CHAPTER VIII

CHEMICAL QUALITY OF GROUNDWATER

INTRODUCTION

Groundwater contains salts in solution. The type and concentration of the constituents depend upon such factors like the origin of water, composition of the water bearing medium, the length of time water has been in contact with the medium, source of recharge, rate of recharge and discharge and the temperature. According to Schoeller (1959) finding water is not everything; the water should be fit for various uses. As such, in any hydrogeological investigation in addition to quantity, quality of groundwater is of vital importance.

The hydrochemical investigations were carried out to study the hydrochemical regimes of groundwater as well as to determine the suitability of groundwater in the research area for domestic, agricultural and industrial uses. The sampled stations include dugwells, tubewells and springs. Details of the techniques adopted and the results of the chemical analysis of groundwater are discussed below.

SAMPLE COLLECTION AND CHEMICAL ANALYSIS

Water samples were collected in polythene bottles of one litre capacity for chemical analysis. Temperature
and pH of the groundwater samples were determined in the field with the help of mercury thermometer and portable pH metre. The temperature of the water varied between 24°C to 25.3°C and 23.5°C to 27°C in the Bhabar and Tarai zones respectively. The water samples were analysed for major cations like sodium, potassium, calcium, magnesium and anions which include carbonate, bicarbonate, chloride and sulphate.

Calcium, magnesium, carbonate, bicarbonate and chloride were determined by volumetric techniques. Sulphate was determined gravimetrically, while potassium and sodium were analysed by flame photometer. In addition to the above analyses, the electrical conductance, hardness and total dissolved solids of the groundwater were also determined.

The results of the chemical analysis of the groundwater samples of the research area are shown in Table 30 and are also represented by graphic method of Collins (1923) (Figs. 89a and 89b). Foster (1950), Hem (1970), Todd (1980) and others also used this method for representing the chemical analysis of water samples. The Table and figures indicate that the groundwater of the Bhabar and Tarai zones show variations in percentages and concentrations of the six ionic constituents that constitute the bulk of the dissolved solids. The pH, electrical


<table>
<thead>
<tr>
<th>Location</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>HCO₃</th>
<th>CO₂</th>
<th>SO₄</th>
<th>Cl</th>
<th>H₂SO₄</th>
<th>NO₃</th>
<th>Fe</th>
<th>Al</th>
<th>Total Hardness</th>
<th>Total Alkalinity</th>
<th>Total Calcium</th>
<th>Total Magnesium</th>
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<tr>
<td>N 12/22 Amritsar</td>
<td>4.84</td>
<td>6.14</td>
<td>0.80</td>
<td>9.20</td>
<td>45.84</td>
<td>13.24</td>
<td>17.73</td>
<td>12.89</td>
<td>155.92</td>
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<td>8.20</td>
<td>5.00</td>
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<td>45.84</td>
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<td>17.73</td>
<td>12.89</td>
<td>155.92</td>
<td>17.23</td>
<td>8.20</td>
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<td>5.00</td>
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<td>12.89</td>
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<td>17.23</td>
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<td>17.73</td>
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<td>5.00</td>
<td>1.45</td>
<td>148.37</td>
<td>72.30</td>
<td>85.10</td>
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</tbody>
</table>

**Results of Chemical Analysis of Water Samples from the Research Area**
FIG. 9a. GRAPHIC REPRESENTATION OF GROUNDWATER CHEMICAL ANALYSIS FOR BHABAR ZONE (after Collins, 1923)
FIG89b GRAPHIC REPRESENTATION OF GROUNDWATER CHEMICAL ANALYSIS FOR TARAI ZONE (after Collins, 1972)
conductivity, total dissolved solids, hardness and the concentration of the individual cations and anions of the groundwater are briefly discussed below.

pH

This is the logarithm of the reciprocal of the effective hydrogen-ion concentration (or the hydrogen-ion activity) per litre of groundwater. The pH of the groundwater samples were determined in the field with portable pH meter. The pH values of groundwater in the research area vary from 7.45 to 8.83 (Table 30) indicating that some of the waters are slightly alkaline in nature. According to Voznaya (1981) the alkalinity of natural waters depends largely upon the presence of carbonates and bicarbonates, and these are contained in appreciable quantities in the groundwater of the research area (Table 30).

ELECTRICAL CONDUCTIVITY (E.C.)

The ability of groundwater to conduct electric current is known as its electrical conductivity (electrical conductance); and is a function of temperature, type of ions present and the concentration of the various ions (Walton, 1970). The unit of measurement of electrical conductivity is micromhos per centimeter at 25°C. At this condition, electrical conductance is a function of concentration and charge of ions present in solution of groundwater. The
electrical conductivity of the groundwater in this work has been determined by using the conductivity bridge Model CB40 at the Chemical laboratory of the Groundwater Cell, Agricultural Department, Punjab (Chandigarh).

The electrical conductance of groundwater in the Bhabar Zone varies from 294 micromhos to 950 micromhos at 25°C (Table 30) except at Billa where locally higher value (3558 micromhos at 25°C) has been observed. In 80 per cent of the analysed groundwater samples from the Bhabar Zone, the electrical conductivity values are below 950 micromhos at 25°C indicating low to medium mineralization of the groundwater. In the Tarai Zone, the electrical conductivity varies from 300 micromhos to 3215 micromhos at 25°C. 64 per cent of the analysed water samples from this zone have conductance values below 1000 micromhos. 27 per cent have conductance values varying between 1000 and 1500 micromhos and only two water samples have conductance values of 1682 and 3215 micromhos at 25°C. The electrical conductivity map of the research area has been prepared (Map 11). The map indicates that groundwater in the Bhabar Zone exhibits lower electrical conductivity and hence lower mineralization than the groundwater of the Tarai Zone. Generally, both the Bhabar and the Tarai zones have low mineralization except in few localities where locally high mineralization values have been observed.
ELECTRICAL CONDUCTIVITY MAP OF THE STUDY AREA

( JUNE 1984 )

SCALE

0  5  10 km

LEGEND

STATE BOUNDARY

BLOCK BOUNDARY

RIVERS / STREAMS

HIGROGRAPH STATIONS

BLOCK HEADQUARTERS

E.C. CONTENT OF 50g/100g (TESTED)
at 25°C
TOTAL DISSOLVED SOLIDS (T.D.S.)

Total Dissolved Solids in a groundwater sample include all solid material in solution, whether ionized or not. It does not include suspended sediments, colloids or dissolved gases (Walton, 1970). The T.D.S. values of groundwater samples of the research area shown in Table 30 have been determined by the residue on evaporation method in the Chemical Laboratory of the Groundwater Cell, Agricultural Department Punjab (Chandigarh). The T.D.S. values of the water samples in the Bhabar zone vary between 171 ppm and 501 ppm except in the village Billa where abnormal local T.D.S. value was observed. In the Tarai Zone T.D.S. values vary from 145 ppm to 976 ppm, with 72 per cent of the water samples having T.D.S. values below 500 ppm. One water sample from Shazadpur village in the Tarai Zone showed abnormally high value.

Generally, total dissolved solids contents of the groundwater in the study area increase from the Bhabar Zone in the North to the southern Tarai Zone; and exhibit variation pattern similar to pattern of variation shown by the electrical conductivity in the Bhabar and Tarai zones, respectively. This is because the Bhabar Zone is composed of cleaner sand and have fewer clay beds than the Tarai Zone farther south. Less soluble material is thus available
in the near surface formation of the Bhabar Zone than available in the Tarai. Groundwater in the Tarai Zone is shallower than in the Bhabar Zone, and the concentration of salts due to higher evaporation from groundwater in the Tarai may increase dissolved solid contents. Another possible explanation for the low mineralization and hence lower T.D.S. and E.C. values of the Bhabar Zone is that it is characterized by steep slopes and forms the principal area of recharge. Water in the Bhabar aquifers flows down gradient. In the Tarai Zone, the concentration of dissolved solids increases markedly as a function of the length of flow path and residence time of groundwater in the aquifers. Hanshaw et al. (1965) also observed that T.D.S. values in the Florida limestone aquifer increased North South away from the recharge zone. Back (1960) remarked that it should be possible to identify the recharge area as those showing the lowest dissolved solid concentrations. According to him an area with high sodium content and with high dissolved solid concentration is likely to be the discharge area, because the amount of dissolved-solids in water would reflect the length of residence of time in the aquifer. This supports the inference drawn earlier from the study of subsurface geological sections of the research area that the Bhabar Zone forms the recharge zone, whereas the Tarai Zone is the discharge area.
Davis and DeWiest (1970) had suggested the following classification of waters on the basis of T.D.S.:

<table>
<thead>
<tr>
<th>Type of Water (after Davis and DeWiest, 1970)</th>
<th>Concentration of Total Dissolved Solids in Parts per Million</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh water</td>
<td>0 – 1,000</td>
</tr>
<tr>
<td>Brackish water</td>
<td>1,000 – 10,000</td>
</tr>
<tr>
<td>Salty water</td>
<td>10,000 – 100,000</td>
</tr>
<tr>
<td>Brine water</td>
<td>More than 100,000</td>
</tr>
</tbody>
</table>

On the basis of the above classification groundwater in the Bhabar and Tarai zones may be classified as fresh since the T.D.S. values for most of the groundwater of the area are below 1,000 ppm. T.D.S. values of water for most domestic and industrial uses should be less than 1,000 ppm, and water for most agricultural uses, should be below 3,000 ppm (Davis and DeWiest, 1970). As such groundwater in the Bhabar and Tarai zones of the research area are suitable for domestic, industrial and agricultural uses. Groundwater, classification according to T.D.S. content (after Hem, 1970) also shows that groundwater in the Bhabar and Tarai zones are fresh and good for irrigation purposes.
TOTAL HARDNESS

The total hardness of water is the concentration of alkali earths, principally Ca\(^{2+}\) and Mg\(^{2+}\) ions expressed in me/l. Strontium and barium may be present but usually in small quantities. Water hardness results from solution of alkali-earth minerals from the soil and from direct pollution of wastes.

In the research area, calcium and magnesium carbonates (limestone and dolomite) are prevalent in small quantities in the Siwalik rocks, but are only sparingly soluble in pure water. Bacterial activities release carbon dioxide in the soil and in percolating rain water. In low pH conditions water containing carbon dioxide and other acidic constituents readily dissolves the insoluble carbonate minerals converting them to soluble bicarbonate.

\[
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(HCO}_3\text{)}_2
\]

Hardness of water is associated with the behaviour of soap towards water, and is a measure of the amount of soap required to produce suds. Since most soap effects result from the presence of calcium and magnesium, hardness is now expressed in terms of these constituents alone. The hardness of water is expressed quantitatively as the equivalent of calcium carbonate, thus,

\[
\text{Total Hardness (TH)} = \text{Ca} \times \frac{\text{CaCO}_3}{\text{Ca}} + \text{Mg} \times \frac{\text{CaCO}_3}{\text{Mg}}
\]
where "hardness as CaCO\textsubscript{3}" or "Total hardness" is measured in parts per million of calcium carbonate. Ca and Mg are in parts per million, whereas ratios are in equivalent weights.

If the values of equivalent weights of CaCO\textsubscript{3}, Ca and Mg in the above equation are substituted, we obtain:

\[ TH = \frac{Ca \times 50}{20.04} + \frac{Mg \times 50}{12.16} = 2.495 \text{Ca} + 4.112 \text{Mg} \]

Hardness in water may be classified as temporary hardness or permanent hardness. Hardness in water resulting from the presence of bicarbonates, e.g. Ca(HCO\textsubscript{3})\textsubscript{2} which can be removed by boiling is referred to as temporary hardness, whereas hardness due to substance like calcium sulphate which is not removed by boiling forms permanent hardness.

Waters containing small quantities of calcium and magnesium salts lather freely with soap and are called soft water (Parkes, 1951). Sawyer and McCarty (1967) classified water on the basis of hardness as CaCO\textsubscript{3} as follows:

<table>
<thead>
<tr>
<th>Hardness (mg/l) as CaCO\textsubscript{3}</th>
<th>Water Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-75</td>
<td>Soft</td>
</tr>
<tr>
<td>75-150</td>
<td>Moderately hard</td>
</tr>
<tr>
<td>150-300</td>
<td>Hard</td>
</tr>
<tr>
<td>Over 300</td>
<td>Very hard</td>
</tr>
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</table>
In the Bhabar and Tarai zones of the research area, "hardness as CaCO₃" varies from 99.89 to 688.59 ppm and 75.00 ppm to 793.15 ppm respectively (Table 30) with most of the values falling below 300 ppm. This implies that the groundwater in the region vary from moderately hard to very hard class of Sawyer and McCarty (1967).

However, Sharma (1979) remarked that hardness of natural water suitable for public supply ranges between 10 ppm to 1800 ppm approximately; thus indicating that groundwater of research area is suitable for various uses.

SODIUM

In the Bhabar Zone of the research area, sodium concentration varies from 24.99 ppm to 94.99 ppm, whereas in the Tarai Zone the range is between 24.78 ppm and 207.4 ppm except at village Billa (Bhabar Zone) and Shazedpur, Wasilpur and Berpura villages (Tarai Zone) where abnormally local high values were observed. The abnormal high concentrations may be attributed to the exchange of calcium in the waters for sodium of base-exchange minerals in the rock materials in those localities in which clay minerals act as natural water softners (BacK, 1960). The average concentration of sodium in both the Bhabar and Tarai zones of the research area does not exceed 99.68 ppm.
Sodium concentration is important in classifying irrigation water. High concentration of sodium salts in the soil develops alkali soil which is not desirable for agricultural purposes as such soil can become deflocculated and tends to reduce soil permeability (Welton, 1970; Todd, 1980). Sodium content is usually expressed in terms of per cent sodium which is defined by the equation:

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

where all ionic concentrations are expressed in milliequivalents per litre (m/lt.).

Wilcox (1955) put forward a classification for irrigation water on the basis of per cent sodium as under:

<table>
<thead>
<tr>
<th>Per Cent Sodium</th>
<th>Water Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 20</td>
<td>Excellent</td>
</tr>
<tr>
<td>20-40</td>
<td>Good</td>
</tr>
<tr>
<td>40-60</td>
<td>Permissible</td>
</tr>
<tr>
<td>60-80</td>
<td>Doubtful</td>
</tr>
<tr>
<td>More than 80</td>
<td>Unsuitable</td>
</tr>
</tbody>
</table>

Per cent sodium in the Bhebar and Terai Zones of the research area varies from 6.24 to 73.8 and 8.74 to 87.34 respectively (Table 30), indicating that the groundwater
of the area on the basis of Wilcox (1955) classification varies from the excellent to doubtful class.

Figure 90 shows a plot of per cent sodium against electrical conductivity after Wilcox (1955). The figure reveals that over 90 per cent of the groundwater samples of the Bhabar Zone and about 84% of the groundwater samples of the Tarai Zone are excellent to good or permissible for irrigation. This indicates that most of the groundwater of the research area is good for irrigation. Only one water sample from the Tarai Zone is unsuitable for irrigation. The analysis also reveals that on the basis of per cent sodium, quality of groundwater for irrigation in Bhabar and Tarai zones can be rated as generally good.

SODIUM HAZARDS:

The U.S. salinity Laboratory Staff (1954) proposed the use of sodium absorption ratio (S.A.R.) for studying the suitability of groundwater for irrigation purposes.

Sodium absorption ratio (S.A.R.) is defined by the following equation:

$$S.A.R. = \frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+})/2}}$$

where all the concentrations are expressed in me/1.
FIG. 90 CLASSIFICATION OF WATER ON BASIS OF ELECTRICAL-
CONDUCTIVITY AND SODIUM PERCENTAGE
(after Wilcox, 1955)
They classified water on the basis of S.A.R. as follows:

<table>
<thead>
<tr>
<th>S.A.R.</th>
<th>Water Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 10</td>
<td>Excellent</td>
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<tr>
<td>10-18</td>
<td>Good</td>
</tr>
<tr>
<td>18-26</td>
<td>Fair</td>
</tr>
<tr>
<td>More than 26</td>
<td>Poor</td>
</tr>
</tbody>
</table>

Except at Wasilpur and Berpura villages of the Tarai Zone where groundwater samples fall in the good water class; values of S.A.R. in the entire Bhabar and Tarai Zones are below 8 indicating that groundwater in the research area are excellent for irrigation.

Figures 9la and 9lb show plots of sodium adsorption ratio against electrical conductivity (U.S. Salinity Laboratory Diagram) to ascertain the salinity and alkalinity hazards in the Bhabar and Tarai zones respectively. Figure 9la depicts that 72.73% of the Bhabar groundwater samples belong to \( C_2S_1 \) class of the U.S. Salinity Laboratory classification, whereas 9% of the water sample belongs to \( C_3S_1 \) and \( C_3S_2 \) classes, respectively. Only one water sample belongs to the \( C_4S_2 \) class in the Bhabar Zone.

In the Tarai Zone (Fig. 9lb) 61.9% of the groundwater samples belong to the \( C_2S_1 \) class, whereas 19%, 4.8%, 9.5%
FIG. 9a. DIAGRAM FOR CLASSIFICATION OF IRRIGATION WATERS IN BHABAR ZONE (AFTER U.S. DEPT. OF AGRIC. HANDBOOK 60, 1954.)

FIG. 9b. DIAGRAM FOR CLASSIFICATION OF IRRIGATION WATERS IN TARAI ZONE (AFTER U.S. DEPT. OF AGRIC. HANDBOOK 60, 1954.)
and 4.8% of the water samples belong to the $C_3S_1$, $C_3S_2$, $C_3S_3$ and $C_4S_2$ classes, respectively.

The above classification indicates that except for groundwater from Shazadpur (Tarai Zone) and Billa (Bhabar Zone) which have very high salinity hazards and low to medium alkali hazards, all other groundwater in the region is free from alkalinity and salinity hazards.

**POTASSIUM:**

Concentration of Potassium in the Bhabar and Tarai Zones varies from 1.0 ppm to 14.03 ppm, and 1.70 to 50.87 ppm respectively. In most cases, potassium concentration is low and generally below 10 ppm. However, in few villages like Billa, Laha (Bhabar Zone); Khera Jattan and Sunderpur (Tarai Zone) very localised higher potassium concentrations were observed, and may have been caused by the leaching of potash fertilizers which is the principal source of added potassium in the soil (Langmuir, 1971); or they may have been added by the absorption and fixation of potassium with associated clay minerals (Whitehouse and McCarter, 1956; Weaver, 1958b) in the clay-rich terrain of the Tarai Zone.

Potassium concentration is essential to animal nutrition but a concentration of 1,000 to 2,000 ppm in stock water is regarded as the extreme limit permissible (Moore, 1950). In the entire research area, the maximum concentration of potassium recorded is 101.49 ppm which is very low in
comparison to Moore's (1950) extreme permissible limit. As such, groundwater in the research area on the basis of potassium content is suitable for domestic and agricultural uses.

**CALCIUM**

The average concentration of calcium in the research area is 28.0 ppm, with individual well concentrations varying from 7.21 ppm to 44.8 ppm in the Bhabar Zone; and 8.00 to 60.12 ppm in the Tarai Zone. The calcium is derived from the leaching of deposits of limestones, sandstones, shales, clays, etc. which form the subsurface lithology of the area and adjoining Siwalik hills.

In the presence of $H^+$ ions calcium carbonate is easily soluble in water. The dissociation of $H_2CO_3$ is one of the most important sources of $H^+$ ions. In the region under investigation, it seems that the following reactions have taken place and account for the calcium carbonate concentration:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$$
Carbon dioxide is readily abundant in the atmosphere, soils and water; and indirectly reflect the concentration of calcium bicarbonate.

Calcium imparts the property of hardness to water and when present with alkalinity or sulfate it may cause boiler scale (Brown et al., 1974). A little calcium carbonate is desirable in water used domestically because of the protective coating that it may form in pipes. A high ratio of calcium to sodium is desirable in water used for irrigation because calcium flocculates the soil colloids and tends to maintain good soil structure and permeability. According to Davis and DeWiest (1970) concentration of calcium in normal potable water ranges between 10 and 100 ppm, and as such 1,000 ppm of calcium may be harmless. As such, groundwater of the research area with calcium concentration varying from 7.21 ppm to 60.12 ppm (Table 30) is potable and harmless for various uses.

MAGNESIUM

The concentration of magnesium in the area varies from 12.89 ppm to 148.35 ppm in the Bhabar Zone and 3.16 to 136.19 ppm in the Tarai Zone. The average concentration of magnesium in the analysed water samples is 38.73 ppm which is very low. The geochemistry of magnesium is similar to that of calcium and is also influenced by the presence of carbon dioxide.
Gypsum and anhydrite are the most important mineral constituents contributing to the presence of sulphates in natural waters (Todd, 1970; El-Hinnawi and Atwa, 1973). Oxidation of sulfide ores also yield substantial amount of sulphates (Todd, 1970).

The concentration of sulphates in the groundwater of the Bhabar Zone of the research area varies from 0 to 102.50 ppm, whereas in the Tarai Zone its concentration varies from 0 to 277.41 ppm.

More than 250 ppm of sulphate is objectionable in water for some industries (Todd, 1970). However, according to the standard of acceptability of water for domestic uses after the Indian Council for Medical Research (ICMR) (1975) highest desirable concentration of sulphate in water is 200 ppm, while 450 ppm is the maximum permissible concentration. The above norms indicate that groundwater in the research area is suitable for industrial and domestic uses in relation to sulphate concentration; except in village Shazadpur (Tarai Zone) where local abnormal concentration of 277.41 ppm was observed. The slightly high concentration of sulphate in the water may be due to the leaching of super phosphate or ammonia sulphate fertilizers which are commonly used in the area by local farmers. However, the sulphate concentration does not exceed the ICMR maximum permissible concentration.
CHLORIDE

Average chloride value in the waters of the research area is about 96.73 ppm, which is too low to create any salinity hazard. In the Bhabar Zone, chloride concentration varies from 17.73 ppm to 92.20 ppm except at Billa where local abnormal concentration was observed. In the Tarai Zone the concentration of chloride ranges between 7.09 ppm and 581 ppm. Local abnormal concentrations exceeding permissible limit of 250 ppm (U.S. Department of Health, Education and Welfare, 1962; and absolute World Health Organization Standard, have been observed in the water of few localities in the region; and may have resulted from pollution of groundwater in the areas by human or animal wastes, and industrial wastes into streams and groundwater reservoir (Brown et al., 1974). Calcium chloride applied to highways can also contribute significant amounts of Cl to groundwater (Langmuir, 1971).

CARBONATE-BICARBONATES AND RESIDUAL SODIUM CARBONATE. (RSC)

Alkalinity in the soil is produced exclusively by carbonate and bicarbonates. The dissociation of bicarbonate to carbonate and to hydrogen ions is effective largely when pH is above 8.2. Below this value carbonate ion combines with hydrogen to form bicarbonate (\(H^+ + CO_3^{2-} \rightarrow HCO_3^-\)). The part of alkalinity titration above pH 8.2 is therefore, a
measure of the carbonate ions, and below 8.2 is a measure of bicarbonate ions. Below pH 4.5, most bicarbonate ions are converted into carbonic acid molecule \( \text{H}^+ + \text{HCO}_3^- = \text{H}_2\text{CO}_3 \).

Sources of carbonate and bicarbonate ions in groundwater include carbon dioxide from the atmosphere, carbon dioxide produced by biota of the soil or by the activity of sulphate reducers and other bacteria in deeper formations, and the various carbonate rocks and minerals. In the Bhabar Zone of the research area, carbonate concentration varies from 0.60 to 6.6 ppm whereas bicarbonate concentration varies from 115 ppm to 579.62 ppm. In the Tarai Zone carbonate and bicarbonate concentrations range between 0.48 to 7.8 ppm and 134.23 to 756.56 ppm, respectively. pH values in the Bhabar and Tarai Zones varies between 7.45 and 8.85 with most of the values ranging between 7.45 to 8.2 which favours the solubility of carbonates, hence more concentration of bicarbonates than carbonates in the area.

Bicarbonate hazard which is caused by the residual sodium carbonate (R.S.C.) in water has been computed by Eaton's method (1950), which proposed that carbonate-bicarbonate in excess of calcium, magnesium on equivalent basis will appear as sodium carbonate.

\[
\text{R.S.C.} = (\text{CO}_3^- + \text{HCO}_3^-) - (\text{Ca}^{2+} + \text{Mg}^{2+})
\]

where all the terms are expressed in m e./lt. respectively.
The Haryana Agricultural University, Hissar uses the following classification for Haryana State, India based on R.S.C. values for irrigation water:

<table>
<thead>
<tr>
<th>R.S.C. m.e./lt.</th>
<th>Water class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 2.5</td>
<td>Fit</td>
</tr>
<tr>
<td>2.5 - 5.0</td>
<td>Marginal</td>
</tr>
<tr>
<td>More than 5.0</td>
<td>Unfit</td>
</tr>
</tbody>
</table>

R.S.C. values (Table 30) of the analysed groundwater samples except locally at Wasilpur, Berpura (Tarai) and Rampur (Bhabar) are generally low, indicating that groundwater in the research area is fit for irrigation on the basis of bicarbonate hazards.

CHEMICAL CHARACTERS OF GROUNDWATER

In order to understand the chemical characters of groundwater in the research area, the results of the chemical analysis shown in Table 30 have been plotted on Piper's (1944) Trilinear diagram for the Bhabar and Tarai zones, respectively (Figs. 92a and 92b). The Trilinear diagram combines two triangular fields at the lower left and lower right, respectively; and an intervening diamond-shaped field. All three fields have scales reading in 100 parts. In the triangular field at the lower left, the percentage reacting values of the three cation-groups (Ca, Mg, Na) are plotted as a single point according to
conventional trilinear coordinates, whereas the three anion-groups ($\text{HCO}_3^-$, $\text{SO}_4^-$, and $\text{Cl}$) similarly expressed as percentages of total anions in milliequivalents per litre; appear as a point in the right triangle. These two points are then projected into the central diamond-shaped area parallel to the upper edges of the central area. The position of this plotting indicates the relative composition of the groundwater in terms of the cation-anion pairs that correspond to the four vertices of the field.

Piper (1944) had interpreted the diamond-shaped field of the trilinear diagram according to Palmer's (1911) classification and had discriminated distinct groundwater types by their plotting in certain sub areas of the diamond-shaped field as shown in Figures 92(i) and 92(ii) respectively for the Bhabar and Tarai zones. Walton (1970) had also suggested the use of this method for differentiation of water types after Piper (1953).

Figures 92(a) and 92(b) reveal that most of the water samples of the Bhabar zone are rich in alkali earths ($\text{Ca}^{2+}$, $\text{Mg}^{2+}$); alkalies ($\text{Na}^+$, $\text{K}^+$) and weak acids ($\text{HCO}_3^-$, $\text{CO}_3^{2-}$). Two water samples (from villages Billa and Burewala) in the area belong to a class where non-carbonate hardness ($\text{Cl}^-$, $\text{SO}_4^{2-}$) exceed 50 per cent. The plot also indicates
FIG. 92a TRILINEAR DIAGRAM SHOWING CHEMICAL CHARACTER OF GROUNDWATER IN THE BHABAR ZONE (after Piper, 1974)

FIG. 92b TRILINEAR DIAGRAM SHOWING CHEMICAL CHARACTER OF GROUNDWATER IN THE TARAI ZONE (after Piper, 1974)
that carbonate alkali (primary alkalinity) in most of
the samples exceed 50 per cent (Fig. 92c) implying that
most groundwater in the area are inordinately soft in
proportion to their content of dissolved solids. Two
water samples from the Bhabar Zone belong to a class
where no one cation-anion pair exceeds 50 per cent
(Fig. 92ic).

In the Tarai Zone (Figs. 92b and 92iia) majority
of the groundwater are rich in alkalies (Na⁺, K⁺) and weak
acids (HCO₃⁻, CO₃²⁻). Fewer groundwater samples from this
zone are rich in alkali earths (Ca²⁺, Mg²⁺) (Fig. 92iia)
as compared with groundwater from the Bhabar Zone. The
higher concentration of alkalies and less alkali earths
in the Tarai Zone as compared to the Bhabar Zone may be due
to predominance of clays in the Tarai Zone. According to
Davis and DeWiest (1966) the weathering of clay minerals
and plagioclase feldspars enriches sodium content in the
soil. One water sample from the village Shazadpur in the
Tarai Zone belongs to the class where non carbonate hardness
(Cl⁻, SO₄²⁻) exceed 50 per cent, while 4 water samples belong
to the class where no one cation-anion pair exceed 50 per
cent (Fig. 92iic). In most of the groundwater of this zone
carbonate alkali exceed 50 per cent indicating that ground-
water is inordinately soft in proportion to their dissolved
solid content. In both the Bhabar and Tarai zones, the plots
FIG. 92 (i) BHABAR ZONE

FIG. 92 (ii) TARAI ZONE

KEY

Area:
1. Alkaline earth exceed alkalies
2. Alkalies exceed alkaline earths
3. Weak acids exceed strong acids
4. Strong acids exceed weak acids
5. Secondary alkalinity (carbonate hardness) exceed 50% i.e. chemical properties of water are dominated by alkaline earths & strong acids
6. Secondary salinity (non-carbonate hardness) exceed 50%
7. Primary salinity (non-carbonate alkali) exceed 50% i.e. chemical properties are dominated by alkalies & strong acids
8. Primary alkalinity (carbonate alkali) exceed 50% i.e. water are inordinately soft in proportion to the content of dissolved solids
9. No one of the cation-anion pairs in Palmer's classification exceeds 50%

FIG. 92 SUB-DIVISION OF DIAMOND-SHAPED FIELD OF PIPER TRILINEAR DIAGRAM AND DIFFERENTIATION OF GROUNDWATER TYPES OF BHABAR AND TARAI ZONES (after Piper, 1944, 1953)
(Figs. 92ic and 92iic) indicate that secondary salinity is absent. Carbonate hardness (secondary alkalinity) is less than 50% in 25% and 24% of the water samples of the Bhabar and Tarai Zones, respectively (Figs. 92ic and 92iic).

Piper (1953) suggested that circles of radii corresponding to total concentration of dissolved solids be drawn with a point of plotting as centre in the diamond-shaped area. However, this was not possible in the present work, as the data plots fall very close to each other (Figs. 92a and 92b).

**CLASSIFICATION OF GROUNDWATER ACCORDING TO HYDROCHEMICAL FACIES**

The concept of hydrochemical facies to understand the chemical characters of groundwater has been used by many workers including Back (1960), Hanshaw et al. (1965), Davis and DeWiest (1970), Walton (1970), Singh and Dogra (1980) and others. Back (1960) had remarked that the concept of hydrochemical facies indicates that the nature and concentration of ions in solution are influenced by the lithology and groundwater flow pattern of the particular region.

The classification of hydrochemical facies put up by Back (1960) as indicated in Table 31 below is followed in this work.
TABLE 31
CLASSIFICATION OF HYDROCHEMICAL FACIES
(After Back, 1960)

<table>
<thead>
<tr>
<th>Cation Facies</th>
<th>Percentage of Constituents (in ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca+Mg</td>
</tr>
<tr>
<td>Calcium-Magnesium</td>
<td>90-100</td>
</tr>
<tr>
<td>Calcium-Sodium</td>
<td>50-90</td>
</tr>
<tr>
<td>Sodium-Calcium</td>
<td>10-50</td>
</tr>
<tr>
<td>Sodium-Potassium</td>
<td>0-10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anion Facies</th>
<th>Percentage of Constituents (in ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bicarbonate - 90-100 0-10</td>
</tr>
<tr>
<td></td>
<td>Bicarbonate-chloride-sulphate - 50-90 10-50</td>
</tr>
<tr>
<td></td>
<td>Chloride-sulphate-bicarbonate - 10-50 50-90</td>
</tr>
<tr>
<td></td>
<td>Chloride-sulphate - 0-10 90-100</td>
</tr>
</tbody>
</table>

The analytical data was plotted in a trilinear diamond-shaped diagram similar to that of Piper (1953) (Fig. 93). Statistical analysis of the figure shows the following characteristic percentage composition of the total ions (in ppm) for the Bhabar and Tarai zones.

**Bhabar Zone**: Ca+Mg = 45.4%, Na+K = 54.6%
HCO$_3$+CO$_3$ = 82.0% Cl+SO$_4$ = 18.0%

**Tarai Zone**: Ca+Mg = 25.0% Na+K = 75.0%
HCO$_3$+CO$_3$ = 95.0% Cl+SO$_4$ = 5.0%
FIG. 93 WATER ANALYSIS DIAGRAM SHOWING HYDROCHEMICAL FACIES OF GROUNDWATER IN THE BHABAR AND TARAI ZONES (after Back, 1960)
The above data on the basis of the classification of hydrochemical facies after Back (1960) (Fig. 93) indicates the predominance of sodium-calcium cation facies with calcium-magnesium occurring in dilute concentrations in the Bhabar Zone. In the Tarai Zone, the cation facies are dominated by sodium-calcium facies. Majority of the Bhabar groundwater samples represent the bicarbonate-chloride-sulphate, anion facies, whereas the anion facies of the Tarai Zone are dominantly bicarbonate facies.

The figure (Fig. 93) thus indicates that the Bhabar Zone is dominated by sodium-calcium - bicarbonate-chloride-sulphate type of hydrochemical facies with calcium-magnesium occurring in dilute concentrations; whereas the Tarai Zone has the sodium-calcium-bicarbonate type of hydrochemical facies. However, sodium concentration in the Tarai Zone is higher than in the Bhabar Zone. This may be attributed to the lithological differences between the Bhabar and the Tarai Zones; the latter being constituted of thicker clay beds. According to Davis and DeWiest (1966), and Walton (1970), the weathering of clay minerals and plagioclase feldspars increase sodium concentration in the soils. The dominance of sodium-calcium cation facies in both the Bhabar and Tarai zones signify that the flow characteristics of the aquifer systems influence the distribution of facies. For instance, sodium facies is developed
by the process of ion exchange in which the clay minerals act as natural water softeners. Water from rainfall and also received by seepage from the emerging streams of the Siwaliks enters the Bhabar recharge area and percolates downward. Some of these emerging streams concentrate calcium and magnesium which are derived from calcareous cement of the Siwalik rocks and from the weathering of boulders, pebbles and sandstones containing feldspars, amphiboles, biotite, etc. into the Bhabar soils. As this water percolates into the Bhabar recharge Zone, calcium-magnesium-bicarbonate facies develops. This occurs in dilute concentrations in the Bhabar Zone. As the water moves through the intercalated clay beds of the Bhabar recharge zone and into the thick clay beds of the Tarai Zone, ion-exchange materials remove calcium and magnesium ions from the water and replace them with sodium ions.

The bicarbonate-chloride-sulphate facies occurring in the Bhabar Zone is due to the dilute solution of the water in the zone which results in the development of any particular facies in response to minor changes in lithologic material. According to Back (1960), small addition of calcareous material changes the bicarbonate-chloride-sulphate facies into bicarbonate facies. This factor may have contributed to the dominance of bicarbonate facies in
the Tarai Zone which are recharged by the Bhabar aquifers. However, bicarbonate ions are derived from solution of \( \text{CaCO}_3 \) carbonate by groundwater made acids by dissolving carbon dioxide gas from the atmosphere and the soil.

It may be inferred from the above analysis that the chemical characters of the groundwater in the research area reflects the combined effect of the chemical activity related to the lithology and the flow pattern within the aquifers of the zone.

SUITABILITY OF GROUNDWATER FOR IRRIGATION, DOMESTIC AND INDUSTRIAL USES

The presence of certain salts in water result to changes in soil structure, permeability and soil aeration, which may affect crop growth. It is, however, difficult to fix specific permissible limits of salt concentration of any irrigation water because of the wide variations in salinity tolerance of different plants (Davis and DeWiest, 1966). The suitability of water for domestic purposes is related to its physical and chemical qualities. Drinking water standards depend on certain local conditions which include climate of the area, drinking/food habits and general health of the local people and as such may not be rigidly uniform. According to Walton (1970), the quality requirements
of waters used in different industrial processes vary widely. He remarked that even within each industry, criteria cannot be established, instead only recommended limiting values or ranges can be stated.

The suitability of groundwater in the research area for various uses has been discussed in the light of per cent sodium, sodium hazards, bicarbonate hazards, total dissolved solids and electrical conductivity; in addition to the concentration of the various cations and anions in consonance with recommended standards of the U.S. Salinity Staff, (1954), U.S. Geological Survey (1974), Indian Council for Medical Research (1975), Haryana Agricultural University, Hissar; U.S. Department of Health, Education and Welfare (1962) and absolute World Health Organization Standards, (1961) etc.

The above results and discussions of chemical analysis of groundwater indicate that the groundwater of the Bhabar and most of the groundwater of the Tarai Zones of the research area are fresh and fit for irrigation, domestic and industrial purposes.