CHAPTER 10

HYDROGEOCHEMICAL CHARACTERISTICS AND CHEMICAL ALTERATION TRENDS
HYDROGEOCHEMICAL CHARACTERISTICS AND CHEMICAL ALTERATION TRENDS

10.1 GENERAL

Each groundwater system has its own characteristic chemical signatures produced as a result of chemical alteration of the meteoric water recharging the system (Back 1966; Drever 1982). The chemical composition of the meteoric water varies within wide limits (Faure, 1998). However, in most of the inland areas of the Indian sub-continent, it is of the Ca-Mg-HCO₃ to Ca-Na-HCO₃ type (Bartarya 1993; Datta and Tyagi 1996; Bhatt and Saklani 1996). The chemical alteration of the meteoric water, on the other hand, depends on several factors, such as interaction with solid phases, residence time of groundwater, mixing of groundwater with pockets of saline water, and anthropogenic impacts (Stallard and Edmond 1983; Dethier 1998; Faure 1998; Subba Rao 2001, Umar and Absar, 2003). The study of a relatively large population of samples from a given area offers clues to various possible trends of chemical alteration which the meteoric water undergoes before acquiring distinct chemical characteristics and attaining a chemical steady state in the aquifer. These identified trends, in turn, may be related to natural and anthropogenic causative factors.

Broadly speaking, the intake of major and minor cations is related to solid-water interaction (Bartarya 1993; Subba Rao 2001). Such a direct relationship between lithology and relative abundances of cations is easily discernible in hard-rock areas (Faure, 1998), for example, in carbonate rock terrain Ca+Mg > Na+K, whereas reverse is the case in areas with arenaceous and crystalline lithologies. In dealing with a groundwater system in alluvium-covered areas, on the other hand, straightforward clues may not be as simple due to the masking of normal chemical alteration trends by anthropogenic influences.

Addition of anions to groundwaters may be through various sources. Dissolution of carbonates and reaction of silicates with carbonic acid account for the addition of HCO₃ to the groundwater, and oxidation of sulphides may be a source of SO₄ (Subba Rao, 2001). Chloride, although present in very low concentrations in a crystalline terrain, may be available for circulating groundwater. The bulk of Cl, however, is derived by groundwater from residues in soils (Karanth, 1987).
The character of groundwater in different aquifers over space and time has proved to be an important technique in solving different geochemical problems (e.g., Chebotarev 1955; Hem 1959; Back et al., 1965; Gibbs 1970; Srinivasamoorthy 2005, Srinivasamoorthy et al., 2008). A number of studies on groundwater quality with respect to drinking and irrigation purposes have been carried out in the different parts of the country (Subba Rao, 2006).

Keeping this in view, the present work deals with hydrogeochemical studies carried out in parts of the Krishni-Hindon interstream region of Western Uttar Pradesh.

10.2 SALIENT FEATURE OF MAJOR ION CHEMISTRY

Some salient features of the major ions chemistry of groundwaters from Krishnii-Hindon interstream falling under the western part of U.P. are being enumerated below. These features are evident through a critical evaluation of the chemical data (Table 2.1a, b, and c).

1. The area has high total dissolved solids (TDS) values, which range from 429 to 1564 mg/l with an average value of 993 mg/l during November 2005.
2. The TDS concentration during June 2006 ranges between 513 and 1712 mg/l, averaging 896 mg/l. All the samples have TDS values higher than the desirable limit (for drinking purpose) of 500 mg/l.
3. Groundwaters are neutral to slightly alkaline in nature, with a pH of 6.8 to 8.5 and 6.9 to 8.5 during November 2005 and June 2006, respectively.
4. Hardness values vary from 136 to 673 mg/l (average value 280 mg/l) and 32 to 457 mg/l (average value 169 mg/l) during November 2005 and June 2006, respectively. Groundwaters, therefore, vary from soft to very hard.
5. Sulphate content varies from 30 to 445 mg/l, averaging 141 mg/l in November 2005 and 44 to 378 mg/l with average value of 172 mg/l during June 2006. Eleven and 22 samples collected during November 2005 and June 2006, respectively, are beyond the highest desirable level of > 200 mg/l in drinking quality water (BIS 1991). The sulphate values of >200 mg/l may be considered anomalous. In general, value of SO₄²⁻ is more in shallow aquifers samples in comparison to deeper aquifer. This may indicates that the shallow aquifer is deteriorated by anthropogenic activities.
6. The Cl\' values are relatively low, averaging 51 in November 2005 and 46 in June 2006. The range of its variation is though very large from 9 to 182 mg/l and 6 to 369 mg/l during November 2005 and June 2006, respectively. Anomalously high chloride value of 369 is reported only in sample no 34 in June 2006. Most of the groundwater samples from deeper aquifer show low values of chloride.

7. Bicarbonate ranges between 156 to 975 mg/l and 245 to 858 mg/l, averaging 536 mg/l and 428 mg/l, during November 2005 and June 2006, respectively. These values show relative consistency.

8. The NO\textsubscript{3}\' analyses were carried out for June 2007 sample only and these concentrations range between zero and 168 mg/l.

9. In two samples the concentration of NO\textsubscript{3}\' is more than the highest desirable limit. A maximum value of 168 mg/l of NO\textsubscript{3}\' is recorded in sample 25D representing Barnawa village. This value exceeds the permissible limit of drinking water standard (BIS 1991).

10. Alkali ions too show large variations in their abundances. Sodium varies from 17 to 322 mg/l in November 2005 and 78 to 378 mg/l in June 2006. Sixteen samples in November 2005 and 24 samples in June 2006 have rather anomalously high Na\textsuperscript{+} values of > 200 mg/l. Potassium is found in low concentration in groundwater since rocks which contain K are relatively resistant to weathering (Golditch, 1938). However, K-salts are widely used in fertilizers and enter groundwater from agricultural land. Potassium values show a range of 0 to 36 and 1 to 90 mg/l during November 2005 and June 2006, respectively. Anomalously high values of > 20 mg/l are reported in five samples in November 2005 and only two samples in June 2006. The highest K value of 90 mg/l is associated with a Na value of 323 mg/l in sample 21 during June 2006.

11. Calcium values range between 20 to 130 mg/l and 3 to 40 mg/l during November 2005 and June 2006, respectively. Ten samples have anomalous Ca values of > 75 mg/l in November 2005. In most of the samples, however, Ca values are relatively consistent. As far as Mg values are concerned, the values range from 4 to 152 mg/l, averaging 34 mg/l in November 2005 and 6 to 103 mg/l during June 2006.
mg/l with average value of 34 mg/l in June 2006. As with Ca values, Mg concentration in most samples also show consistency.

12. Alkalis are the dominant cationic species when compared to Ca$^+$ and Mg$^+$. This statement holds good for both pre monsoon and post monsoon set of samples.

13. The HCO$_3^-$ is the most dominating anionic species in the groundwaters of the study area. Only 20 samples have concentration of SO$_4^{2-}$ together with Cl$^-$ equal to that of HCO$_3^-$. This statement holds good for both pre monsoon and post monsoon samples.

10.3 RELATIVE ABUNDANCE OF MAJOR IONS

In order to evaluate the relative abundances of major cations and anions various X-Y plots have been prepared. As seen in (Fig. 10.1) alkalis are more abundant than Ca+Mg. This feature is also seen on the L-L diagram (Fig 9.5a and 9.5b). However, samples from June 2006 season show concentration on higher side which indicate temporal enrichment of Na+K. A noteworthy point emerging from this plot is that except for sample no 38, all the samples collected in June 2006 plot above equal concentration line. The majority of samples from deeper locations show relatively less concentration of alkalis and Ca+Mg in both the seasons. Samples of November 2005 tend to plot closer to 1:1 line in comparison to samples of June 2006. The majority of samples of both the seasons have overwhelming abundance of alkalis. It is only in November, 2005, i.e. that some, precisely speaking 16, samples have Ca+Mg>Na+K.

Based on relative abundances of the major anions, HCO$_3$ and Cl (Fig. 10.2), groundwater of the area is indicated to be of three types. Four samples of June 2006, i.e. 26, 35, 36 and 36D, plot on HCO$_3$ = Cl line. Only sample no 34 (June 2006) depict abundance of chloride over bicarbonate (Cl$^-$>HCO$_3^-$. The remaining samples of both the season have overwhelming abundance of HCO$_3$ (HCO$_3$ >> Cl). Thus, temporal variations are indicated in both bicarbonate and chloride, though not substantial.
Figure- 10.1 Relationship between alkalis and Ca+Mg

Figure- 10.2 Relationship between HCO$_3$ and Cl
Relative abundances of Cl and SO$_4$ are shown in (Fig.10.3). The feature that emerges from the plot is that except for a very small number of samples, SO$_4$ is far more abundant than Cl. This chemical attribute, i.e. SO$_4$ $>$ Cl may be taken as a characteristic feature of groundwaters of the area.

![Figure 10.3 The relation between Cl and SO$_4$](image)

**10.4 CHEMICAL CHARACTERISTICS OF GROUNDWATER**

HCO$_3$ − Cl+SO$_4$ plots (Fig.10.4) clearly show that bicarbonate is the most abundant anionic species (HCO$_3$ $>$ Cl+SO$_4$) in both the seasons. Very few samples fall near 1:1 line that represents HCO$_3$ $\approx$ Cl+ SO$_4$.

To assess bonding affinities of Na+K and Cl, their equivalent concentrations have been plotted against one other (Fig. 10.5). It is seen that all the samples of both the seasons plot above the equal concentration line. Slight changes in concentration levels are recorded in pre and post monsoon samples. As Cl would normally tend to be associated with alkalies, rather than Ca and Mg, it may be inferred that Cl has been consumed in forming alkali chlorides.
Figure- 10.4 Relative abundance of Cl+SO₄ and HCO₃

Figure- 10.5 Alkalis Vs Cl plot
This further implies that alkalis would be available in plenty to get associated with HCO₃ and SO₄. It is therefore logical to expect that aqueous species, such as, alkali bicarbonates and alkali sulphates may also exist.

Significantly, HCO₃-enriched groundwater samples with HCO₃ concentration of 5 or more meq/l give evidence of having excess alkalis which may be available for bonding with anions other than Cl (Figures 10.2, 10.4 and 10.5). This group of samples may therefore have Na-HCO₃ as one of the aqueous species.

The natural bonding affinity between Ca+Mg and HCO₃ is evaluated in Figure 10.6. The fact which readily emerges out from the figure is that about 80% of the samples show excess of HCO₃ (dominance of HCO₃ over Ca+Mg). The excess HCO₃ would be tied up with excess of Na+K as clearly shown in Figure 10.5. Samples with Ca+Mg>HCO₃, in all likelihood, may have a tendency to have a bond between Ca+Mg and SO₄ in samples characterized by excess of SO₄ (Fig 10.4). Therefore some uncommon species like Na- HCO₃ and Ca-Mg-SO₄ may be present in the groundwaters of the study area.

Relative abundance of SO₄ in groundwater of the area necessitates plotting equivalent alkalis concentration against SO₄ (Figure 10.7). Few samples, mainly in November 2005, plot close to the equal concentration line, implying the possibilities of the existence of aqueous species, such as, Na-SO₄. Remaining samples of both the season show overwhelming abundance of alkalis over SO₄ (Na+K>>SO₄). This implies that alkalis - SO₄ species may only be trivial in significance.

It is evident from preceding discussion that all the major aqueous species such as, Na-Cl, K-Cl, Na-HCO₃ , Na-SO₄ , Ca-HCO₃, Mg-HCO₃, Ca-SO₄ and Mg-SO₄ are likely to be present in groundwaters of the study area.
Figure- 10.6 Biocarbonate Vs Ca+Mg plot

Figure- 10.7 Relationship between alkalis and SO$_4$
10.5 TRACE ELEMENTS DISTRIBUTION IN GROUNDWATER

Trace elements in groundwater are defined as chemical elements dissolved in water in minute quantities, always or almost always, in concentration less than 1 milligram/litre (USGS, 1993). Many of the trace elements are also known as heavy metals. Essential trace elements are required by man in amounts ranging from 50 micrograms to 18 milligrams per day. Acting as catalytic or structural components of larger molecules, they have specific functions and are indispensable for life.

Some metals present in trace concentration are important for physiological functions of living tissue and regulate many biochemical processes. The same metals, however, at increased concentration may have severe toxicological effects on human being (Chapman 1992). At the same time the deficiency of trace elements are also harmful. Domestic and industrial waste-water and agricultural activities are also responsible for the higher concentration of heavy metals in the groundwater. Trace metals can be toxic and even lethal to humans even at relatively low concentrations because of their tendency to accumulate in the body (Domenico 1998).

A characteristic feature of most trace metals in water is their tendency to form hydrolyzed species and to form complexed species by combining with inorganic anions such as HCO$_3^-$, CO$_3^{2-}$, SO$_4^{2-}$, Cl$^-$, F$^-$ and NO$_3^-$ . In groundwater environments contaminated with dissolved organic compounds, organic complexes may also be important (Freeze and Cherry 1979).

Trace element studies of groundwater have attracted the attention for a variety of reasons (Gibbs, 1977), such as:

(I) Their significance related to public health problems
(II) Their need in plant growth
(III) Academic interest to understand the mechanism of metal transport in aqueous environment

A set of 13 trace metals comprising Cu, Zn, Ni, Fe, Mn, Co, Cr, Se, Cd, As, B, Ag and Pb were analysed in 18 groundwater samples collected from study area. The trace metals for analysis were chosen for analysis keeping in view their impact on human health. The concentrations of various trace elements are given in Table 10.1. Comparisons of the data obtained are made with WHO 1994 and BIS 1991 drinking water standards (Table 9.4).
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BDL: Below detection level
Copper (Cu): Copper is an essential element in human metabolism and is considered to be non-toxic up to 0.05 mg/l concentration in drinking water (BIS 1991, WHO 1993). Copper levels in drinking-water are usually low at only a few micrograms per litre, but copper plumbing may result in greatly increased concentrations. Concentrations can reach several milligrams per litre following a period of stagnation in pipes.

The intake of copper from food is normally 1-3 mg/day. In adults, the absorption and retention rates of copper depend on the daily intake; as a consequence, copper overload is unlikely. Acute gastric irritation may be observed in some individuals at concentrations in drinking water above 3 mg/litre. The greatest danger of toxicity arises when children consume acidic beverages that have been in contact with copper container. However, few patients with Wilson’s disease (hepatolenticular degeneration) were adversely affected by the estimated average intake of copper (Schienberg and Strenleib 1965). The Cu concentrations in the study area range between 0.027-0.132 mg/l and thus all samples are well within the maximum permissible limit of 1.5 mg/l for Cu.

Zinc (Zn): Zinc is an essential trace element found in virtually all food and potable water in the form of salts or organic complexes. Zinc is an essential and beneficial element in human metabolism. The diet is normally the principal source of zinc. Although levels of zinc in surface and ground water normally do not exceed 0.01 and 0.05 mg/litre, respectively, concentrations in tapwater can be much higher as a result of dissolution of zinc from pipes (APHA 1992).

The daily requirement of pre-school aged children is 0.3 mg Zn/kg of body weight. The daily adult human intake average is 0-15 mg/kg. Zinc deficiency leads to dwarfism, dermatitis and loss in taste. Water containing zinc at concentration in excess of 5 mg/l has an undesirable astringent taste and may develop a greasy film on boiling (WHO 1993). The concentration of Zn in the potable water should not exceed the range 5-15 mg/l. The Zn concentration in the study area ranges from 0.106 to 3.99 mg/l. The observed zinc values are up to an order of magnitude lower than its highest desirable limit of 5 mg/l. The groundwaters therefore are clearly Zn-deficient.
**Nickel (Ni):** The concentration of nickel in drinking-water is normally less than 0.02 mg/litre. Nickel released from taps and fittings may contribute up to 1 mg/litre. In special cases of release from natural or industrial nickel deposits in the ground, the nickel concentration in drinking-water may be even higher. The average daily dietary intake is normally 0.1-0.3 mg of nickel but may be as high as 0.9 mg with an intake of special food items (WHO 1993). Higher concentration of nickel, as both soluble and sparingly soluble compounds, is now considered as a human carcinogen in relation to pulmonary exposure (WHO, 1993). The concentrations of Ni in the study area range between 0.043-0.092 mg/l.

**Iron (Fe):** Iron is one of the most abundant metals in the earth's crust. It is found in natural fresh waters at levels ranging from 0.5 to 50 mg/l (WHO, 1994). Iron may also be present in drinking-water as a result of the use of iron coagulants or the corrosion of steel and cast iron pipes during water distribution. Iron is an essential element in human nutrition. Estimates of the minimum daily requirement for iron depend on age, sex, physiological status and iron bioavailability and range from about 10 to 50 mg/day. The Fe in potable water should not exceed the range 0.3-1.0 mg/l (BIS 1991). Groundwater under anaerobic condition dissolves mineral of Iron and increase the iron content of it (Kalicharan 2007).

The Fe concentration in the study area range between 0.365-1.765 mg/l. Four out of 18 samples have Fe concentration of >1.0 mg/l. Sample 11 of location Bitawada shows highest concentration of 1.76 mg/l. The high concentrations of iron may cause toxic effect to human health.

**Manganese (Mn):** Manganese is one of the more abundant metals in the earth's crust and usually occurs together with iron. Dissolved manganese concentrations in ground and surface waters that are poor in oxygen can reach several milligrams per litre. On exposure to oxygen, manganese can form insoluble oxides that may result in undesirable deposits and colour problems in distribution systems (APHA 1992).

The Mn concentration in drinking water should range between 0.05-0.5 mg/l. In the study area it ranges between 0.024-0.513 mg/l. Higher concentrations of Mn may cause neurological syndrome resembling manganese encephalopathy (Anon. 1977). Iron and manganese play a biochemical role in the life cycles of plants and
animals; their presence in the groundwater in higher concentration is undesirable for all uses (Ballukraya and Ravi, 1999).

**Cobalt (Co):** Cobalt is required for the manufacture of red blood cells and in preventing anaemia. An excessively high intake of cobalt may damage the heart muscles, and may cause an over production of red blood cells or damage to the thyroid gland (http://www.anyvitamins.com/cobalt-info.htm). Cobalt concentrations in the study area range between 0.00172-0.00597 mg/l.

**Chromium (Cr):** Chromium is widely distributed in the earth's crust. Total chromium concentrations in drinking water are usually less than 2 µg/ litre, although concentrations as high as 120 µg/litre have been reported (WHO, 1993).

Trivalent chromium rarely occurs in drinking water. Most water borne chromium is in the hexavalent form. Hexavalent Cr is much more toxic than trivalent one and has no nutritional value. Hexavalent chromium may pose disorders of skin and cancer in respiratory track (Goel 1997). High concentration of groundwater may cause ulceration of nasal septum and dermatitis (Singh and Bhayana, 1986). The highest desirable level of chromium concentrations in the drinking water is 0.05 mg/l. The Cr concentrations in the study area range between 0.0532-0.07578 mg/l, and thus, all the samples have concentration levels approaching the highest desirable limit.

The cause of these relatively high Cr concentrations is not known. Normally, higher Cr values may be expected in terrains characterized by the presence of basic rocks. In the area of study, confined to Gangetic plains, the only suggestion that may be offered is that Cr in groundwater is of anthropogenic origin probably from paper mills.

**Selenium (Se):** Selenium levels in drinking water vary greatly in different geographical areas but are usually much less than 0.01 mg/litre. Selenium is an essential element for humans and forms an integral part of the enzyme glutathione peroxidase and probably other proteins as well (WHO 1993). Selenium concentration in drinking water should range in between 0.01-0.1 mg/l according to BIS 1991. In the study area, its concentration ranges from 0.0032 to 0.0271 mg/l and is, therefore, well with in the permissible limit. Only two samples have more than desirable level
i.e. 0.01 mg/l. Small amount of selenium is beneficial but large amount is toxic. The potential health effects are hair or finger nail loss and numbness in fingers or toes if Se exceeds the prescribed limit.

**Cadmium (Cd):** Cadmium is one of the most toxic metal to man and animal (Friberg et al., 1974). It is released to the environment in wastewater and its sources may be fertilizers and local air pollution. Contamination in drinking water may also be caused by impurities in the zinc of galvanized pipes and solders and some metal fittings, although levels in drinking water are usually less than 1 µg/litre.

Cd accumulates primarily in the kidneys and has a long biological half life in humans of 10-35 years, thus causing pathological changes of kidney, tubules and glomerular changes (Itokawa et al., 1974; Colucci et al., 1975). There is evidence that cadmium is carcinogenic. Cadmium also causes effects on cardio vascular system and also causes gastro intestinal upset, renal dysfunction, hypertension, growth inhibition, genetic defects and testicular tumors. Drinking water containing excessive cadmium leads to the occurrence of “itai-itai” disease among the Japanese (Kobayashi, 1970). The recommended permissible limit of Cd in drinking water is 0.01 mg/l (BIS 1991). The concentration of Cd in the study area ranges between 0.00004-0.004 mg/l which is well within the permissible limit.

**Arsenic (As):** Arsenic is widely distributed throughout the earth's crust and it is toxic in nature. It is introduced into groundwater from industrial effluents, atmospheric deposition and also from pesticides which are widely used in the study area. The excess arsenic damages the skin, causes circulatory system problems and results in an increased risk of cancer. The desirable level of arsenic is 0.05 mg/l according to BIS 1991. The concentration of As in the study area ranges from 0.0013 to 0.024 mg/l, which is well within the permissible limit.

**Boron (B):** Boron compounds are released into water from industrial and domestic effluents. It is usually present in drinking water in concentrations of <1 mg/litre, but some higher levels have been found as a result of naturally occurring boron (WHO 1984). Long-term exposure of humans to boron compounds leads to mild
gastrointestinal irritation. The maximum permissible limit of B is 5 mg/l (BIS, 1991). In the study area its concentration ranges from 0.13 to 0.51 mg/l.

Silver (Ag): The concentration of silver in groundwater from the study area varies between 0.001 to 0.024 mg/l. All samples have values less than the maximum permissible limit of 0.05 mg/l. Ag is derived partially from agricultural sources (as an impurity in fertilizers) and partly from lithological sources particularly due the presence of clay layers in the alluvium (Pawar and Nikumbh, 1999).

Lead (Pb): Lead concentration in natural waters increases mainly through anthropogenic activities (Goel, 1997). The possible sources of lead in groundwater are mainly diesel fuel consumed extensively in farm lands, discarded batteries, paint and leaded gasoline. Lead is also used in some pesticides such as lead arsenate.

Lead is present in tap water to some extent as a result of its dissolution from natural sources, but primarily from household plumbing systems containing lead in pipes, solder, fittings, or the service connections to homes. The amount of lead dissolved from the plumbing system depends on several factors, including pH, temperature, water hardness, and standing time of the water, with soft, acidic water being the most plumbo-solvent.

Lead is one of the hazardous and potentially harmful pollutants. It has its impact both on man and animals. Infants, children up to six years of age and pregnant women are most susceptible to its adverse effects. Lead is toxic to both the central and peripheral nervous systems, including sub-encephalopathic neurological and behavioral effects. Its consumption in higher quantity may cause hearing loss, blood disorders, hypertension and eventually it may prove to be fatal (WHO, 1993 and BIS 1991).

The most common symptoms of lead poisoning are anemia, severe intestinal cramps, paralysis of nerves, loss of appetite and fatigue (Train, 1979). Lead toxicity also causes irreversible damage to the brain in children.

The Pb concentration in drinking water is permissible up to 0.05 mg/l according to BIS 1991. The Pb concentration in the study area ranges between 0.0283 and 0.1831 mg/l. Out of 18 samples analysed, 6 have concentration levels higher than
the permissible limit of 0.05 mg/l. Interestingly, high Pb concentrations are reported where Fe concentrations are high too.

The higher concentration of Fe, Mn and Pb at locations Bitawada, Daha and Budhana, respectively, is attributed to industrial pollution. High concentration of these metals in some of the samples of shallow aquifer water may cause health hazards to the inhabitants of the area. The increasing concentration of these undesirable metals in the groundwater of the study area is mainly originating from industrial effluents of sugar mills, pulp and paper factories, cooperative distilleries and municipal waste water.

10.6 CHEMICAL CHARACTERISTICS OF SOIL

Generally the soils of the region are dark brown to brown in colour. Soil texture is an important character which determines the water retention and transmission properties of soils. Based on the texture, the soils are identified as sandy loam and loam (Survey of India, 2003). Generally, these soils allow slow infiltration of water through them.

The soils of the region have pH values of ranges from 6.81 to 7.45 indicating acidic to alkaline character. Seven out of 9 samples collected (Figure 10.8), show alkaline nature. Salinity of the soils are determined from electrical conductivity (EC). Its ranges from 100 to 300 micro mhos/cm. The analysis reveals the low electrical conductivity values indicating the non-saline character of the soils. The results of the important physical and chemical constituents determined are tabulated in Table 10.2.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Name of Villages</th>
<th>Colour</th>
<th>pH</th>
<th>EC (µS/cm at 25°C)</th>
<th>HCO₃</th>
<th>Cl</th>
<th>SO₄</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Budhina Kalan</td>
<td>DBr</td>
<td>6.81</td>
<td>200</td>
<td>28</td>
<td>71</td>
<td>0.14</td>
<td>58</td>
<td>67</td>
<td>131</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>Sisauli</td>
<td>DBr</td>
<td>7.01</td>
<td>100</td>
<td>171</td>
<td>43</td>
<td>0.34</td>
<td>54</td>
<td>34</td>
<td>136</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td>Lisadhi</td>
<td>DBr</td>
<td>7.12</td>
<td>100</td>
<td>110</td>
<td>21</td>
<td>0.42</td>
<td>54</td>
<td>58</td>
<td>114</td>
<td>62</td>
</tr>
<tr>
<td>4</td>
<td>Bantikhera</td>
<td>Br</td>
<td>7.26</td>
<td>100</td>
<td>98</td>
<td>28</td>
<td>0.29</td>
<td>49</td>
<td>24</td>
<td>131</td>
<td>37</td>
</tr>
<tr>
<td>5</td>
<td>Kudana</td>
<td>Br</td>
<td>7.45</td>
<td>300</td>
<td>122</td>
<td>32</td>
<td>0.50</td>
<td>54</td>
<td>29</td>
<td>136</td>
<td>39</td>
</tr>
<tr>
<td>6</td>
<td>Tikri</td>
<td>Br</td>
<td>7.12</td>
<td>100</td>
<td>110</td>
<td>28</td>
<td>0.52</td>
<td>58</td>
<td>24</td>
<td>149</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>Bawana</td>
<td>DBr</td>
<td>6.97</td>
<td>100</td>
<td>85</td>
<td>36</td>
<td>0.39</td>
<td>44</td>
<td>29</td>
<td>151</td>
<td>25</td>
</tr>
<tr>
<td>8</td>
<td>Budhana</td>
<td>DBr</td>
<td>7.01</td>
<td>100</td>
<td>98</td>
<td>39</td>
<td>0.50</td>
<td>42</td>
<td>30</td>
<td>138</td>
<td>40</td>
</tr>
<tr>
<td>9</td>
<td>Nagwa</td>
<td>Br</td>
<td>7.15</td>
<td>100</td>
<td>92</td>
<td>32</td>
<td>0.61</td>
<td>29</td>
<td>28</td>
<td>97</td>
<td>36</td>
</tr>
</tbody>
</table>

DBr- Dark Brown
Br- Brown

Table 10.2: Chemical analysis of soil in mg/100gm
The analysis reveals that the soils are rich in Na, K and Ca contents due to the use of NPK and gypsum fertilizers in huge quantity in the study area.

10.7 DISSOLVED SILICA

Twelve samples were analysed for dissolved silica content (Figure 10.8). This was done with an intention to have an idea about the depth of origin of groundwater and comment on its characteristics, such as, residence time and interaction with solid phases, i.e. granular zone or bedrock. It needs to be mentioned here that conventionally silica analysis is not performed as part of groundwater studies in India or other countries. This is in spite of the fact that a relatively rich literature exists on relationship of silica with parameters, such as, temperature, regional heat flow values and depth.

Median value of SiO\textsubscript{2} in groundwaters is 17 mg/l and rock types with which groundwater is in contact over a longer period are the principal factor controlling its concentration levels (Davis, 1964). Swansberg and Morgan (1978) applied silica geothermometer to over 70,000 non-thermal groundwater samples of USA and unequivocally showed that there is a strong correlation between silica geotemperatures for a given region and the known regional heat flow. They arrived at a relationship

Silica derived temperature in groundwater (T in °C) = mq + b

Where q is the regional heat flow in mWm\textsuperscript{-2} and m and b are constants with values of 0.67 °C m\textsuperscript{2} mW\textsuperscript{-1} and 13.2 °C, respectively. Constant b is related to the mean air temperature and m is related to the depth to which water descends. Swansberg and Morgan (1978) in their study demonstrated that the estimated depth of the occurrence of the groundwater in deep steady state was of the order of 1.4 to 2.0 km.

In another study, Marchand et al., (2002) have convincingly demonstrated that silica content of groundwater increases due to increased contact with Si-rich material and that the silica content is directly proportional to the residence time of water underground. They also showed that waters evidently originating at deeper levels had higher silica values than in shallow groundwaters.
Figure- 10.8 Location of soil samples and samples analysed for silica
Boughton and McCoy (2006), on the other hand have shown in their exhaustive study of the Morgan County, West Virginia, USA that a relationship exists between observed temperatures of groundwater discharges and their silica content.

A number of silica geothermometers have been proposed. The one which seems to be appropriate for groundwater systems is given by Fournier (1983). This equation takes into account the solubility of chalcedony and given below:

\[ t^\circ C = \left[ \frac{1032}{4.69 - \log \text{SiO}_2} \right] - 273.15 \]

Fournier (1983) has given another equation which is based on solubility of quartz. The equation is:

\[ t^\circ C = \left[ \frac{1309}{5.19 - \log \text{SiO}_2} \right] - 273.15 \]

Results of silica analysis and temperatures deduced using the two thermometries are given in Table 10.3.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Location</th>
<th>Depth (m)</th>
<th>SiO₂ (mg/l)</th>
<th>Cl (mg/l)</th>
<th>TDS (mg/l)</th>
<th>Temperature °C Quartz</th>
<th>Temperature °C Chalcedony</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fatehpur</td>
<td>50</td>
<td>34</td>
<td>20</td>
<td>693</td>
<td>85</td>
<td>54</td>
</tr>
<tr>
<td>2</td>
<td>jasoi</td>
<td>40</td>
<td>31</td>
<td>17</td>
<td>526</td>
<td>81</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>Sisauli</td>
<td>40</td>
<td>36</td>
<td>26</td>
<td>1022</td>
<td>87</td>
<td>56</td>
</tr>
<tr>
<td>4</td>
<td>Budhana</td>
<td>74</td>
<td>36</td>
<td>21</td>
<td>863</td>
<td>87</td>
<td>56</td>
</tr>
<tr>
<td>5</td>
<td>Lank</td>
<td>83</td>
<td>37</td>
<td>101</td>
<td>564</td>
<td>88</td>
<td>57</td>
</tr>
<tr>
<td>6</td>
<td>Bitawada</td>
<td>28</td>
<td>24</td>
<td>60</td>
<td>598</td>
<td>71</td>
<td>40</td>
</tr>
<tr>
<td>7</td>
<td>Nagwa</td>
<td>15</td>
<td>35</td>
<td>12</td>
<td>1427</td>
<td>86</td>
<td>55</td>
</tr>
<tr>
<td>8</td>
<td>Daha</td>
<td>70</td>
<td>45</td>
<td>99</td>
<td>888</td>
<td>97</td>
<td>66</td>
</tr>
<tr>
<td>9</td>
<td>Barnawa</td>
<td>50</td>
<td>30</td>
<td>247</td>
<td>613</td>
<td>81</td>
<td>47</td>
</tr>
<tr>
<td>10</td>
<td>Phughana</td>
<td>86</td>
<td>2</td>
<td>14</td>
<td>924</td>
<td>N.A</td>
<td>N.A</td>
</tr>
<tr>
<td>11</td>
<td>Biral</td>
<td>30</td>
<td>8</td>
<td>111</td>
<td>862</td>
<td>32</td>
<td>N.A</td>
</tr>
<tr>
<td>12</td>
<td>Shikarpur</td>
<td>18</td>
<td>9</td>
<td>30</td>
<td>559</td>
<td>36</td>
<td>N.A</td>
</tr>
</tbody>
</table>

Also given in the Table are Cl and TDS values to be related to those of silica in Figures 10.9 and 10.10, respectively. Silica values obtained have also been used to draw a distribution map (Figure 10.11). Such a map is rather an overambitious attempt since it is based on 12 samples only, but the purpose is to understand broad patterns which may be related to other parameters.
Figure- 10.9 SiO₂ Vs Cl plot

Figure- 10.10 SiO₂ Vs TDS plot
Figure 10.11 Distribution of silica values
As expected, temperatures determined using chalcedony thermometry are lower than those of quartz thermometry. This is related to solubility behavior of the two silica polymorphs and thermodynamic parameters (Fournier, 1983). In general, temperatures estimated using the former, i.e. chalcedony thermometry; seem to be more logical and realistic.

Temperatures likely to exist at deeper reservoir conditions, as estimated by the chalcedony equation, are highest for Daha, i.e. 66 °C. For Fatehpur, Jasoi, Sisauli, Budhana, Lank and Nagwa, it ranges between 50 and 57 °C, averaging 55 °C. Inferred temperature is lower at 39 °C for Bitawada. The thermometry is not applicable to samples 10, 11 and 12 from Phughana, Biral and Shikarpur because of anomalously low silica values.

There is a tendency of higher silica values of >30 mg/l in the northern, and particularly, in the southern parts of the area (Figure 10.11). This, in turn, implies higher silica geo-temperatures (Table 10.3). The trend, however, can not be called unequivocal as sample representation in the central part of the area is rather poor.

At least one feature emerges out. There is a discernible 'high' around Daha. Since samples were collected in June, 2007, when the ambient temperature was in excess of 30 °C, a silica temperature of 66 °C would mean a temperature of about 35 °C over and above the average air temperature which, in turn, would correspond to a depth of about 1000 m taking into account an average heat flow value of 30 °C/km (GSI, 1991). Other samples, characterized by silica values of >30 mg/l and temperature averaging around 55 °C, as mentioned above, would, by the same token correspond to a depth of about 800 m.

Another anomaly is in the form of exceedingly small silica values obtained for samples from Phughana, Biral and Shikarpur. These values are far too smaller than the values normally found in groundwaters (Davis, 1964; Boughton and McCoy, 2006), and that is why thermometries do not apply to these. As a matter of fact, the values of 2 to 9 mg/l tend to characterize river water rather than subsurface water. A value of 2 mg/l for Phughana is particularly enigmatic as it has been recorded in the deepest, i.e. 86 m deep well (Table 10.3). If the analysis for silica (carried out in Geological Survey of India Laboratory at Lucknow) is right, the only hypothesis that may be offered is that these three wells, ranging in depth from 18 to 86 m, discharge basically the water that has reached aquifers as a result of the influent nature of the
two rivers. Further, it would mean that this water has relatively short residence time
which has precluded rock-water interaction. This seems particularly so in case of
Shikarpur, adjacent to the right bank of river Hindon, as its chemistry matches quite
well with that of the river water (Chapter 9).

For the other two sites, i.e. Phughana and Biral, on the other hand, chloride
and sulphate values are strikingly lower than those in river Krishni. The possibility
that descending (inflowing) river water has mixed with groundwater in different
proportions is not tenable as the silica in that case would have been higher than the
observed values. Water level contour maps (Figures 6.5a, 6.5b, 6.6a and 6.6b) and
maps showing horizontal inflow from streams (Figures 7.2a and 7.2b) depict influent
tendency of river Krishni, but the same is not consistent with the silica value at
Phughana. Biral could represent a mixture of river water and some component of
relatively low TDS subsurface water so as to account for silica and Cl values of 9 and
85, respectively.

Phughana probably represents an analytical error or is grossly undersaturated
with respect to silica for reasons not known.

Silica values have been related to Cl and TDS concentrations in Figures 10.9
and 10.10, respectively. On SiO₂ – Cl plot, samples 1, 2, 3, 4 and 7 occupy a small
cluster defined by moderate SiO₂ content of 31 to 37 mg/l and relatively low Cl values
of 12 to 25 mg/l. These may be termed as groundwaters that have attained their silica
values through interaction with the solid phase at temperatures averaging around 55
°C at depth of about 800 m. The chloride content of these samples is though somewhat
lower than that expected in normal groundwaters. This itself is an indication of
relative paucity of surface and near-surface components of water in these samples. On
SiO₂ – TDS plot (Figure 10.10), these samples plot in nearly a straight vertical line
indicating that silica values have nothing to do with TDS values and any TDS value
of 500 to >1400 mg/l may be possible for nearly identical SiO₂ concentration. This, in
turn, also implies that Cl also have no relationship with TDS and that the latter is not
related to water – rock interaction. In other words the implication is that TDS may be
related to anthropogenic rather than geogenic phenomenon.

Samples 5, 6, 8, 10 and 12 tend to suggest the normal SiO₂ – Cl relationship as
a result of water – rock interaction. Phughana value being doubtful, Shikarpur and
Daha samples mark the end-members of this trend. Samples from Barnawa and Biral
(samples 9 and 11) are peripheral to river Krishni and are anomalously enriched in Cl probably due to inflow from highly contaminated river. Such a possibility for Biral has already been mentioned above.

Silica values, thus, help us understand that TDS values observed are mainly derived through anthropogenic influences and that the groundwaters sampled for the present study, in general, are derived from about 800 to 1000 m depth. This implies that we probably do not have a representative of groundwater characterized by the residence in the bedrock, i.e. quartzites belonging to the Delhi Super Group, which is inferred to lie at a depth of about 1300 m in the study area (Chapter 3).

10.8 DISCUSSION

Hydrogeochemistry of the area located between Krishni and Hindon rivers in Muzaffarnagar district, forming a part of the Ganga Plain in western Uttar Pradesh, studied over a period covering two pre- and one post-monsoon seasons of years 2005 to 2007, provide us an opportunity to study the characteristic trends with respect to temporal and spatial variations in geochemical parameters and relate them to various natural and anthropogenic causes.

The groundwaters of the area, in nutshell, are characterized by the dominance of alkalis and relative abundance of sulphate. The alkalis are almost always higher than the cumulative concentration of Ca + Mg. Sulphate, on the other hand, has average values of 141 to 172 mg/l during post- and pre-monsoon seasons, respectively, with rather anomalous values of >200 mg/l reported in a number of samples.

It is imperative to have an idea of the possible sources of alkalis and sulphate that give the groundwater in the area its characteristic signature. Sodium values are >100 mg/l in the vast majority of the samples. Values as high as >300 mg/l have been reported. Potassium values are also on the higher side, in general, and the highest values recorded are 66 to 90 mg/l. Both these values for Na and K are difficult to be acquired through water–rock interaction alone. This may be said with confidence drawing parallelism with geothermal systems which are also groundwater systems but at elevated temperatures. In some of the geothermal systems in India, for example, Chhumathang in Ladakh region of J&K, water–rock interaction in granitic bedrock (reservoir) at temperatures exceeding 150 °C has yielded Na and K values of only
about 300 and 30 mg/l, respectively (GSI, 1991). It is, therefore, difficult to conceive that interaction of groundwater in granular zones could result in alkali values as observed in the area.

Under such circumstances other sources have to be looked into for Na and K supply to the groundwater. A clue is obtained from the analysis of water soluble components of soil (Table 10.2). The values for the two alkali ions are 29 to 58 and 23 to 67 mg/100 g. Although part of these values could possibly be due to dissolution of wind-blown salts but the bulk of it is evidently due to anthropogenic influences. Potassium is a component of NPK (nitrogen, phosphorous and potash) fertilizer used abundantly in the area. Sodium, although not part of this fertilizer combination, may find its way as impurities in some of the fertilizers, particularly, urea. This has been observed in the eastern part of the Ganga Plain in Kanpur and Unnao districts of Uttar Pradesh (GSI, personal communication).

Sodium, along with Cl, may also be added to the system through sewage pollution and leachate percolation (Umar and Ahmed, 2007). Sodium and Cl may also be contributed from discharges from paper and acid factories. Yet another source of Na in the groundwater of the area may be through discharges from sugar factories, where NaOH is used for increasing the pH of the lagoon water during the course of effluent treatment.

As far as the source of sulphate is concerned, it has already been discussed in details in the previous Chapter (Section 9.8.1). In addition to sugar factories, occasional use of gypsum fertilizer is another source for SO₄ in the groundwater.

The source of other cations and anions may also be discussed here in brief. Calcium and Mg may be derived through dissolution of calcareous concretions which occur as small lensoidal bodies in the area of studies (Chapter 5). Calcium may also be derived from gypsum fertilizer. It may also be added to the system as lime used in sugar factories for drying SO₂ is discarded and it eventually finds its way in to the system through infiltration of rain water or inflow of river water (Section 9.8.1). The source of Cl may be in wind-blown salts, impurities in fertilizers and sewage pollution. Bicarbonate, in addition to the normal course of its entry in to the system in root-respiration zone, may also be added to the system through dissolution of calcareous material. However, the fact that Krishni river has anomalously high bicarbonate content of 1190 to 1250 mg/l, which is in excess of all cations put
together (Chapter-9), suggests that there is some additional source of this anion in the form of discharges from various industries. This inference is arrived at due to the fact that such a high HCO₃ content in the river water is otherwise inexplicable. The source of this excess bicarbonate in the river water, however, is not understood at this stage. A possibility may be that the hydrated lime, discarded after the use in the effluent treatment plant (Chapter-9), reacts with CO₂ that may be available through decaying of organic wastes to form Ca(HCO₃)₂. This conjecture gets some support from the fact that Krishni river has Ca values of 180 to 240 mg/l, which are in stoichiometric proportion to observed bicarbonate values. It is this high bicarbonate in the river water that eventually finds its way in groundwater due to the influent nature of the river.

A comparison of pre-monsoon and post-monsoon concentrations provides clues to temporal variations. This is particularly conspicuous in cations. Only one sample has Ca + Mg > Na + K during the pre-monsoon season, but during the post-monsoon season as many as 16 samples show this trend. This may be related to the fact that infiltration of rain water after the monsoon spell causes a dilution effect in aquifers resulting in increasing the relative abundance of Ca + Mg.

As far as the existence of the possible ionic complexes is concerned, Cl would tend to form alkali chlorides. Calcium and Mg would primarily be liganding with HCO₃ to form alkaline earth bicarbonates. Excess of alkalis would be associated with HCO₃, the most abundant anion. In some instances with Ca + Mg > Na + K, the latter could form some sulphates too. Thus, various ionic complexes, such as, Na-Cl, K-Cl, Na-HCO₃, Na-SO₄, Ca-Mg-HCO₃ and Ca-Mg-SO₄ may be present in the groundwater of the area. It is inferred that alkali bicarbonates would be the most dominant ionic complex in the area.

Temporal variations are conspicuous as depicted in L-L diagrams for November, 2005 and June, 2006 (Figures 9.5a and 9.5b). As far as spatial variations are concerned, there are discernible differences in samples from close to the river banks and those collected from the area lying between the two rivers. These differences are related to hydrological variations in the area, such as, influent nature of the streams, directions of groundwater movement and lateral and vertical permeability of the medium. Chemical alteration trends have been discussed in details, but in nutshell, the meteoric water, which is scarcely identified in the area,
tends to alter its chemical composition more in response to anthropogenic influences than natural processes, i.e. water-rock interaction and dissolution of solid phase.

10.9 INFERENCES

Based on relative abundances of the major anions $\text{HCO}_3$ and $\text{Cl}$, groundwater of the area are of three types, i.e. 1) $\text{HCO}_3 = \text{Cl}$, 2) $\text{Cl} > \text{HCO}_3$, and 3) $\text{HCO}_3 >> \text{Cl}$. Groundwater is characterized by the abundance of alkalis and relative enrichment in sulphate and this is the characteristic feature of these groundwaters.

Sodium and K would tend to form alkali chlorides. Calcium and Mg would be in the company of $\text{HCO}_3$ to form alkaline earth bicarbonate complexes. Alkalis would be associated with $\text{HCO}_3$, the most abundant anion. Some $\text{Ca} + \text{Mg}$ could form sulphates. Various ionic complexes, i.e. Na-Cl, K-Cl, Na-$\text{HCO}_3$, Na-$\text{SO}_4$, Ca-Mg-$\text{HCO}_3$ and Ca-Mg-$\text{SO}_4$ are, therefore, likely to be present in the groundwater of the area. Alkali bicarbonates would probably be the most dominant ionic complex in the area.

Analysis of some samples for silica has revealed that the groundwater could have residence in aquifers lying 800 to 1000 m bgl. Plot of silica with TDS and Cl suggest that the source for chemical species in groundwater is not predominantly through water-rock interaction.

It appears that the source of major cations and anions is dominantly through anthropogenic activities. For sulphate there is convincing evidence that it is contributed by sugar factories. The other anions and all the major cations may be contributed through natural processes as well as through factory and sewage discharges, discarded leachate and chemicals, fertilizers and organic waste.

There is temporal, as well as, spatial variation in the chemistry of groundwater. The former is particularly pronounced for cations. Post-monsoon period seems to be characterized by relative dilution. Spatial variations are discernible in the form of changes observed in samples collected from near the rivers and those from the central part of the area. Chemical alteration of meteoric water is conspicuous in the form of significant increase in TDS, but these alterations are predominantly anthropogenic rather than geogenic.

Trace elements studies have been carried out on 18 groundwater samples. Higher concentration of Iron, Mn, and Lead at location Bitawada, Daha and Budhana
respectively, and it is attributed to the Industrial pollution. The increasing concentration of these undesirable metals in the groundwater of the study area is mainly responsible for industrial effluents of sugar mill, pulp and paper, cooperative distilleries, municipal waste water and other miscellaneous industries.

Chemistry of the water-soluble component of soils has indicated that it is affected by the excessive use of fertilizers in the area. Water percolating through these soils is likely to impart these chemical signatures on groundwater.