CHAPTER - 7
CLASSIFICATION OF GROUNDWATER AND ITS CHEMICAL ATTRIBUTES FOR VARIOUS APPLICATIONS

7.1 GENERAL

In the past, water quality concerns were often neglected or studied only for academic interest because good quality water supplies were abundant and readily available. Water quality in an area is a function of physical and chemical parameters that are greatly influenced by geological formations and anthropogenic activities. Agricultural activities, population growth, rapid industrialization and unplanned urbanization in the Ganga Plain have resulted in various geo-environmental hazards causing deterioration of groundwater quality in many ways. Understanding the quality of groundwater is particularly important as it determines the factors governing the suitability of water for drinking, domestic, agricultural and industrial purposes (Subramani et al. 2005).

Groundwater is not pure water because it usually contains dissolved mineral ions. The type and concentration of these dissolved minerals can affect the usefulness of groundwater for various purposes. If certain mineral constituent are present in excessive amounts, some type of treatment may be necessary to either change or remove the dissolved mineral before the water can be used for the intended purposes.

Quality of water, therefore, has become one of the important environmental issues. Groundwater is an important source of water for domestic, agricultural and industrial consumption. Quality of groundwater demands as much as its quantity and it is described by its physical, chemical and biological characteristics. These characteristics are interlinked. Quality of groundwater and its suitability for drinking and irrigation purposes is important for its safe and effective use. Several studies have been made on the quality and chemical characteristic of groundwater of Ganga basin (Umar and Ahmed, 2000; William et al. 2001; Ravenscraft et al. 2005; Umar, 2006; Umar et al. 2006; Ahmed, 2008; Saha, 2009; Saha et al. 2009; Joshi et al. 2009; Ghose et al. 2009; Khan, 2009; Dhakyanika and Kumara, 2010).
7.2 COMPOSITION OF METEORIC WATER

The role of the chemistry starts from the time precipitation occurs on the land and hydrological cycle sets in. The chemistry of the meteoric water is the starting point for all subsequent chemical alterations that the meteoric water is subjected to during infiltration and as a result of water – rock interaction and also as a consequence of anthropogenic influences.

There is no dearth of literature on chemical attributes of rainwater (Mouli et al. 2005 and numerous sources available on internet). Bicarbonate is the only ionic species of dissolved inorganic carbon present in a significant amount (Freeze and Cherry, 1979), which is derived as a result of dissolution of CO₂ from the atmosphere. Bicarbonate ion may have highly variable concentration levels in rainwater depending upon the season, location and duration of the rainfall and values as high as 50 mg/l have been reported.

Sulphate may also be present in rainwater. The source of this anion is related to industries spewing sulphur in to the atmosphere as particulate S and gaseous SO₂. This leads to increased concentration of H⁺ and SO₄²⁻ in rain water, as shown in following reactions:

\[ S + O \rightarrow SO_2 (g) \]

\[ SO_2 (g) + H_2O + \frac{1}{2} O_2 \rightarrow SO_4^{2-} + 2H^+ \]

In 51 rainwater samples collected across the United States (http://www.people.carleton.edu/~bhaileab/EnvironmentalGeology/RainWater.pdf), SO₄ values from traces to 5.20 mg/l have been recorded.

Other anions reported from rainwater are Cl⁻ and NO₃⁻, with concentration levels of 0.10 to 4.20 and 0.15 to 8.16 mg/l, respectively, in the study carried out in USA(http://www.people.carleton.edu/~bhaileab/EnvironmentalGeology/RainWater.pdf). Concentration of Cl⁻ seems to be directly related to the proximity to marine environment. Nitrate probably is contributed from the atmosphere which contains nitrogen oxides contributed from terrestrial industrial, vehicular and anthropogenic sources.

As far as major cations, Na, K, Ca and Mg, are concerned, a study carried out in Dhanbad, Jharkhand, India, by Singh et al. (2007) suggests that concentration
levels of cations in rainwater is relatively high in dry months before and after the monsoon period. It is lower during the monsoon. Major anions, SO₄, Cl, F and NO₃, also show similar trends but not as well defined as that for cations.

It has been convincingly suggested that terrestrial sources are equally important as marine and anthropogenic sources of cations and anions recorded in rainwater. The study carried out in USA suggests that factors, such as closeness to the coast, contribution of soil dust to atmosphere, industrial emission and burning of wastes are responsible for the observed chemistry of rainwater. The source for Na and Cl is unequivocally the salts derived from marine environment. It has been argued that even inland areas, far from the coast, have availability of marine salts depending on type and direction of prevalent winds, which may be incorporated as chemical constituents of rainwater (Mouli et al. 2005).

Calcium and Mg concentrations in rainwater are in all likelihood, at least partially, related to soil moisture evaporation. This may also yield some CO₂ to the atmosphere, which eventually transforms to HCO₃ in precipitation. Soil dust may contribute not only all the major cations, but also anions, to the atmosphere, which may eventually be carried downward as chemical species of rainwater.

7.3 CHANGES IN THE CHEMISTRY OF SHALLOW GROUNDWATER

Precipitation and infiltration processes play an important role in determining the chemical characteristics of the groundwater in an unconfined aquifer. The soil zone that supports plant life is one of the most important components in the study of groundwater chemistry. It is in the soil zone that recharge water first enters and comes in contact with inorganic and organic solids and gases and it is here that most significant chemical changes occur. Naturally occurring dissolved organic compounds are typically present in minor or trace quantities in the soil zone. By far the most abundant organic compounds in shallow groundwater are humic and fulvic acids. Important groundwater gases, in addition to carbon dioxide, include oxygen, hydrogen sulfide and methane. Organic carbon in the soil also affects the inorganic chemistry of groundwater because the oxidation of organic matter produces CO₂ gas which reacts with water to produce carbonic acid. The presence of carbonic acid imparts acidic character to water and makes it a more aggressive agent of weathering.
and dissolution. The increase in the level of anionic carbon species enhances ion complexing (Deutch, 1997).

\[ O_2 + \text{Organic Matter} \rightarrow CO_2 \]
\[ H_2O + CO_2 = H_2CO_3 \]
\[ H_2CO_3 = H^+ + HCO_3^- \]

While presence of carbonic acid makes groundwater attack silicate and carbonate minerals, thus acquiring major cations, such as, Ca, Mg, Na and K, dissociation of carbonic acid results in the formation of bicarbonate ion. Release of these cations and silica from silicate matrix involves very slow process of water-rock interaction. Groundwater, on the other hand, in the presence of CO₂ dissolves carbonates of Ca and Mg (Karanth, 1987):

\[ CaCO_3 + H_2O + CO_2 = Ca\ (HCO_3)_2 \]
\[ MgCO_3 + H_2O + CO_2 = Mg\ (HCO_3)_2 \]

Carbonates may also be attacked by acidic groundwater with sulphuric acid, which may be generated as a result of oxidation of sulphides or due to mixing of industrial effluents. This causes redistribution of carbonate/bicarbonate species in the groundwater:

\[ CaCO_3 + H_2SO_4 = CaSO_4 + H_2CO_3 \]
\[ H_2CO_3 = H^+ + HCO_3^- \]
\[ HCO_3^- = H^+ + CO_3^- \]

Agricultural contaminants also cause substantial changes in shallow groundwater geochemistry and liquid - solid interaction controlling environment. These aspects have received some what less attention. The quality of alluvial groundwater in rural areas is sensitive to the contaminants originated from the agricultural chemicals, such as, fertilizers, pesticides (Kelly, 1997; Stigter et al. 1998; Kraft et al. 1999). Chemical fertilizers tend to contribute NO₃, SO₄, P, Ca, Na, K and Cl to groundwater either as a result of direct dissolution or through agricultural return water. While NO₃ comes from sources, such as, ammonia or nitrate fertilizer, SO₄ and Ca are added as a result of the use of gypsum powder to counter the menace of alkalinity. Potassium and P are necessary ingredients of NPK fertilizer, commonly used in Ganga Plain. Sodium and Cl often find their way to groundwater channels as impurities in fertilizers, particularly nitrogen-rich fertilizers.
Other sources causing discernible changes in the chemistry of shallow groundwater resources are related to disposal of municipal wastes, including sewage, and discharges from industries. These anthropogenic and industrial sources contribute anions, such as, SO$_4$, Cl, NO$_3$ and some hazardous trace metals. Leather, textile and chemicals and fertilizers industries, in particular, play a detrimental role in deteriorating the chemical quality of groundwater.

7.4 PHYSICO-CHEMICAL ATTRIBUTES OF GROUNDWATER

The properties of groundwater of the area under study, in terms of fundamental parameters, such as, pH, hardness, total dissolved solids and EC are given below.

7.4.1 Electrical Conductivity

The electrical conductivity with 400 µmhos/cm at 25° C is considered suitable for human consumption (WHO, 1984), while more than 1500 µmhos/cm at 25° C may cause corrosion of iron structures.

Electrical conductivity of groundwater in the alluvium aquifer increases depending on the depth and groundwater flow direction (Celik et al. 2006). On the basis of electrical conductance, groundwater is classified (Table-7.1) as given by Sarma and Narayanaswamy (1981):

<table>
<thead>
<tr>
<th>Class</th>
<th>EC (µS/cm at 25° C)</th>
<th>Post-monsoon 2005</th>
<th>Pre-monsoon 2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Conductivity</td>
<td>&lt; 500</td>
<td>60% (33 Samples)</td>
<td>40% (22 Samples)</td>
</tr>
<tr>
<td>Medium Conductivity</td>
<td>500 - 1000</td>
<td>33% (18 Samples)</td>
<td>49% (27 Samples)</td>
</tr>
<tr>
<td>Class I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium Conductivity</td>
<td>1000 - 3000</td>
<td>7% (4 Samples)</td>
<td>11% (6 Samples)</td>
</tr>
<tr>
<td>Class II</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High Conductivity Class III</td>
<td>&gt; 3000</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

In the study area, Electrical Conductivity values ranges between 200-1400µS/cm during November 2005. The EC values during June 2006 ranges between 300-1500 µS/cm. The correlation between instrumentally determined EC values and...
calculated TDS values (correlation coefficient ‘r’ being 0.612) is not very good, as it should be, and this may possibly be due to some instrumental error in EC values.

7.4.2 Hydrogen Ion Concentration (pH)

Values of pH were measured at well sites, which range between 6.8 to 8.6 and 6.2 to 8.4 during post-monsoon 2005 and pre-monsoon 2006, respectively (Table-2.1a and 2.1b). The groundwater thus is mildly acidic to slightly alkaline in nature. From the point of view of human consumption, all the samples may be considered fit, as they are neither acidic nor strongly alkaline.

7.4.3 Hardness

In the area of study the hardness value varies from 115 to 743 mg/l. The average value is 309 mg/l. It was found that 28 samples are higher than desirable limit for drinking purposes of >300 mg/l during November 2005 field survey (Table-7.2). The groundwater, therefore, comes under the category of moderately hard to very hard. During June 2006 field session, hardness ranges between 8-630 mg/l with an average value of 163 mg/l. Sample no.1, 8, 10, 23, 26, 29, 31 and 32 shows the value above the desirable limit mentioned above. Thus for this time period groundwater falls under soft to very hard category. However, except samples 1 and 4 collected in November, 2005 and sample 29 of June 2006, all the samples analysed are indicated to be with in the permissible limit of drinking water standard (BIS, 1991).

<table>
<thead>
<tr>
<th>Hardness of CaCO₃ (mg/l)</th>
<th>Water Class</th>
<th>Post-monsoon 2005</th>
<th>Pre-monsoon 2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 75</td>
<td>Soft</td>
<td>0</td>
<td>5% (21 Samples)</td>
</tr>
<tr>
<td>75 – 150</td>
<td>Moderately hard</td>
<td>5% (3 Samples)</td>
<td>45% (5 Samples)</td>
</tr>
<tr>
<td>150-300</td>
<td>Hard</td>
<td>44% (24 Samples)</td>
<td>44% (21 Samples)</td>
</tr>
<tr>
<td>&gt; 300</td>
<td>Very hard</td>
<td>51% (28 Samples)</td>
<td>6% (8 Samples)</td>
</tr>
</tbody>
</table>

7.4.4 Total Dissolved Solids (TDS)

Total dissolved solids (TDS) have been calculated by summing up all the major cations and anions (Table-2.1a and 2.1b) and this is probably the reason that the correlation between TDS and instrumentally determined EC is not excellent as it
usually should be. Lack of correlation between the two may possibly be due to unsystematic instrumental error in determining EC. TDS values for November, 2005 samples range from 667 to 1824 mg/l. Thirty four out of 55 samples have values of >1000 mg/l, the average value for the samples being 1133 mg/l. The TDS values during June 2006 range between 566 to 1952 mg/l with an average value of 1057 mg/l. During this season 25 groundwater samples have TDS value of >1000 mg/l (Table-7.3).

Table-7.3: Classification of water based on TDS

<table>
<thead>
<tr>
<th>Category</th>
<th>TDS (mg/l)</th>
<th>Post- monsoon 2005</th>
<th>Pre- monsoon 2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh water</td>
<td>0- 1,000</td>
<td>38% (21 Samples)</td>
<td>55% (30 Samples)</td>
</tr>
<tr>
<td>Brackish water</td>
<td>1,000- 10,000</td>
<td>62% (34 Samples)</td>
<td>45% (25 Samples)</td>
</tr>
<tr>
<td>Saline water</td>
<td>10,000- 100,000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Brine water</td>
<td>&gt; 100,000</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

TDS values of <500 mg/l are generally considered to be good. Drinking water becomes significantly unpalatable at TDS value >1000 mg/l. From this point of view, therefore, groundwater in the study area is not really ideal.

Distribution of TDS values for post-monsoon period for the year 2005 is shown in Figure-7.1a. Similar plot for the pre-monsoon period of 2006 is given in Figure-7.1b. Two very distinct zones of TDS values of 1200 to > 1600 mg/l are observed in the area in the pre-monsoon 2006 plot (Figure-7.1b). The more prominent of the two zones is located in the northern part, where a relatively large area of TDS content of > 1400 mg/l encompasses three pockets characterized by TDS values of > 1600 mg/l. The western high TDS pocket extends northwestward from Baraut towards the left bank of river Yamuna. The other high TDS zone is located in the southeastern part of the area on the right or western bank of river Hindon east of village Rataul.

In the post-monsoon 2005 period (Figure-7.1a), the distribution of TDS values is markedly different compared to that in the succeeding pre-monsoon period. In general, higher TDS values are relatively scattered in November, 2005. Evidently TDS values tend to concentrate in the northern half of the study area in the intervening period between the successive monsoons.
7.5 CLASSIFICATION OF GROUNDWATER

The major ion composition of groundwater was used to classify groundwater into various types based on the dominant cations and anions (Deutsch, 1997). The groundwater of the study has been classified on the basis of Piper’s Trilinear and L-L diagrams.

7.5.1 Piper’s Trilinear Diagram

Hydrogeochemical facies are distinct zones that have cation and anion concentrations describable within defined composition categories. The definition of a composition category is commonly based on subdivisions of the trilinear diagram in...
the manner suggested by Back (1961) and Back and Hanshaw (1965). Plotting of post-monsoon samples on Piper’s Trilinear Diagram (Figure-7.2a) reveals:

- Based on relative abundance of anions, 76% samples are bicarbonate type, 20% are without any dominant anionic signature and the remaining 4% are sulphate type.
- On the basis of cationic species 69% of the samples are rich in alkalis, 27% lack any dominant cationic signature and 4% have relative abundance of Ca and Mg.
In pre-monsoon samples (Figure-7.2b), the observed trend on Piper’s Diagram in terms of relative abundance of cationic and anionic species is as follows:

- Bicarbonate is the most abundant anion in 66% of the samples, followed by 29% with no dominant anionic species and 5% with relative abundance of sulphate.
- Alkalis dominate over other cations in 85% of the samples and 15% of the remaining samples do not have any dominant cationic signature.
The majority of the samples, therefore, are "alkali bicarbonate type" with Na having an overwhelming abundance over K. The remaining samples are of "mixed type" with composition varying from mixed alkali bicarbonate type to alkali-Cl-SO₄ type.
7.5.2 L-L Diagram

The chemical classification of groundwater has been attempted on L-L diagram, given by Langelier and Ludwig (1942). Both, post-monsoon – 2005 (Figure-7.3a) and pre-monsoon – 2006 (Figure-7.3b) samples have been plotted to discern any conspicuous changes in the overall chemical behavior of groundwater during the two major seasons of the year which are marked by distinct variations in parameters, such as, recharge of the system, land use, interaction with surface water bodies and water use, particularly in terms of the quantity withdrawn. The presence of different chemical species has given unique chemical signature to the groundwater. The post-monsoon – 2005 plot (Figure-7.3a) helps in identifying three different chemical types of groundwater. Meteoric signatures in the form of relative abundances of Ca, Mg and HCO₃ have been completely obliterated and none of the samples plot in the Ca – Mg – HCO₃ field of unaltered meteoric water.

Group I samples occupy the central part of the plot and thus exhibit “mixed chemical characteristics” as all the major cations and anions have their noticeable presence. Bulk of the samples belongs to this Group. Barring 5 samples which are peripheral, the remaining samples form a conspicuous cluster occupying the centre of the plot, which encompasses 30 out of 55 samples (54%). Group I samples may conveniently be put under the category of “Mixed Type”.

Group II samples seem to have the same affinity as those of Group I in as far as the relative abundances of cations is concerned. The only discernible difference between the two Groups is that the latter shows relative enrichment of HCO₃ at the expense of the other major anions Cl and SO₄. These samples, based on their chemical characteristics, may be classified as “Mixed Bicarbonate Type”. Group II samples may be considered nearest representative of meteoric water. Group III, on the other hand, is identified as a distinct chemical type by virtue of the relative abundance of alkalis with HCO₃ having preponderance over other anions Cl and SO₄. This Group may, therefore, be designated as “Alkali Bicarbonate Type”.

At the first glance the pre-monsoon scenario – 2006, depicted in Figure-7.3b, does not appear to be significantly different from that of the immediately preceding post-monsoon season (Figure-7.3a), as the samples plot in the same zone. A closer look, however, reveals that if 4 samples (samples 4, 8, 31 and 35) are excluded, two clusters
are observed. The upper cluster corresponds to the Group I, identified above, while the lower one is more akin to Group III or Alkali Bicarbonate Type.

Figure-7.3a: Langelier and Ludwig (L-L) diagram of November, 2005 samples

Figure-7.3b: Langelier and Ludwig (L-L) diagram of June 2006 samples
7.6 SUITABILITY OF GROUNDWATER FOR HUMAN CONSUMPTION

The quality of water has become one of the important environmental issues of the twenty first century and therefore an understanding of chemical quality of groundwater is essential for determining its usefulness for various purposes, such as, domestic consumption, industrial uses and agricultural purposes. The water which is not suitable for drinking may be good for irrigation and the water unsuitable for irrigation may be quite suitable for industrial purposes (Goel, 1997). Each use of water has its own limits on the degree of pollution it can accept. Every use of water requires a certain minimum quality of water with regard to the presence of dissolved and suspended materials of both chemical and biological nature. The minimum quality of water should ensure no harm to the user.

The World Health Organization (1984), Indian Standard drinking water specification (BIS, 1991) and Indian Council of Medical Research (ICMR) have laid down drinking water standards, which assure, in general, the protection of human health. Accordingly, the concentration of various major and trace elements in the groundwater samples of the study area are compared with the drinking water standards of WHO (1994) and Indian Standard Drinking Water Specification (BIS, 1991) as summarised in Table-7.4.

7.6.1 Drinking Water Quality from the Point of View of Major Ions

Total dissolve solids (TDS) of samples from the study area are above the desirable limit of 500 mg/l in both seasons. All the samples, however, have TDS content lower than the maximum permissible limit of 2000 mg/l.

While in 2 samples of November 2005 the \(\text{SO}_4^2-\) content is more than its maximum permissible limit in drinking water (BIS, 1991), its concentration levels in June 2006 are within the permissible limit. As a matter of fact, \(\text{SO}_4^2-\) concentration of > 200 mg/l is not considered good and continuous intake of such water may not be good for human health. As many as 13 post-monsoon and 9 pre-monsoon samples have values exceeding 250 mg/l. The high intake of \(\text{SO}_4^2-\) may result in gastrointestinal irritation and respiratory problems to the human system (Maiti, 1982; Subba Rao, 1993; Subramani et al. 2005).

The concentration of \(\text{Cl}^-\) in post-monsoon samples collected in 2005 is below the maximum desirable limit. In pre-monsoon season, though, the concentration of \(\text{Cl}^-\)
in 4 samples is above the highest desirable limit, but way below the maximum permissible limit (BIS, 1991) in drinking water. The fact that about 30% of the samples studied have Cl values of > 100 mg/l is significant from the point of view of the water being potable. This is because in association with high Na values (about 50% samples have Na concentration exceeding 200 mg/l) Cl may impart bad taste to water (http://www.env.gov.bc.ca/wsd/plan_protect_sustain/groundwater/library/groundfactsheets/pdfs/cl (020715)_fin2.pdf).

Only one set of samples collected in June 2007 were analyzed for NO3. The highest recorded value of 78 mg/l is lower than the maximum permissible limit of 100 mg/l for this ion (Table-7.4).

It is worthwhile to discuss Na too though this is one of the ions for which desired or permissible limits are not given by BIS or WHO. Data available from net (www.wikipedia.com) based on available literature from Water Stewardship Information Series, U. S. A. Environmental Protection Agency and Minnesota Pollution Control Agency for the period from 1999 to 2008 clearly indicate that high Na values in drinking water are not advisable due to the known role of this element in hypertension, heart diseases and kidney-related problems. Environment Protection Agency of USA, as a matter of fact, recommends a value of 20 mg/l of Na in the ideal drinking water based on the routine requirement of Na by human body and availability of Na through other solid intakes. The Canadian drinking water quality objective for Na is an Aesthetic Objective (AO) of 200 mg/l. The water with a Na value of more than this is not categorized as drinking water meant for continuous consumption. If this standard is taken in to consideration, the situation in the study area is far from being normal. The highest Na values for the post- and pre-monsoon seasons are recorded at 382 and 398 mg/l, respectively and about 45% of the samples have Na concentration of > 200 mg/l.

Sodium is accompanied by rather anomalous and unusual concentration of the other alkali ion K in the study area. Values as high as > 100 to 264 mg/l are recorded, and 10 to 12 samples have value of > 30 mg/l. For an element which is known to have concentration levels of < 1 to 5 mg/l in groundwater, in general, values of even 10 mg/l are high. Although no information are available on maximum permissible limit of K in drinking water, yet the area under study may safely be categorized as the one with abnormal distribution of K values.
Role of potassium in cellular and electrical functions of human body are well known (http://hkpp.org/general/potassium_health.html). Its excess in drinking water, however, is not a cause of major worry as human renal system is well equipped to get rid of surplus K from the body.

Calcium and Mg are ions in groundwater which, in general, are not discussed in context of human health. It is, however, imperative to discuss the distribution of these two ions in the area as there are clear indications of calcium deficiency and anomalous Ca/Mg ratio. Calcium values measured in the two sets of samples (November, 2005 and June, 2006) give average values of 43 mg/l and 19 mg/l, respectively. All the 55 samples collected in 2006 have Ca values less than the prescribed lower limit where as 49 out of 55 samples collected in 2005 have recorded such values. The study area, therefore, is a clear case of calcium deficiency. This is one of the significant outcomes of this study that calls for research in greater detail to understand the manifestation of this chemical attribute of groundwater in field. It is a common knowledge that calcium is an essential element for the growth, upkeep and maintenance of the human skeletal structure and its deficiency may be causing a menace for the human health. Several epidemiological studies (Riggs et al. 1967) suggest that Ca-deficiency in groundwater, particularly when not compensated by oral intake, may be conducive for diseases like osteoporosis and even rickets. The symptoms for the latter are however more pronounced when Ca-deficiency is coupled with deficiency of vitamin D.

The average Mg concentration in the two sets of samples remains more or less consistent at 49 mg/l and 48 mg/l, respectively. The maximum permissible limit of 100 mg/l (Table-7.4) is exceeded by only three samples each collected during the two seasons. These Mg values of > 100 mg/l in only 5% of the samples do not pose any threat to human health and may only contribute to an increase in hardness and get manifested in the form of some deposits in pipes and pots. Sixteen samples collected in November, 2005 and 14 collected in June, 2006 (about 30% of the samples collected), however, have Mg concentrations lower than the lowest recommended value of 30 mg/l (Table-7.4). Several epidemiological studies have suggested that Mg-deficiency may result in coronary diseases and increases the risk of acute myocardial infarction (AMC). Moreover, Mg when consumed as chloride may cause

7.6.2 Trace Metals Concentration and Drinking Water Quality

Trace metals concentration in groundwater in the study area have been dealt with in Chapter 8. However, it was considered relevant to discuss rather anomalous and apparently hazardous concentration of some of the metals here in this section dealing with the quality of groundwater for drinking purposes.

Table-7.4 summarizes the prescribed limits of various trace metals and their observed concentration ranges in the study area.

The concentration of Mn, Fe and Se are higher in 2, 4 and 6 samples, respectively. Manganese and Fe concentrations are generally not considered toxic and no adverse symptoms are reported on human health when water having higher concentration of these elements is consumed over long periods. Moreover, values of Fe and Mn reported in the study area are rather restricted and not alarmingly high (www.wikipedia.com).

Twenty one out of 22 samples have Cr concentration higher than the permissible limit according to BIS (1991) and this is really very significant information that has come through this study. That Cr is carcinogenic, particularly when present in hexavalent state, is now very well understood by those dealing with medical geology (Sawyer and Mc Carty, 1978). Chromate salts are associated with cancer of the lungs i.e. bronchogenic carcinoma, and also exhibits corrosive action to the skin and mucous membrane (Umar and Ahmad, 2000).

The concentrations of Al in all the 22 samples are above the maximum permissible limit of 0.2 mg/l (Table-7.4). As a matter of fact, 21 out of 22 samples analyzed have Al concentrations ten times or even higher than the maximum permissible limit. Fortunately, Al is not considered toxic, in general, if consumed in higher quantities but there is no research to substantiate this argument. There had been suggestions that consumption of Aluminum in appreciably high quantities may be a factor conducive for Alzheimer Disease (AD), but again there is no strong scientific evidence in favor of this argument (www.wikipedia.com). There is probably a strong
Table-7.4: Range of concentration of various major and trace elements in shallow groundwater samples and their comparison with W.H.O. (1994) and B.I.S. (1991) Drinking Water Standards

<table>
<thead>
<tr>
<th>Constituents</th>
<th>BIS (1991) (mg/l)</th>
<th>W.H.O. (1994) (mg/l)</th>
<th>Values in Study Area (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Highest desired level</td>
<td>Maximum permissible level</td>
<td>Highest desired level</td>
</tr>
<tr>
<td>pH</td>
<td>6.5-8.5</td>
<td>6.5-9.5</td>
<td>7.8-5</td>
</tr>
<tr>
<td>Total Hardness</td>
<td>300</td>
<td>600</td>
<td>100</td>
</tr>
<tr>
<td>TDS</td>
<td>500</td>
<td>2000</td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>75</td>
<td>200</td>
<td>75</td>
</tr>
<tr>
<td>Magnesium</td>
<td>30</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>250</td>
<td>1000</td>
<td>200</td>
</tr>
<tr>
<td>Sulphate</td>
<td>200</td>
<td>400</td>
<td>200</td>
</tr>
<tr>
<td>Fluoride</td>
<td>0.6-1.2</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Nitrate</td>
<td>45</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>0.05</td>
<td>1.5</td>
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</tr>
<tr>
<td>Iron</td>
<td>0.3</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>Lead</td>
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<td>--</td>
<td>0.1</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.1</td>
<td>0.5</td>
<td>0.05</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>0.1</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Cobalt</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>0.05</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>0.1</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.01</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.03</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>
need to take up this study too on the source and geochemical behavior of this omnipresent metal.

Lead values are higher than the permissible limits in 7 samples. These high values are associated with high Fe values but the significance of this association is not understood. It may be speculated that it may relate to the influence of piping used in wells. Most common symptoms of lead poisoning are anemia, severe intestinal pain, paralysis of nerves, loss of appetite and fatigue (Train, 1979). Lead toxicity also causes irreversible mental damage in children.

Selenium also needs to be mentioned here. Six samples show concentration higher than the desirable limit, though much less than the maximum permissible limit and therefore it is not alarming at all. It is such an element which causes adverse effects when it is deficient in intake and there is every possibility that some of the samples with values of 0.005 to 0.008 may actually represent its deficiency. Higher concentration of Se may result in decay of hair, nails and teeth and neurological and skin disorders (www.wikipedia.com; Morris et al. 1983).

The area is intensively cultivated with the wide use of chemical fertilizers and pesticide. Moreover, house hold wastes, sewage and industrial effluents are the other sources of pollution of surface and subsurface water bodies.

7.7 QUALITY OF WATER FOR IRRIGATION PURPOSES

The suitability of groundwater for irrigation is contingent on the effects of the mineral constituents of water on both the plant and soil. Salt may harm plant growth physically by limiting the uptake of water through modification of osmotic processes, or chemically by metabolic reactions such as those caused by toxic constituents. Effects of salts on soils in causing changes in soil structure, permeability and aeration directly affect plant growth (Todd, 1980).

The irrigation water containing a high proportion of sodium will increases the exchange of sodium content of the soil, affecting the soil permeability, and texture making the soil hard to plough and unsuitable for seeding emergence (Triwedy and Goel, 1984; Sujatha and Reddy, 2003). If the percentage of Na\(^+\) with respect to Ca\(^{++}\) + Mg\(^{++}\) + Na\(^+\) is considerably above 50% in irrigation waters, soils containing exchangeable calcium and magnesium take up sodium in exchange for calcium and magnesium causing deflocculation and impairment of the quality and permeability of
soils (Karanth, 1987). Soil amendments, such as, gypsum or lime may correct the situation.

The total dissolved content, measured in terms of specific electrical conductance gives the salinity hazard of irrigation water. The electrical conductivity is a measure of salinity hazard to crop as it reflects the TDS in the groundwater. Parameters such as Sodium Absorption Ratio (SAR) and Residual Sodium Carbonate (RSC) were estimated to assess the suitability of groundwater for irrigation. The salt present in the water, besides affecting the growth of plants directly, also affects soil structure permeability and aeration, which indirectly affect plant growth (Mohan et al. 2000; Umar et al. 2001).

**7.7.1 Sodium Adsorption Ratio (SAR) Criterion**

The interpretation of water quality suitable for the irrigation purposes are given by Richard (1954) in the form of EC versus SAR values. Electrical Conductivity (E.C.) has been treated as index of salinity hazards and sodium adsorption (SAR) as index of sodium hazards. SAR is calculated from the ionic concentration (in meq) of sodium, calcium and magnesium according to following relationship (Karanth, 1987).

\[
\text{SAR} = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}}
\]

The SAR values of the groundwater samples of the area are given in Table-2.2a and 2.2b. The data has been plotted in (Figure-7.4a and 7.4b) to observe the suitability of water for irrigation purposes. The SAR value ranges from 0.80 to 11.08 with an average value of 4.93 in the samples collected during November 2005 (Table-2.2a). The analytical data of post-monsoon 2005 plotted (Figure-7.4a ) on the US salinity diagram (Richards 1954) show that 73% samples fall in C2S1, 11% in C3S1, 7% fall C2S2, 5% fall in C3S2 and 4% in C1S1 respectively. Four samples fall in C2S2 and 3 in C3S2, respectively, and except these 7 samples, the remaining samples fall in good to excellent class from the point of view of irrigation.

During pre-monsoon 2006 field session, the SAR values range from 1.68 to 16.39 (Table-2.2b), average value being 6.24. Therefore the possibility of sodium hazard may be high in the area. The analytical data show that 62% of the groundwater
samples fall in the field of C2S1 (Figure-7.4b). These medium salinity and low sodium water can be used for irrigation on almost all the types of soils if a moderate amount of leaching occurs. Eighteen percent of the samples fall in C3S1 category. These high salinity and low sodium water can not be used on soils with restricted drainage. Even with adequate drainage, special management for salinity control may be required. Water of C2S2 category accounts for 5% of the water samples. These are characterized by medium salinity and medium sodium content and may be used on coarse-textured or organic soil with good permeability. About 15% of water samples plot in C3S2 field. These are high salinity and medium sodium waters requiring good drainage (Karanth, 1987). The quality classification of groundwater is given below in Table-7.5 (USSL, 1954).

![Figure-7.4a: SAR Vs E.C. (November, 2005)](image-url)
Table-7.5: Quality Classification of Irrigation Water (after USSL 1954)

<table>
<thead>
<tr>
<th>Water</th>
<th>Salinity Hazard E.C (Micromhos/cm at 25°C)</th>
<th>SAR Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent</td>
<td>&lt;250</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Good</td>
<td>250-750</td>
<td>10-18</td>
</tr>
<tr>
<td>Fair</td>
<td>750-2250</td>
<td>18-26</td>
</tr>
<tr>
<td>Poor</td>
<td>&gt;2250</td>
<td>&gt;26</td>
</tr>
</tbody>
</table>

7.7.2 Residual Sodium Carbonate (RSC) Parameter

Eaton (1957) suggested that the excess sum of carbonate and bicarbonate in groundwater over the sum of calcium and magnesium also influences the suitability of groundwater for irrigation. This is denoted as residual sodium carbonate (RSC), which is calculated as follows (Raghunath, 1987):
\[ \text{RSC} = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \]

where the concentrations are reported in meq/l.

Water with RSC below 1.25 is good; 1.25 - 2.5 is marginal or tolerable and above 2.5 is not suitable for irrigation purposes. The classification of irrigation water according to the RSC value is presented in Table-7.6. If RSC > 2.5, irrigation water may cause formation of salt peter (KNO₃).

The value of residual sodium carbonate have been calculated (Table-2.2a and 2.2b) and compared with above classification. It is inferred that 29% and 24% samples in post-monsoon 2005 and pre-monsoon 2006, respectively, are good quality. The remaining samples fall in doubtful to unsuitable quality in both the seasons.

### Table-7.6: Quality of Groundwater Based on Residual Sodium Carbonate (RSC)

<table>
<thead>
<tr>
<th>RSC (meq/l)</th>
<th>Quality</th>
<th>Post-Monsoon 2005</th>
<th>Pre-Monsoon 2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1.25</td>
<td>Good</td>
<td>16</td>
<td>13</td>
</tr>
<tr>
<td>1.25-2.5</td>
<td>Doubtful</td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td>&gt;2.5</td>
<td>Unsuitable</td>
<td>32</td>
<td>31</td>
</tr>
</tbody>
</table>

#### 7.8 CHEMICAL QUALITY OF RIVER DISCHARGES

Seven samples collected from river discharges were analyzed to assess their quality and relationship with the groundwater regime, particularly in terms of any indications for interaction between surface water bodies and groundwater reservoirs (Table-2.3). These samples, collected from rivers Yamuna, Hindon and Krishni, show 'mixed' characters and plot outside the field of 'meteoric' or Ca – Mg – HCO₃ type water (Figure-7.5). While samples from river Yamuna plot as a cluster, the upstream sample from river Hindon is conspicuously different from the other two samples.

Samples from Yamuna are relatively dilute with TDS of < 500 mg/l. This aspect is significant from the point of view that all the 110 groundwater samples collected during November, 2005 and June, 2006 have TDS value of > 500 mg/l, the average value being > 1000 mg/l (Table-7.3). This implies that in its influent part of the course, river Yamuna would tend to dilute the groundwater and when its behavior
would be effluent, it would be reflected in higher TDS content in its discharge. The Yamuna samples are relatively uniform in chemical composition in having SO$_4$ and HCO$_3$ as the dominant anions, the former being marginally more abundant. As far as cations are concerned, these samples have Na > Ca > Mg. There is a possibility that water of chemical quality similar to that of river discharge (from the point of view of concentration of major cations and anions), discharging from some of the wells is being used for drinking purpose.

![Figure-7.5: Langelier and Ludwig (L-L) diagram for June 2007 river samples](image)

Samples collected from river Hindon are chemically different. The upstream sample collected from Barnawa has a TDS value of 1035 mg/l, which is dominated by the HCO$_3$ content of > 500 mg/l. Sulphate also shows rich value of 190 mg/l. Among the cations, Na is overwhelmingly abundant compared to Ca, Mg and K. The two downstream samples of Baleni and Gauna, on the other hand, have TDS values of < 500 mg/l, similar to that in Yamuna samples, but have comparatively lower concentration of alkalis and HCO$_3$ (Figure-7.5), and have SO$_4$ as the dominant ion. An exceptionally and rather anomalously high SO$_4$ content of 263 mg/l is recorded at Gauna.
The sample collected from river Krishni serves as an example of the extent to which the quality of river discharge could get deteriorated as a result of anthropogenic influences. A TDS value of 2600 mg/l is the net result of anomalously high values of all the ions. This is particularly so for HCO₃, SO₄, Na and K.

7.9 DISCUSSION

One of the evident characteristics of the groundwater of the study area is their relatively high TDS content which is always > 500 mg/l. In the 2005 collection season as many as 62% samples record TDS values of > 1000 mg/l, whereas in the pre-monsoon season of 2006 about 45% samples fall under this category. Taking into consideration TDS values of > 1200 mg/l, 23 and 10 samples collected in the successive years have recorded such values. Higher values, in general tend to concentrate in the northern half of the area in pre-monsoon period of 2006 (Figures-7.1a and 7.1b). Based on these rather anomalously high TDS values it may be inferred that the role of water – rock interaction as a mechanism for the acquisition of solutes by groundwater is not substantial and processes, such as, anthropogenic activities, dissolution of some naturally occurring materials or mixing with deep-seated brines may have a more dominant role to play.

Another significant feature is that TDS values, in general, show a decrease in the pre-monsoon season of 2006 (55% samples with TDS of <1000 mg/l) compared to values observed in the post-monsoon season of 2005 (38% samples with TDS of < 1000 mg/l). In other words, TDS decrease in a period of about 6 months. It needs to be noted that during this period of November, 2005 to June, 2006 there were hardly any rains which could have accounted for some dilution of groundwater. There were only sparse short duration post-monsoonal showers in the months of January and February, accounting for not even 5% of the annual rainfall of 566 mm (average of recorded values at Baraut and Baghpat stations) for the year 2006.

An evaluation of data indicate that with this tendency of decrease in TDS from an average value of 1133 mg/l in 2005 to 1057 mg/l in 2006, there had been a redistribution of chemical species resulting in spatial changes in TDS concomitantly. For example, in November, 2005 high TDS values of >1400 mg/l were observed at locations 1, 5, 6, 13, 14, 21, 22 and 40. In 2006, such values are recorded at locations 10, 11, 12, 13, 21, 22, 41, 45, 48, 49 and 51. What emerges is that high TDS values
encompassing locations 1, 5, 6, 13 and 14 in 2005 have apparently shifted northwards defining an even more conspicuous ‘high’ (Figures-7.1a and 7.1b).

It is difficult to offer a straightforward explanation for this marked change in TDS having both temporal and spatial attributes. An approximation may be arrived at for a mixing model using a mass balance equation to be solved for ‘x’ that stands for the fraction of the post-monsoon 2005 groundwater involved in the mixing.

\[
[(\text{Cl in 2005 samples}) \times x] + [(\text{Cl in mixing water}) \times (1-x)] = \text{Cl in 2006 samples}
\]

Taking the average Cl values of 85, 29 and 71 mg/l for groundwater samples of 2005, discharges from rivers Yamuna/Hindon and 2006 groundwater samples, respectively, it may be calculated that mixing of post-monsoon 2005 groundwater and river water in a ratio of 75:25 would result in Cl content as observed in pre-monsoon period 2006.

Taking this model of general dilution of groundwater during the period from November, 2005 to June, 2006 in to consideration would imply an across the board decrease in the concentration levels of all the major ions. This, however, is not the case. While average Na values tend to increase in pre-monsoon period of 2006, Mg does not show any change. Moreover, applicability of this model would also assume that both the rivers are influent during the bulk of their respective courses.

It may be inferred therefore that the changes observed in groundwater chemistry over a period of about 6 months from November, 2005 to June, 2006 are due to a combination of factors, such as, mixing/dilution, precipitation/dissolution, irrigation, cation exchange, climatic influences and various anthropogenic factors. These aspects and relative roles of various processes are dealt with in greater details in a subsequent section.

Chemistry of river discharges provides some interesting information. Except for a sample from river Krishni and the upstream sample from river Hindon, the remaining 5 samples (3 from Yamuna and 2 from Hindon) have TDS values of < 500 mg/l, less than half of the average TDS values measured in groundwater samples over two sample collection seasons. This implies that the influent drainage would result in diluting the groundwater and effluent behavior of these streams would result in an increase in TDS of river discharge. A scenario akin to the former situation has been discussed above in the context of mass balance approximation. Very high TDS in
Krishni (2661 mg/l) may be related to pollution from industrial and household effluents and wastes, but in the upstream sample of Hindon it may be, at least partially, due to the effluent nature of the stream in the limited stretch. This is particularly so as downstream samples of Hindon are dilute and groundwater (sample 41) in the immediate vicinity of Hindon upstream sampling point has a TDS of 1330 to 1542 mg/l.

7.10 SUMMARY

Groundwater in the study area has ‘Low to Medium (Class I)’ electrical conductivity and bulk of the samples are moderately hard to hard.

In general, TDS values are high, averaging >1000 mg/l for both the sets of samples, post-monsoon value being higher. There is a clear tendency of redistribution of TDS and higher values concentrate in the northern half of the area in pre-monsoon period of 2006. Based on these rather anomalously high TDS values (as high as >1800 mg/l and averaging > 1000 mg/l) it may be safely inferred that the role of water – rock interaction as a mechanism for the acquisition of solutes by groundwater is not substantial and processes, such as, anthropogenic activities, dissolution of some naturally occurring materials or mixing with deep-seated ascending brines may have a more dominant role to play.

A general decrease in average TDS during a period of about 6 months from November, 2005 to June, 2006, when there were hardly any rains, could imply dilution of groundwater due to interaction with surface water bodies or shallow groundwater.

A mass balance equation suggests such dilution to the extent of 25%. A combination of factors, such as, precipitation/dissolution, irrigation, cation exchange, and influences of climatic and various anthropogenic factors, rather than dilution alone, explain the observed chemical changes in a more lucid way.

Based on conventional Piper’s Trilinear Plot, the samples show an overwhelming abundance of alkalis over Ca and Mg. Presence of all the anions is indicated but HCO₃ tends to dominate over SO₄ and Cl.

On L-L Diagram, broadly speaking, three chemical types of groundwater are identified. These are ‘mixed’, ‘mixed bicarbonate’ and ‘alkali bicarbonate’ types. Chemical signatures of meteoric origin of groundwater are completely obliterated as a
result of the acquisition of solutes in varying but substantial concentrations through various natural and anthropogenic processes. The latter two types more or less merge in to one group in pre-monsoon period of 2006.

As far as quality of water for drinking purposes is concerned, it is not ideal from the points of view of concentration of both major ions and trace metals. TDS are on higher side. Sulphate concentration, though within the maximum permissible limit, is on higher side, 13 post-monsoon and 9 pre-monsoon samples having values exceeding 250 mg/l. The high intake of SO$_4^{2-}$ may result in gastrointestinal irritation and respiratory problems to the human system.

High Na values in drinking water are not advisable due to the known role of this element in hypertension, heart diseases and kidney-related problems. For the two sets of samples the average Na values are 186 and 208 mg/l, respectively. The highest Na values for the post- and pre-monsoon seasons are recorded at 382 and 398 mg/l, respectively and about 45% of the samples have Na concentration of > 200 mg/l. Sodium concentration in groundwater, therefore, is clearly at a perilous level from the point of view of human health.

Calcium values measured in the two sets of samples (November, 2005 and June, 2006) give average values of 43 mg/l and 19 mg/l, respectively. All the 55 samples collected in 2006 have Ca values less than the prescribed lower limit whereas 49 out of 55 samples collected in 2005 have recorded such values. The study area, therefore, is a clear case of calcium deficiency which may be conducive for diseases like osteoporosis and even rickets, the latter of course when Ca-deficiency is coupled with the deficiency of vitamin D.

Chromium is carcinogenic when present in hexavalent state and 21 out of 22 samples have Cr concentration higher than the permissible limit according to BIS (1991). This is really very significant information that has come through this study and needs to be explored in greater details.

The concentrations of Al in all the 22 samples are above the maximum permissible limit of 0.2 mg/l (Table-7.4). As a matter of fact, 21 out of 22 samples analyzed have Al concentrations ten times or even higher than the maximum permissible limit. Although in general Al is not considered toxic but there had been suggestions that when consumed in higher proportion Al may be conducive for
Alzheimer Disease (AD). Distribution of Al, its source and the chemical species it occurs in, are also some of the aspects that need to be taken up in future studies.

The SAR value ranges from 0.80 to 11.08 with an average value of 4.93 in the samples collected during November 2005. With the exception of 7 samples (13%), the remaining samples fall in good to excellent class from the point of view of irrigation. During pre-monsoon 2006 period, the SAR values range from 1.68 to 16.39, average value being 6.24. Therefore the possibility of sodium hazard in the area is relatively high. About 20% samples have moderate to high salinity associated with moderate Na values. These samples are not ideal for agricultural activities.

It is inferred based on RSC that 29% and 24% samples in post-monsoon 2005 and pre-monsoon 2006, respectively, are of good quality and suitable for irrigation. The remaining samples fall in doubtful to unsuitable quality in both the seasons. SAR and RSC estimates suggest that the area, in general, has tendency for depositing alkalis as NaHCO₃, Na₂CO₃, Na₂SO₄ and KNO₃.

Seven samples collected from river discharges were analyzed to assess their quality and relationship with the groundwater regime, particularly in terms of any indications for interaction between surface water bodies and groundwater reservoirs. River Krishni and the upstream sample from river Hindon show conspicuous effect of pollution. The remaining 5 samples from are with TDS of < 500 mg/l. This implies that in influent part of their courses rivers would tend to dilute the groundwater and their effluent behavior would be reflected in higher TDS content in their discharge.