 | 185               | 118        | 70 | 70 |
| 2     | Jarwai   | S-2                  | HP     | 7.49| 671               | 429        | 255| 175|
| 3     | Tendua   | S-3                  | BW     | 7.57| 570               | 365        | 250| 150|
| 4     | Guma     | S-4                  | HP     | 6.96| 661               | 423        | 260| 140|
| 5     | Bana     | S-5                  | River  | 7.3 | 625               | 400        | 190| 165|
| 6     | Kara     | S-6                  | HP     | 7.53| 836               | 535        | 295| 255|
| 7     | Kara     | S-7                  | River  | 7.58| 690               | 442        | 185| 155|
| 8     | URLA     | S-8                  | HP     | 7.4 | 656               | 420        | 265| 220|
| 9     | Urula    | S-9                  | HP     | 7.34| 1049              | 671        | 435| 230|
| 10    | Sarora   | S-10                 | HP     | 7.27| 1685              | 1078       | 465| 300|
| 11    | Gondwara | S-11                 | BW     | 7.33| 1239              | 793        | 375| 290|
| 12    | Bhanpuri | S-12                 | HP     | 7.25| 1654              | 1059       | 480| 275|
| 13    | Birgaon  | S-13                 | HP     | 7.48| 1346              | 861        | 300| 245|
| 14    | Raw-bhata| S-14                 | BW     | 7.67| 1475              | 944        | 215| 280|
| 15    | Urkura   | S-15                 | HP     | 7.27| 1890              | 1210       | 520| 275|

Table 1. Physicochemical parameters in the water of Raipur Industrial area.
The chemical analysis results are within ±10 percent errors. The physicochemical parameters, anions, cations, and heavy metals results are parameter wise discussed below.

### 4.1 Physico-chemical Analysis of groundwater samples

#### 4.1.1 pH

pH measures the intensity of acidity or alkalinity of water assessed based on hydrogen ion concentration. The groundwater samples' pH values of the present study ranged from 6.9 to 7.7, with an average value of 7.4. It shows that the water in the study area is neutral. The BIS acceptable limit for drinking is 6.5 to 8.5, respectively and all the water samples are suitable for the drinking purpose collected from the study area.

The correctness of the chemical analysis result is checked through ionic charge balance is calculated for the EC and major ions, i.e., calcium, magnesium, sodium and potassium, carbonate, bicarbonate, chloride, sulfate, and fluoride [7]. It is observed that all the chemical analysis results are within ±10 percent errors. The physicochemical parameters, anions, cations, and heavy metals results are parameter wise discussed below.

| S.no. | Location | Location | HCO₃ | Cl | SO₄ | F | Ca | Mg | Na | K |
|-------|----------|----------|------|----|-----|---|----|----|----|---|
| 1     | Atari    | S-16     | HP   | 6.97 | 268 | 172 | 125 | 65 |
| 2     | Jarwai   | S-17     | HP   | 7.13 | 1004 | 643 | 400 | 155 |
| 3     | Dhaneli  | S-18     | BW   | 7.31 | 1315 | 842 | 375 | 230 |
| 4     | Girod    | S-19     | HP   | 7.54 | 1203 | 770 | 345 | 250 |
| 5     | Baroud   | S-20     | HP   | 7.62 | 510  | 326 | 185 | 160 |

| Min   | 6.96   | 185   | 118  | 70   | 65  |
| Max   | 7.7    | 1890  | 1210 | 520  | 300 |
| Ave   | 7.4    | 976.6 | 625  | 299.5| 204.3|

BIS Acceptable Limit: 6.5 - 500
BIS permissible Limit: 8.5 - 1500

| S.no. | Location | Location | HCO₃ | Cl   | SO₄ | F | Ca | Mg | Na | K |
|-------|----------|----------|------|------|-----|---|----|----|----|---|
| 6     | Kara     | S-21     | HP   | 6.96 | 268  | 172 | 125 | 65 |
| 7     | Kara     | S-22     | HP   | 7.13 | 1004 | 643 | 400 | 155 |
| 8     | Urla     | S-23     | HP   | 7.31 | 1315 | 842 | 375 | 230 |
| 9     | Urala    | S-24     | HP   | 7.54 | 1203 | 770 | 345 | 250 |
| 10    | Sarora   | S-25     | HP   | 7.62 | 510  | 326 | 185 | 160 |
| 11    | Gondwara | S-26     | HP   | 6.96 | 268  | 172 | 125 | 65 |
| 12    | Bhanpuri | S-27     | HP   | 7.13 | 1004 | 643 | 400 | 155 |
| 13    | Birgaon  | S-28     | HP   | 7.31 | 1315 | 842 | 375 | 230 |
| 14    | Rawa-bhata | S-29   | HP   | 7.54 | 1203 | 770 | 345 | 250 |
| 15    | Urkura   | S-30     | HP   | 7.62 | 510  | 326 | 185 | 160 |
| 16    | Sakra    | S-31     | HP   | 6.96 | 268  | 172 | 125 | 65 |
| 17    | Sondra   | S-32     | HP   | 7.13 | 1004 | 643 | 400 | 155 |
| 18    | Dhaneli  | S-33     | HP   | 7.31 | 1315 | 842 | 375 | 230 |
| 19    | Girod    | S-34     | HP   | 7.54 | 1203 | 770 | 345 | 250 |
| 20    | Baroud   | S-35     | HP   | 7.62 | 510  | 326 | 185 | 160 |

| S.no. | Location | Location | HCO₃ | Cl   | SO₄ | F   | Ca | Mg | Na | K |
|-------|----------|----------|------|------|-----|-----|----|----|----|---|
| 16    | Sakra    | S-16     | HP   | 6.97 | 268  | 172 | 125 | 65 |
| 17    | Sondra   | S-17     | HP   | 7.13 | 1004 | 643 | 400 | 155 |
| 18    | Dhaneli  | S-18     | BW   | 7.31 | 1315 | 842 | 375 | 230 |
| 19    | Girod    | S-19     | HP   | 7.54 | 1203 | 770 | 345 | 250 |
| 20    | Baroud   | S-20     | HP   | 7.62 | 510  | 326 | 185 | 160 |

| Min   | 6.96   | 185   | 118  | 70   | 65  |
| Max   | 7.7    | 1890  | 1210 | 520  | 300 |
| Ave   | 7.4    | 976.6 | 625  | 299.5| 204.3|

BIS Acceptable Limit: 6.5 - 500
BIS permissible Limit: 8.5 - 1500

Table 2. Major ions in ground and surface water of Raipur Industrial area.
4.1.2 Electrical Conductivity (EC). The results show that EC values of the Raipur industrial area vary from 185 to 1890 μS/cm with an average of 976.6 μS/cm at 250C. The comparative high conductivity value > 1500 μS/cm is observed at Urkura, Sarora, and Bhanpuri hand pump water with obtained values are 1890, 1685 and 1654 μS/cm at 250C respectively. The relation between dissolved solids and EC is EC*K=TDS, where EC is in microsiemens/cm. TDS is the total dissolved solids in milligrams per liter, and K is the proportionality constant, which remains mostly in between 0.55 and 0.75 [8]. The samples' TDS value lies in the range of 118 to 1210, with an average of 625 mg/l. The BIS recommended TDS value is 500-2000 mg/l for drinking purposes, and all the obtained TDS values are within the BIS permissible limit at the study area.

4.1.3 Total Hardness (TH). The water containing excess hardness is not desirable for potable water as it forms scales on water heater and utensils when used for cooking and consumes more soap during washing of clothes [9]. The water samples' total hardness value ranges from 70 to 520, with an average concentration of 299.5 mg/l as CaCO3; which is found within the BIS maximum permissible limits of 600 mg/l for the drinking purpose.

4.1.4 Total Alkalinity (TA). Total alkalinity is due to the presence of carbonate, bicarbonate, and hydroxide ions. The weathering of rocks is the potential source of alkalinity. High alkalinity imparts a bitter taste, harmful for irrigation as it damages soil and hence reduces crop yields. The study area's alkalinity ranges from 65 to 300 mg/l with an average concentration of 204.3 mg/l as CaCO3, which is within the maximum permissible limits (600 mg/l) for the drinking purpose.

4.1.5 Bicarbonate (HCO3−). Bicarbonate is the dominating anion among all the anions in the study area. The bicarbonate concentration varies between 79.0 and 366 mg/l, with an average concentration of 249.2 mg/l in all the collected water samples. The bicarbonate ions have produced the alkalinity and hardness in water.

4.1.6 Chloride (Cl−). The high chloride content in water may be due to the pollution from chloride rich effluent of industries, sewage, and municipal waste. The water samples' chloride content is in the range of 14.2 to 337.3 mg/l, with an average value of 136.0 mg/l, which is well within the BIS maximum permissible limits of 1000 mg/l for drinking water purpose.

4.1.7 Sulphate (SO4²−). BIS has prescribed an acceptable limit of 200 mg/l, and this limit is extended up to 400 mg/l provided magnesium does not exceed 30 mg/l. the chemical analysis results show that the sulfate concentration observed from 0.5 to 145.4 with an average of 57.9 mg/l that is within the prescribed limit set by BIS for drinking purposes.

4.1.8 Fluoride (F). Fluoride content is essential for the development of normal bones and teeth. Excessive fluoride gets deposited on teeth, causes dental fluorosis, deposited on bones, causes skeletal fluorosis, and Crippling fluorosis [10]. In the present study, the fluoride content in the Raipur industrial area's ground and surface water varies from trace to 1.1 with an average concentration of 0.2 mg/l, which is below the BIS acceptable and permissible limit 1.0 and 1.5 mg/l, respectively. The river water samples were collected from two locations, Bana and Kara, show fluoride concentration 0.2 and 1.1 mg/l, respectively. Differences in fluoride concentration are huge in between Bana and Kara river water samples; it may be due to some industrial effluents containing high fluoride are mixed with the river water at Kara. In the Kara area, fluoride concentration is high in river water but does not pose any alarming situation.

4.1.9 Calcium and Magnesium (Ca & Mg). The sources of calcium and magnesium in natural water are various types of rocks, industrial waste, and sewage. The calcium concentration in the groundwater ranges from 24 to 176, with an average concentration of 86.7 mg/l, and magnesium concentration varies
from 2.4 to 52.8, with an average concentration of 19.9 mg/l. It is observed that in all the locations, the value of calcium and magnesium were found within the maximum permissible limits of BIS.

4.1.10 Sodium and Potassium (Na & K). The range of sodium ions in water samples varies from 6 to 207, with an average concentration of 55.0 mg/l. The range of potassium ions in water samples varies from 0.5 to 12 mg/l, with an average value of 2.5 mg/l. An exceptionally high sodium concentration is 207 mg/l, which is more than the WHO recommended limit observed at Rawabhata hand pump water.

4.1.11 Heavy Metals in groundwater. The presence of heavy metals in groundwater and surface water in the environment of Raipur industrial area is presented in Table-3. The obtained chemical analysis results are also compared with the Indian standard [6] specification for drinking purposes. The heavy metal concentration in groundwater and surface water is discussed below.

| S. No. | Location   | Source | Fe  | Zn  | Pb  | Mn  | Cu  | Cr  |
|--------|------------|--------|-----|-----|-----|-----|-----|-----|
| 1      | Atari      | BW     | bdl | 0.11| bdl | bdl | bdl | 0.01|
| 2      | Jarwai     | HP     | bdl | 0.28| bdl | bdl | bdl | 0.01|
| 3      | Tendua     | BW     | bdl | 0.03| bdl | bdl | bdl | Bdl |
| 4      | Guma       | HP     | 0.58| 0.06| bdl | bdl | 0.01| Bdl |
| 5      | Bana       | River  | bdl | 0.01| 0.04| 0.20| bdl | 0.01|
| 6      | Kara       | HP     | 0.22| 0.44| bdl | 0.01| bdl | 0.02|
| 7      | Kara       | River  | bdl | 0.00| 0.03| 0.30| bdl | 0.03|
| 8      | Urala      | HP     | bdl | 0.08| bdl | bdl | 0.01| 0.02|
| 9      | Urala      | HP     | bdl | 0.06| bdl | 0.42| bdl | 0.02|
| 10     | Sarora     | HP     | bdl | 0.03| bdl | bdl | 0.02| 0.02|
| 11     | Gondwara   | BW     | bdl | 0.00| bdl | bdl | 0.02| 0.02|
| 12     | Bhanpuri   | HP     | bdl | 0.31| bdl | bdl | 0.02| Bdl |
| 13     | Birgaon    | HP     | bdl | 0.04| 0.07| 0.01| Bdl | 0.01|
| 14     | Rawa-bhata | BW     | bdl | 0.05| bdl | bdl | bdl | 0.03|
| 15     | Urkura     | HP     | bdl | 0.16| bdl | 0.25| bdl | Bdl |
| 16     | Sakra      | HP     | 1.35| 1.05| bdl | 0.18| 0.02| Bdl |
| 17     | Sondra     | HP     | 0.60| 1.17| bdl | bdl | bdl | Bdl |
| 18     | Dhaneli    | BW     | 0.08| 0.01| bdl | bdl | bdl | 0.02|
| 19     | Girod      | HP     | 0.61| 0.34| bdl | 0.21| 0.01| Bdl |
| 20     | Baroud     | HP     | 0.00| 0.73| 0.07| bdl | bdl | Bdl |

|      | Minimum    | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
|      | Maximum    | 1.35 | 1.17 | 0.07 | 0.42 | 0.02 | 0.03 |
|      | Average    | 0.17 | 0.25 | 0.01 | 0.08 | 0.01 | 0.01 |
|      | BIS Acceptable Limit | 0.3 | 5   | 0.01 | 0.1 | 0.05 | 0.05 |
|      | BIS permissible Limit | NR | 15  | NR  | 0.3 | 1.5 | NR  |

4.1.11.1 Iron (Fe). According to BIS (2012) [6] the acceptable and maximum permissible limit for Fe has been set at 0.3 mg/l. Excess of set limit causes objectionable taste, stains laundry and plumbing fixtures. However, excessive concentrations can be harmful or even fatal to some forms of crops and aquatic life. In the study area, the iron content has been found below the detection limit in most water samples and ranging from 0.0 to 1.35 mg/l, whereas in three locations, Guma, Sankra, Giraud, and Sondra, Iron content exceeded the permissible limit.

4.1.11.2 Zinc (Zn). Zinc is an essential micronutrient and beneficial element for human bodies. The Bureau of Indian Standards prescribes permissible limits as 5 - 15.0 mg/l. The concentration of zinc above 5.0 mg/l cause a bitter taste to water. In the study area, the zinc concentration varies from trace to 1.17 mg/l in all kinds of water samples. That shows at all locations, zinc concentration is within the BIS prescribed limit.
4.1.11.3 **Lead (Pb).** Lead is highly toxic to humans in relatively low concentrations. The acceptable limit of lead in drinking water is 0.01 mg/l, and no relaxation is given for the maximum permissible limit. In the study area high lead concentration is observed at four locations, i.e., Kara, Bana, Birgaon and Baraud where the observed concentrations are 0.03, 0.04, 0.07, and 0.07 mg/l, respectively. In the rest of the locations, lead is found below the BIS acceptable limit.

4.1.11.4 **Manganese (Mn).** The BIS acceptable and permissible recommended limit of manganese is 0.1 to 0.3, respectively, for the drinking purpose. A high concentration of manganese (above permissible limit) in groundwater is objectionable for domestic purposes as it imparts inky flavor to water. The deficiency of manganese seriously affects the leaf of the plants and encourages diseases like chlorosis and narcosis. The manganese in water samples of the Raipur industrial area has been ranging between not detectable to 0.42 mg/l. Only at one location Urla industrial area is recorded at 0.42 mg/l above the BIS permissible recommended limit. In the rest of the area, manganese concentration is observed either within the limit or below the detection limit.

4.1.11.5 **Copper (Cu).** Copper is one of the essential elements for the human body, and on the other hand, it may be toxic in elevated concentrations. At higher pH, copper may become more toxic. The concentration of copper in the water of the Raipur industrial cluster is ranged between not traceable to 0.02 mg/l. It shows that copper concentrations at all the locations in the study area's water are within the BIS recommended limit 0.05 to 1.5 for the drinking purposes.

4.1.11.6 **Chromium (Cr).** The minimum chromium concentration in water samples collected from the study area is below the traceable limit, while the maximum concentration is observed at 0.03 mg/l with an average concentration of 0.01 mg/l. That indicates at all of the locations, the chromium concentration is below the BIS recommended limit. Chromium concentration in small amounts is essential to mammals but in excess (0.01 mg/l as maximum permissible limit fixed by BIS) can cause digestive problems, intestinal diseases, carcinogenic acuity (cancer), can produce coetaneous and nasal mucous membrane ulcer and dermatitis, etc. Hexavalent chromium causes lung tumors.

4.2 **Types of water**

Piper trilinear diagram is very useful in the investigation of chemical characters of water solution in the hydrologic system. Different types of water within the range group formations are due to groundwater flow characteristics through the aquifer system and the effect of local recharge [11]. The water types are interlinked with the geology of the area and distribution of facies with the hydrogeological controls. The Piper trilinear diagram of groundwater and surface water of the Raipur Industrial area is presented in Figure-2.

It has been observed that most of the water in and around Raipur industrial area is a mixed type. Calcium is dominating cation in most of the places, while sodium is dominating only at Rawabhabata. In the anion side, bicarbonate is dominating, and in some samples, chloride and sulfate are also dominating at the study area.
4.3 Groundwater quality for irrigation purposes

To know the suitability of groundwater for irrigation purposes, various parameters such as soluble sodium percentage, sodium adsorption ratio, residual sodium carbonate, percent sodium, Kelley’s ratio, magnesium ratio, and permeability index (SSP, SAR, RSC, %Na, KR, MR and PI) have been calculated [12] and presented in Table-4. The suitability of water regarding calculated irrigation parameters is plotted in the US Salinity diagram and Wilcox diagram. The usefulness of the water for irrigation purposes is discussed below.

Table 4. Irrigation Water Quality parameters of Raipur Industrial cluster.

| S.No. | Location       | Source | SSP % | SAR | RSC | %Na | KR | MR | PI   |
|-------|----------------|--------|-------|-----|-----|-----|----|----|------|
| 1     | Atari          | BW     | 23.2  | 0.5 | 0.0 | 25.3| 0.3| 14.1| 88.2 |
| 2     | Jarwai         | HP     | 17.8  | 0.7 | -1.6| 18.3| 0.2| 25.3| 48.0 |
| 3     | Tendua         | BW     | 8.8   | 0.3 | -2.0| 9.0 | 0.1| 19.8| 40.5 |
| 4     | Guma           | HP     | 15.1  | 0.6 | -2.4| 16.0| 0.2| 17.1| 42.5 |
| 5     | Bana           | River  | 28.4  | 1.1 | -0.5| 32.3| 0.4| 20.8| 62.7 |
| 6     | Kara           | HP     | 21.3  | 0.9 | -0.8| 21.6| 0.3| 26.9| 51.6 |
| 7     | Kara           | River  | 38.4  | 1.7 | -0.6| 41.3| 0.6| 24.1| 67.8 |
| 8     | Urala (Bendri)| HP     | 16.0  | 0.6 | -0.9| 16.2| 0.2| 39.3| 49.4 |
| 9     | Urala          | HP     | 18.8  | 1.0 | -4.1| 18.9| 0.2| 36.5| 38.9 |
| 10    | Sarora         | HP     | 32.7  | 2.1 | -3.2| 32.9| 0.5| 47.0| 50.6 |
| 11    | Gondwara       | BW     | 28.6  | 1.6 | -1.7| 29.0| 0.4| 26.4| 51.6 |
| 12    | Bhanpur        | HP     | 28.4  | 1.7 | -4.1| 28.5| 0.4| 8.2 | 45.9 |
| 13    | Birgaon        | HP     | 42.4  | 2.5 | -1.1| 42.6| 0.7| 29.7| 63.7 |
| 14    | Rawa-bhata     | BW     | 67.8  | 6.2 | 1.3 | 68.1| 2.1| 36.9| 85.6 |
| 15    | Urkura         | HP     | 27.8  | 1.8 | -4.9| 28.2| 0.4| 22.9| 44.2 |
| 16    | Sakra          | HP     | 9.5   | 0.2 | -1.2| 9.9 | 0.1| 19.8| 50.9 |
| 17    | Sondra         | HP     | 14.0  | 0.7 | -4.9| 14.3| 0.2| 40.9| 33.1 |
| 18    | Dhaneli        | BW     | 26.5  | 1.4 | -2.9| 26.8| 0.4| 25.1| 47.6 |
| 19    | Girod          | HP     | 29.6  | 1.6 | -1.9| 29.8| 0.4| 18.6| 52.5 |
| 20    | Baroud         | HP     | 14.0  | 0.4 | -0.5| 14.4| 0.2| 29.5| 55.7 |
4.3.1 US Salinity Diagram. US salinity laboratory [13] classification evaluates the irrigation water quality based on its electrical conductivity (EC) as the indicator of its salt concentration, and SAR as the indicator of its relative sodium activity. All the water samples fall in C2 & C3 category, which implies salinity hazard is medium to high. As far as sodium hazard is concerned, all samples were falls under S1 and S2 category suggesting low to medium sodicity (Figure-3).

Atari’s water sample is a fall in C1-S1 (low sodium hazard & low salinity hazard) class that indicates the water is suitable for irrigation purposes. Other than these, some of the water samples are fall in C2-S1 (low sodium hazard and medium salinity hazard) class that indicates the water has a low medium suitable for irrigation purposes. Most of the water sample fall C3-S1 category that shows the water has high salinity and low sodium hazard class medium suitable for irrigation purposes. Only a water sample of Rawabhata fall in C3-S2 region that indicates the water of this location has high salinity and medium sodium hazard class and less suitable for irrigation.

![US Salinity Diagram](image)

**Figure 3.** US Salinity diagram of ground and surface water of Raipur Industrial area.

4.3.2 Wilcox diagram. Wilcox [14] has proposed a (bivariate %Na versus EC in μS/cm) diagram with five category classification for irrigation water. The computed values of percent sodium and electrical conductivity in μS/cm have plotted a diagram that is given in Figure-4. The Wilcox diagram exhibited that in most of the locations, groundwater and surface water either fall in excellent to the good category or good to permissible category and suitable for the irrigation purpose at the study area. Whereas water samples collected from Rawabhata fall in the permissible to doubtful category and less suitable for irrigation.
Figure 4. Wilcox diagram of ground and surface water of Raipur Industrial area.

4.3.3 Soluble Sodium Percentage (SSP). Soluble Sodium Percentage (SSP) of the water is calculated by applying the equation given below in which the values are expressed in meq/l.

\[ \text{SSP} = \frac{\text{Na} \times 100}{\text{Ca} + \text{Mg} + \text{Na}} \]

The sodium in water replaces Ca in the soil by base exchange process, decreasing the soil permeability. Water with less than or equal to 50 SSP value is of good quality, and more than 50 is not suitable for irrigation as permeability will be very low. Most of the water is suitable for irrigation purposes at the study area except Rawabhata where the high value of SSP observed 67.8 and water is unsuitable for irrigation.

4.3.4 Sodium Adsorption Ratio (SAR). SAR being a measure of alkali/sodium hazard to crops is an important parameter for assessing groundwater suitability for irrigation purposes. Richard's (1954) has given the following formula for calculation of SAR value, where all ions in meq/l

\[ \text{SAR} = \frac{[\text{Na}]}{\sqrt{\left(\frac{[\text{Mg}]}{2} + [\text{Ca}]\right)}} \]

The suitability of the water for irrigation decreases with increasing SAR value. Specifically, the sodium reacts with soil and reducing its permeability. The groundwater samples are having SAR value < 10 and come in excellent class that indicates the concentration of sodium, calcium, and magnesium is appropriate and quality of groundwater is suitable for irrigation. In all the water samples of study area, having SAR value is less than 10 hence suitable for irrigation purposes.

4.3.5 Residual Sodium Carbonate (RSC). The sodium hazard in the soil is also increased if the water contains high concentrations of bicarbonate ions. The bicarbonate values are conveniently expressed in terms of Residual Sodium Carbonate. The excess sum of carbonate and bicarbonate content in groundwater over the sum of calcium and magnesium content influences water’s suitability for irrigation purposes. This is expressed as Residual Sodium Carbonate (RSC) and is calculated using the following formula, all ions in meq/l

\[ \text{RSC} = (\text{CO}_3^- + \text{HCO}_3^-) - (\text{Ca}^{++} + \text{Mg}^{++}) \]

All the water samples of the study area with Residual Sodium Carbonate (RSC) value < 1.25 and groundwater are suitable for irrigation purposes with respect to RSC value.
4.3.6 Percent Sodium (%Na). Irrigation water with a high concentration of dissolved Na+ involves base-exchange reactions with the soil’s alkaline earth metals. These reactions reduce the permeability and cause poor internal drainage and air circulation in the soil. Sodium content in natural water is expressed in terms of percent sodium (%Na) is calculated by using the following formula, where all ions in meq/l

\[ \text{Na} \% = \frac{[\text{Na}] + [\text{K}]}{([\text{Na}]+ [\text{K}]+ [\text{Mg}]+[\text{Ca}])} \times 100 \]

Most of the study area's water samples are suitable for irrigation purposes except Rawa-Bhata where % Na is recorded 68.1, which is unsuitable for irrigation purposes.

4.3.7 Kelley’s Ratio. Kelley proposed a cation based formula to quantify the sodium problem of irrigation water [15]. This formula, known as Kelley’s ratio, is expressed as follows, where all ions in meq/l

\[ \text{Kelley Ratio} = \frac{[\text{Na}]}{([\text{Mg}]+[\text{Ca}])} \]

Water having Kelley’s ratio greater than one is considered as unfit for irrigation purposes. Table 4 shows that more or less all the samples are having KI ratio less than one that means mostly water of study area is suitable for irrigation purpose, except Rawa Bhata where KI value is recorded 2.1 which shows that water is unfit for irrigation purpose.

4.3.8 Magnesium Ratio (MR). Magnesium Ratio (MR) is calculated by applying the following equation in which the ions are expressed in meq/l.

\[ \text{MR} = \frac{(\text{Mg} \times 100)}{([\text{Ca}]+[\text{Mg}]+[\text{Na}])} \]

MR value >50 is considered unsuitable for irrigation. In the study area, calculated magnesium ratio is less than 50 in all the water samples that indicate water is suitable for irrigation.

4.3.9 Permeability Index (PI). Doneen (1964) formulated an equation to determine the permeability index (PI) to study the suitability of water for irrigation as continuous moisture application may affect soil permeability by precipitation of some aspects in the topsoil, thus reducing void space hindering water dynamics. The PI can be determined by applying the following formula in which all the ions are in meq/l.

\[ \text{PI} = \frac{([\text{Na}]+(\sqrt{\text{HCO}_3})}{([\text{Ca}]+\text{Mg}+\text{Na})} \times 100 \]

PI = 25%-75% - Class-II - suitable for irrigation
PI >75% -Class-I - unsuitable for irrigation

Most of the samples calculated PI value is between 25% & 75%, showing that water is coming in the class-II category and suitable for irrigation. Whereas in two locations Atari and Rawabhata water have calculated PI value 88.2 and 85.6, respectively. In those areas, water (PI value >75%) comes in Class-I and unsuitable for irrigation.

4.4 Groundwater quality for industrial purposes

Groundwater quality needs to be assessed with reference to its utility for industrial purposes as the majority of the industries consume vast quantities of water in various processes. Water within specific quality is a must to protect the necessary machinery from scaling or corrosion effects. The know the suitability of water for industrial purposes, the corrosive ratio, Lingelier saturation index, and Ryznar stability Index (CR, LSI, RSI) are computed and presented in Table-5.
Table-5. Industrial parameters of ground and surface water of Raipur Industrial area.

| S. No. | Location   | Source | CR  | LSI  | RSI  |
|--------|------------|--------|-----|------|------|
| 1      | Atari      | BW     | 0.2 | -1.8 | 10.9 |
| 2      | Jarwai     | HP     | 0.4 | -0.8 | 8.9  |
| 3      | Tendua     | BW     | 0.4 | -1.0 | 9.3  |
| 4      | Guma       | HP     | 0.6 | 0.3  | 8.0  |
| 5      | Bana       | River  | 0.4 | -0.6 | 8.9  |
| 6      | Kara       | HP     | 0.3 | -0.5 | 8.5  |
| 7      | Kara       | River  | 0.6 | -0.9 | 9.3  |
| 8      | Urla (Bendri) | HP | 0.3 | -2.1 | 10.2 |
| 9      | Urala      | HP     | 0.6 | 0.2  | 7.8  |
| 10     | Sarora     | HP     | 0.8 | 0.6  | 7.3  |
| 11     | Gondwara   | BW     | 0.5 | 0.0  | 7.9  |
| 12     | Bhanpuri   | HP     | 0.9 | 0.3  | 7.4  |
| 13     | Birgaon    | HP     | 0.7 | -0.8 | 8.9  |
| 14     | Rawa-bhata | BW     | 0.8 | -0.2 | 8.3  |
| 15     | Ukura      | HP     | 1.1 | 0.6  | 7.1  |
| 16     | Sakra      | HP     | 0.5 | -0.5 | 9.4  |
| 17     | Sondra     | HP     | 0.9 | -0.3 | 8.5  |
| 18     | Dhaneli    | BW     | 0.8 | -0.4 | 8.4  |
| 19     | Girod      | HP     | 0.5 | -0.1 | 7.9  |
| 20     | Baroud     | HP     | 0.3 | -1.2 | 9.6  |

Minimum 0.2 -2.1 7.1
Maximum 1.1 0.6 10.9
Average 0.6 -0.5 8.6
Good <1 <-2 <6
Corrosive >1 >2 >>8

4.4.1 Corrosivity Ratio (CR). The Corrosivity ratio (CR) is calculated using the under mentioned formula in which the ions are in mg/l units.

\[
CR = \frac{Cl/35.50 + 2(SO_4/96)}{2(HCO_3 + CO_3/100)}
\]

The CR value of water with less than or equal to 1 is considered good where as more than 1 indicates corrosive nature and is not fit for transportation through metal pipes [16,17] and it is not suitable for industrial or domestic purposes. Most of the water samples of the study area are non corrosive in nature and suitable for industrial purposes except Urkura where CR value is recorded 1.1 which is not suitable for industrial purposes with respect to corrosivity Ratio.

4.4.2 Langelier saturation Index (LSI). LSI is a measure to study the suitability of water for industrial purposes with reference to these affects. LSI helps in predicting the calcium carbonate stability of water and its ability to precipitate or dissolve. Apart from damaging the instruments / machinery, the scaling or corrosion properties of ground water will also bodily damage the house hold pipelines, fixtures water boilers thus it is essential to study the calcium carbonate stability of water by determining LSI value which is calculated using following formula,

\[
LSI = pH - pHs
\]

Based on the LSI value the following classification can be made (Carrier 1965)

2.0 : Scale forming but non-corrosive
0.5 : Slightly scale forming and corrosive
0.02 : Balanced but pitting - corrosion possible
-0.5 : Slightly corrosive but non-scale forming
-2.0 : Serious corrosion
The positive value of LSI indicates over-saturation of water thus tendency of CaCO₃ deposition and a negative saturation leads to tendency for corrosion. The saturation index is used to evaluate the scale forming and scale dissolving tendencies of water. If the saturation index is zero (pH=pHₛ), the water is in equilibrium and there is no net tendency of either scaling or corroding. All the water samples of study area are non corrosive in nature and suitable for industrial use with respect to LSI value.

### 4.4.3 Ryznar stability Index

The Ryznar stability Index (RSI) is another method of identifying dissolving or precipitation CaCO₃ nature of the ground water. It can be assessed using the equation mentioned below.

\[
\text{RSI} = 2(\text{pH}_s) - (\text{pH}_w)
\]

Where, pHₛ is the pH at saturation in CaCO₃ and pHₔ is the measured pH of water.

The RSI value of </=6 indicates increasing tendency for scale forming with a decreasing index, where as a value of >>7 suggest formation of no corrosion protective film. Water with RSI of >>8 suggest tendency for corrosion. Most of the water samples calculated RSI value is more than the eight and water has corrosive in nature at study area. Whereas in few locations, recorded RSI value is between 7 and 8 which is suitable for industrial supply.

### 4.4.4 Temporal variation

The chemical quality of surface water and groundwater varies with time and environmental conditions. The temporal variation in surface water quality and groundwater quality in between the previous study and present study surmised in Table-6 and parameter wise discussed below.

The pH value is getting low due to the water samples collected only around industries in current study. The minimum and maximum conductivity recorded low in this year but the average conductivity value is higher than the previous study. Similarly average concentration of bicarbonate, chloride, sodium, calcium, magnesium and total hardness is also recorded higher than the previous study. Few of the parameters like fluoride and sulphate are recorded low compared to the previous study it may be due to the affected area being away from the present study area.

**Table 6. Details of previous (2011-12) and present (2016-17) water quality data of Raipur.**

| Year | 2011-12 (n=61) | 2016-17 (n=20) | BIS 10500 :2012 (Acceptable limit) | BIS 10500 :2012 (Permissible limit) |
|------|----------------|----------------|-------------------------------------|--------------------------------------|
| Parameters | Min-Max | Mean | Min-Max | Mean | |
| pH    | 7.6-8.7 | 8.1 | 6.9-7.7 | 7.4 | 6.5 | 8.5 |
| EC (µS/cm) | 276-2650 | 755 | 185-1890 | 976.6 | - | - |
| HCO₃⁻ (mg/l) | 67-366 | 176.1 | 79-366 | 249.2 | 200 | 600 |
| Cl⁻ (mg/l) | 7-422 | 88 | 14.2-337.3 | 136.0 | 250 | 1000 |
| F (mg/l) | 0.1-2.2 | 0.4 | 0.0-1.1 | 0.2 | 1.0 | 1.5 |
| SO₄²⁻ (mg/l) | 5.575 | 83.1 | 0.5-145.4 | 57.9 | 200 | 400 |
| NO₃⁻ (mg/l) | 1-125 | 25.5 | - | - | 25 | 45 |
| Na (mg/l) | 4-240 | 53.4 | 6-207 | 55.0 | - | - |
| K (mg/l) | 1.6-26 | 5.5 | 0.5-12 | 2.5 | - | - |
| Ca (mg/l) | 12-250 | 67.6 | 24-176 | 86.7 | 75 | 200 |
| Mg (mg/l) | 1-61 | 17.2 | 2-4-52.8 | 19.9 | 30 | 100 |
| TH (mg/l) | 50-800 | 239.0 | 70-520 | 299.5 | 200 | 600 |
| Fe (mg/l) | 0.16-1.78 | 0.66 | bdl-1.35 | 0.17 | - | 0.3 |
| Mn (mg/l) | 0.03-0.12 | 0.28 | bdl-0.42 | 0.08 | 0.1 | 0.3 |
| Cu (mg/l) | 0.03-0.07 | 0.05 | bdl-0.02 | 0.01 | 0.05 | 1.5 |
| Zn (mg/l) | 0.01-0.86 | 0.12 | bdl-1.17 | 0.25 | 5 | 15 |
| Pb (mg/l) | bdl-0.05 | 0.01 | bdl-0.07 | 0.01 | - | 0.05 |

The heavy metals like iron manganese and copper are recorded low in the present study. Zinc concentration is enhanced, and no changes have been observed in lead concentration. Overall it is
observed that most of the ions are increasing with time and situation while in a few of the ion concentrations have no changes observed with time. However, some of the parameters are recorded low in the current study as compared to previous.

5. Conclusion
The groundwater in the study area is neutral to slightly alkaline. Its classification is based on the major ions, total alkalinity, and total hardness show that groundwater is suitable for drinking and domestic purposes. In respect to heavy metals, most of the groundwater is potable and heavy metals are within the acceptable limit except at few places where high iron, lead, and manganese are observed. The groundwater is suitable for irrigation purposes with reference to various computed parameters such as soluble sodium percentage (SSP), sodium adsorption ratio (SAR), residual sodium carbonate (RSC), percentage of sodium (%Na), Kelley ratio (KI), magnesium ratio (MR), and Permeability Index (PI) etc. Groundwater is bicarbonate and mixed type. Similarly, industrial parameters i.e., CR, RSI and LSI are calculated for determining the corrosive and scaling ability of groundwater samples in the study area, indicating most of the samples are non-corrosive except in few locations where water is corrosive. It is observed that most of the ions are increasing with time and circumstances, while in a few of the ions have no changes occurs in concentration.

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