CHAPTER - 9
DATA CORRELATION AND SYNTHESIS

9.1 SIGNIFICANT OUTCOMES OF THE STUDY

The present study has helped in arriving at some significant findings which are being listed out here succinctly to tie them up together with a view to present a consolidated picture.

- The study area is a part of the vast central Ganga Plain, delimited in the east and the west by Hindon and Yamuna rivers, respectively. Climatic changes are influencing the area and based on the analysis of the data for more than 100 years, there is a trend of declining rainfall, particularly, during the last two decades. These two decades have been marked by large scale demography related changes and massive industrialization. More than 96% of the water requirements are now taken care of through groundwater resource.

- Depth to bed rock is about 1000 m and the shallowest of the three major aquifer zones extends to a depth of 126 m bgl. The other two aquifers occur in the depth range of 130 to 260 m and 275 to 425 m, respectively. A fourth aquifer in the depth range of 625 to 675 m is reported in the area east of river Hindon.

- The top clay layer overlying the first aquifer is persistent but there are clay lenses at deeper level too. Calcareous nodules occur within clay beds. Depth to water table varies from 8.62 m to 29.16 m, deeper water table conditions being in the northeastern part.

- Water level fluctuations in 2006 were on the positive side but in 2007 about 73% of the wells showed negative fluctuation due to poor monsoonal recharge and higher rate of withdrawal due to enhanced requirement for irrigation purposes.

- The Eastern Yamuna Canal (EYC) acts as a water divide and the flow of groundwater is, in general, towards east on its left bank and towards west on the right bank. On the eastern bank, westerly flow is also inferred on the right bank of river Hindon defining a major trough which is obviously related to over-exploitation. Seepages from canal are manifested as groundwater mounds.
• Total recharge in the area of study in a period of 3 years averages 497 MCM and the average total discharge for the same period is 700 MCM, leaving a deficit balance of 203 MCM. The average stage of groundwater development is 141%.

• The steady state simulation employing MODFLOW 4.1 gives the following values. The direct recharge to the Hindon-Yamuna watershed is 358.0 MCM. The total annual draft through pumping is 393.8 MCM. The sub-surface horizontal inflows and outflows are 3.9 and 20.7 MCM, respectively. Inflows from rivers Hindon and Yamuna are 30.0 and 24.2 MCM, whereas base flows are 1.7 and 0.43 MCM, respectively.

• Based on 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. There is neither temporal nor spatial consistency in the distribution of TDS values.

• 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.

• There are clear indications that Na, K, Cl and SO₄ have been added to the system mainly through anthropogenic activities.

• Sodium could have been derived as a result of water-rock interaction and cation exchange but the bulk of it, however, may have been acquired as a result of infiltration of water in zones of reh soil and from sewage and industrial waste. Sugar and related industries may also be a contributor. Potassium comes mainly from fertilizers and its anomalously high values suggest partial fixation of K in soils and its retention in the groundwater.

• There is drastic depletion in concentration of Ca in the pre-monsoon season of 2006. This may be explained as a result of precipitation of carbonate and cation exchange.

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• Bicarbonate has been acquired through water-solid phase interaction and dissolution of CO₂ in percolating groundwater. Its distribution, both spatially and temporally, is prone to changes due to precipitation and dissolution of carbonates in different seasons. As surplus HCO₃ is recorded in some samples, it may be speculated that source for this anion also lies in some anthropogenic activities.

• Sulphate values as high as 342 to 457 mg/l in 4 samples and >30% samples with concentration exceeding 200 mg/l clearly indicate that addition of this anion to the groundwater system is through anthropogenic activities and the biggest culprit in this regard is the booming sugar industry in the area.

• Chloride values, though averaging 85 and 71 mg/l in the two successive sampling seasons, are at times as high as 227 to 369 mg/l and bulk of it is related to human activities.

• Ionic species likely to occur in the groundwater in the study area are Ca-HCO₃, Mg-HCO₃, Ca-SO₄, Na-Cl, Na-SO₄, Na-HCO₃ and K-Cl.

• Anomalously high concentration levels for Al and Cr and relatively high values are reported for Mn, Fe and Pb. High values of Pb and Fe are often associated and this may be because of the pipes used in wells. High Cr values may be related to industrial influence. The cause of high Al values in all the 22 samples is not known at this stage.

9.2 ZONAL DISTRIBUTION OF CHEMICAL SPECIES

While trying to collate the data and work out various factors controlling the distribution of chemical constituents, it was considered imperative to have an idea about the zone-wise distribution of major cations and anions. The area has been divided in to northeastern, northwestern, central and southern zones for comparing the broad chemical similarities and dissimilarities (Table-9.1). Significant features that emerge from this comparison are:

• Compared to other zones there is relative preponderance of Na in the Northeastern Zone, which at least partially may be the manifestation of cation exchange, as has
been discussed earlier. There is consistency in the distribution of pre- and post-monsoon values of HCO₃ and SO₄.

Table 9.1: Zone-wise distribution of major cations and anions (mg/l)*

<table>
<thead>
<tr>
<th>ZONES</th>
<th>Northeastern Zone</th>
<th>Northwestern Zone</th>
<th>Central Zone</th>
<th>Southern Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>WELLS</td>
<td>9 to 12, 41 to 50 and 55 (15 wells)</td>
<td>36 to 38 and 51 to 54 (7 wells)</td>
<td>1 to 8, 13 to 18, 30 to 32, 34, 39 and 40 (20 wells)</td>
<td>19 to 29, 33 and 35 (13 wells)</td>
</tr>
<tr>
<td>Na 2005 mg/l</td>
<td>217</td>
<td>138</td>
<td>205</td>
<td>145</td>
</tr>
<tr>
<td>Na 2006 mg/l</td>
<td>262</td>
<td>171</td>
<td>180</td>
<td>211</td>
</tr>
<tr>
<td>Ca 2005 mg/l</td>
<td>43</td>
<td>20</td>
<td>47</td>
<td>48</td>
</tr>
<tr>
<td>Ca 2006 mg/l</td>
<td>14</td>
<td>22</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>HCO₃ 2005 mg/l</td>
<td>562</td>
<td>460</td>
<td>621</td>
<td>500</td>
</tr>
<tr>
<td>HCO₃ 2006 mg/l</td>
<td>576</td>
<td>443</td>
<td>457</td>
<td>507</td>
</tr>
<tr>
<td>SO₄ 2005 mg/l</td>
<td>176</td>
<td>124</td>
<td>225</td>
<td>156</td>
</tr>
<tr>
<td>SO₄ 2006 mg/l</td>
<td>198</td>
<td>232</td>
<td>160</td>
<td>166</td>
</tr>
</tbody>
</table>

* 2005 and 2006 refer to post-monsoon and pre-monsoon samples collected in November, 2005 and June, 2006, respectively

- The Northwestern Zone is characterized by the lowest Ca values in the post-monsoon period of 2005. In fact, when data from individual wells are compared, Ca shows consistency and its average values for the two sets of samples vary between 20 and 22 mg/l. As a possible corollary to this, HCO₃ values are also lowest and consistent in this zone. As a matter of fact when compared to the Northeastern Zone, all the major ions in the Northwestern Zone, with the exception of Ca and SO₄ in pre-monsoon season, show depletion. This is probably a chemical evidence that seepage from EYC is more to the west than east. Another significant feature of this zone is that it shows large scale addition of SO₄ from an average value of 124 mg/l (November, 2005) to an average value of 232 mg/l (June, 2006). This addition of SO₄ and also of Ca may be related to anthropogenic factors, mainly related to sugar industry, as discussed in a later section.
• The Central Zone shows most conspicuous changes. Contrary to the trend in other zones, Na in pre-monsoon collection of 2006 is lower than that in the post-monsoon, 2005. The same is true for HCO₃ and SO₄. Both the anions show considerable decrease in their concentration level in pre-monsoon period. The observed chemical trends in this zone may possibly be a consequence of clusters of industries at Baghpat in the west and Sarai in the east.

• Substantial enrichment is noticed in the concentration of Na in the pre-monsoon period (June, 2006) in the Southern Zone. On the other hand, post-monsoon Na value is relatively low, similar to the corresponding value in the Northwestern Zone. Calcium values are relatively high.

9.3 INFLUENCE OF GEOLOGICAL PARAMETERS

Two geological features, the upper most persistent clay layer and occurrences of calcareous nodules in clay beds and lenses within the granular zone, particularly in the southern part, are significant from the point of view of observed chemical attributes of groundwater. Clay layer is thickest in the northern part of the area and in the northeastern part it attains the maximum recorded thickness of 51 m (Figures-4.2 and 4.3).

The presence of clay horizon may be considered conducive from the point of view of cation exchange, which is capable of modifying concentration levels of Na and Ca as indicated in the equation (Tedaldi and Loehr, 1992) given below:

\[ \text{Ca}^{++} + 2 \text{Na} \text{(exchanged)} = 2 \text{Na}^{+} + \text{Ca} \text{(exchanged)} \]

The equilibrium for the equation given above is far to the right as long as there is appreciable Na⁺ on the exchange sites of clay. The removal of Ca⁺⁺ from solution by exchange with Na⁺ may cause the groundwater to become or remain under-saturated with respect to other calcium facies, such as, calcite and gypsum.

It is not the clay itself but its constituents, such as, clay minerals (illite, smectite) and its associated humus content and oxides of iron which control the Cation Exchanging Capacity (CEC) on clay mineral surfaces. The northeastern part of the area, therefore, by
virtue of having a considerable thickness of clay, presents an ideal scenario for cation exchange involving Na and Ca, resulting in relative enrichment of the former and depletion of the latter, in the groundwater. There is some indication for this process in the Northeastern Zone (Table-9.1) in the pre-monsoon period. The highest recorded Na value of 262 mg/l seems to have some contribution from groundwater-clay interaction. It needs to be pointed out here that the contribution of this process in acquisition of Na ions by groundwater may, however, be relatively insignificant.

Such suggested trends of Na enrichment in groundwater as a result of cation exchange are not uniform and consistent. This entire process and resultant distribution of Na and Ca in soil and groundwater depends on the equation

\[
\left(\frac{C_{\text{Ca}}}{N_{\text{Na}}}\right) = K \left(\frac{C_{\text{Na}}}{N_{\text{Na}}}\right)^2
\]

where \((C_{\text{Ca}})\) and \((N_{\text{Na}})\) refer to “activities” of Ca and Na, respectively, on clay exchange sites and \((C_{\text{Na}})\) and \((N_{\text{Na}})\) refer to the “activities” of Ca and Na in groundwater in equilibrium with clay surface. Equilibrium constant of the equation is denoted by K. Values of \((C_{\text{Ca}})\) and \((N_{\text{Na}})\) for various clay minerals are available from standard tables dealing with thermodynamic properties of minerals and values of \((C_{\text{Na}})\) and \((N_{\text{Na}})\) are related to their respective concentrations in groundwater. If \(N_{\text{Na}}\) is high, \(C_{\text{Na}} / N_{\text{Na}}^2\) would have a lower value and the value of K would be large. Under such circumstance, \(N_{\text{Na}}\) may replace \(C_{\text{Ca}}\) and/or \(M_{\text{Mg}}\) on clay exchange sites in order to maintain equality on the two sides of equation given above.

Role of thick clay bed in being conducive for cation exchange in the northeastern part of the area can not be ruled out but what seems to be a distinct possibility is that trends may be changing with time, seasons and site-specific parameters (Tyagi, 2003). Irrigation with sodic water would lead to an increase in Exchangeable Sodium Percent (ESP) in soils. In the early stages of sodic irrigation in regions characterized by relative abundance of clay fraction in the soil, such as, the Northeastern Zone in the study area, large amounts of divalent cations are released from the exchange sites. In the monsoonal season the irrigation is by far more dilute rainwater. This regularly alternating irrigation
by sodic water in the dry season and rainwater during monsoon may induce cycles of precipitation and dissolution of salts and resultant increase and decrease in concentration levels of Na and Ca.

The presence of kankar, carbonate concretions and nodules is the other factor which may have a bearing on Ca and HCO$_3$ values in the groundwater. Solubility of CaCO$_3$ is inversely proportional to temperature at constant partial pressure of CO$_2$ (Boughton and McCoy, 2006). This implies that at high temperature solubility of CaCO$_3$ will decrease and carbonate will precipitate under near surface conditions causing depletion in Ca and HCO$_3$ values in the groundwater. Winter months, with temperature going down to 5 to 10°C, may, by virtue of this relationship, be conducive for dissolution of pre-existing carbonates thus increasing the concentration levels of Ca and HCO$_3$ values in the groundwater. Carbonate deposition and dissolution is an omnipresent phenomenon in groundwater systems (Boughton and McCoy, 2006) and observed large variations in Ca values in November, 2005 as compared to those of June, 2006 in the study area may at least partially be related to this alternating dissolution and precipitation of carbonates during successive winter and summer seasons, respectively.

9.4 HYDROLOGICAL PARAMETERS AND WATER CHEMISTRY

Various hydrological parameters that may influence the distribution of major cations and anions are permeability related factors, contribution from surface water bodies, groundwater flow regime and the possibility of mixing of groundwater from different aquifers.

Permeability attains significance when acquisition of solutes is mainly as a result of water-rock interaction, particularly, in terrains dominated by hard rock. This definitely is not the case here.

The isopermeability map (Figure-4.15) shows that the major portion of the area is covered by the zone having permeability values of 30-40 m/day. Higher and lower permeability is inferred in small patches particularly in the vicinity of river courses. Chemical data do not suggest any obvious relationship with this inferred permeability map.
Based on zonal distribution of hydraulic conductivity (Figure-6.1), it appears that broadly speaking the northern part, comprising Baghpat, Baraut, Rithaura and area to the northeast of Krishni river, has relatively lower permeability with hydraulic conductivity values averaging 26 m/day. The rest of the area has an average K value of 35 m/day suggesting better permeability conditions. There is some vague relationship between this permeability zonation and distribution of chemical species. The northern, less permeable, part is characterized by relative abundance of Na and its marked enrichment during pre-monsoon period. Presence of thick and persistent clay beds in this part, which have facilitated cation exchange resulting in release of Na to groundwater from clay exchange sites, may have rendered lower overall permeability to this part. There is difference in temporal distribution of SO₄ too in the northern and southern parts but its relationship with permeability related conditions is not clear.

Surface water – groundwater interaction is capable of resulting in discernible changes in groundwater chemistry due to influent behavior of rivers and seepage from canals. Khan (2004) reported the two rivers to be effluent in nature. The flow direction as inferred now is relatively altered and this seems to be the consequence of overexploitation of the resource and impact of Eastern Yamuna Canal (EYC) which acts as the groundwater divide in the area. River Yamuna, as inferred in the present study, is influent in nature in the northern part and beyond that it is effluent throughout the study area. River Hindon is influent throughout its course, except the patch in its lower reaches in the southern part where it evidently becomes effluent.

Except for a sample from river Krishni and the upstream sample from river Hindon, which are clearly affected by surface pollution, the remaining 3 samples from Yamuna and 2 samples from Hindon, have TDS values of < 500 mg/l. Groundwater has TDS generally exceeding 800 mg/l, averaging 1000 mg/l (Chapter-7). Therefore an influent drainage would result in diluting the groundwater. The effluent behavior of surface drainage, on the other hand, would result in an increase in TDS of river discharge which may only be picked up through very closely spaced sampling of streams.
There is some chemical evidence for the effluent nature of river Yamuna in the bulk of its run in the study area, except in the northern part. Taking Cl as the conservative ion, the fraction of groundwater input in the discharge of Yamuna between sites 2Y and 3Y (Table – 2.3, Figure – 2.2) may be calculated. Taking Cl at site 2Y at 31 mg/l and average Cl value of 78 mg/l in the groundwater (Table-8.2), it may be calculated that for an observed Cl value of 40 mg/l at site 3Y, groundwater and Yamuna water (2Y) have to be mixed in a ratio of 0.20:0.80. In other words, between sites 2Y and 3Y, north and south of Baghpat, respectively, the Yamuna discharge has about 20% contribution from groundwater outflows. The chemical evidence using Cl or TDS is, however, not unequivocal for Yamuna being effluent, as inferred from hydrological characteristics (Chapter-4).

Very high TDS value of 2661 mg/l in the only sample collected from river Krishni (Table-2.3) 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 speculation is supported by the occurrence of groundwater (sample 41) with TDS of 1330 to 1542 mg/l, in the immediate vicinity of Hindon sampling point. Downstream samples of Hindon are dilute and this does not seem to be consistent with Hindon being influent except in the extreme southern part as downstream samples would have retained high TDS recorded in its upper reaches. A possibility that may be considered is that at sampling site 1H (Barnawa), where TDS value is 1035 mg/l, the collected sample has pollutants/contaminants in colloidal state. Downstream samples, 2H and 3H, seem to be relatively far more dilute due to settling down of colloidal matter in the stream bed.

That EYC acts as an N-S groundwater divide may now be evaluated in the light of chemical data. Chemical differences across the canal in Northeastern and Northwestern Zones (Table-9.1) have already been discussed above. It seems the same relationship continues along the length of the canal. When broad chemical characteristics of 17 wells located to the west of EYC are compared with those of the 38 wells located to the east of it, this is clearly seen that western wells have lower TDS, Na and Cl values. This is akin to the situation discussed above and implies that bulk of about 150 MCM (per annum)
water entering the groundwater system as canal seepage, affects the western part more than the eastern. This water with a TDS of about 400 mg/l would cause dilution. Mass balance equation shows that this mixing of groundwater and canal seepage has to be in a ratio of 0.95:0.05.

In situations when inland groundwater occurrences are characterized by very high TDS values a possibility that needs to be considered is of the occurrence of deep aquifers of saline water and their mixing with shallow groundwater. Such saline water bodies are reported from parts of Mathura and Agra districts of Uttar Pradesh in the Yamuna Plain and Gurgaon, Sohna and some other districts of Haryana (Central Ground Water Board Website). Indications of the existence of a saline groundwater body are also reported from the adjoining area of Ganganagar in district Meerut, 54 km east of Baghpat, across river Hindon. The groundwater encountered in the deepest exploratory well drilled by CGWB in an aquifer in the depth range of 625 to 675 m has Na and Cl values of 1150 and 1980 mg/l, respectively (Khan, 2004). Sodium and Cl concentrations are almost in equimolar proportion implying the existence of Na-Cl as the major ionic species. This saline water body may be extending to the area of study, however, its contribution to the shallow groundwater may be ruled out in the light of chemical evidence of relative paucity of Na-Cl as a major ionic species.

9.5 CLOSED BOX APPROXIMATION OF CHEMICAL CHANGES

An attempt may be made to evaluate the effect of recharge and discharge on the chemistry of groundwater in the area. Average recharge and draft values for the years 2005, 2006 and 2007 (Chapter-5) may be taken and a closed box model may be developed to get a broad view of resultant signatures on the chemistry of groundwater. The average recharge for the period of study is 497 MCM. It has three components, monsoon and non-monsoonal precipitation, input through irrigation and canal seepage; in a ratio of 0.35:0.35:0.30, respectively. Assigning TDS values of 93, 1095 and 429 mg/l and Cl values of 15, 78 and 35 mg/l to the three components (Table-8.2), respectively, and assuming 20% concentration of TDS and Cl on account of evaporation of the water
being used for irrigation, it may be calculated that the cumulative recharge to the groundwater system would have TDS value of 610 mg/l and Cl value of 50 mg/l.

A closed box may now be conceived assuming it to have 10,000 MCM of groundwater with Cl and TDS values of 78 and 1095 mg/l. Chemical effects of recharge at the rate 497 MCM per annum and discharge at the rate of 700 MCM per annum may now be simulated. It is seen that the effect of recharge and discharge at the given rates would be progressive dilution of groundwater and depletion in the quantity of groundwater in the box. For example, at the end of 5th year the box has 8985 MCM (depleted by 1015 MCM) groundwater with Cl and TDS values of 72 and 985 mg/l, respectively. In other words, groundwater is depleted in TDS by 110 mg/l.

The implication of this model is that recharge tends to ameliorate the concentration levels of solutes in the groundwater but additions of chemical species through uncontrolled anthropogenic processes keep on deteriorating the quality. As the things stand now the box becomes an open box or a closed box which keeps on changing its initial chemical parameters.

9.6 INFILTRATION THROUGH SALINE SOIL

Saline soil constitutes about 21 km² of the study area of more than 1345 km². It consists of white encrustations which are more or less superficial and consist predominantly of Na₂CO₃. Anomalously high Na values in groundwater suggest that these saline soils may also be one of the sources of Na as well as HCO₃. These saline encrustations may be dissolved in rainwater or irrigation water and then carried downward in solution to become part of the groundwater in the area. Taking a very conservative estimate of only 1 mm thick layer of saline patches being available for dissolution, it may be calculated that the mass of Na₂CO₃ dissolved would be 47,000 tons. For this calculation specific gravity value has been taken at 2.25 g/cm³, which is for monohydrated sodium carbonate. Taking the governing equation, as given below and molar quantities of other reactants in proportion of 47,000 tons of Na₂CO₃, it may be calculated that 20400 tons of Na and 54080 tons of bicarbonate ions would be released to the groundwater.
Dissolution of saline encrustations would be most effective during the monsoon season therefore its effect on shallow groundwater chemistry is likely to be witnessed late in the post-monsoon period. Saline patches are likely to reappear as a result of capillary action during peak summer months.

The possibility that Na enrichment observed in pre-monsoon 2006 samples is, at least partially, on account of dissolution of saline soil can not be ruled out. This process may also account for addition of Cl and SO₄ to the groundwater as saline soils, in addition to Na₂CO₃, also have Na₂SO₄ and NaCl in traces.

9.7 INFLUENCE OF FERTILIZERS

The source of K, which in a number of samples has concentration levels of 30 to 264 mg/l, is in all likelihood in NPK fertilizers used particularly before the sowing season of wheat and to some extent during the early stage of sugarcane cultivation. According to the information available from the District Statistical Report, the amount of N, P and K used in fertilizers during the year 2007 was 276 x 10⁵, 79 x 10⁵ and 13 x 10⁵ kg, respectively. As the area under cultivation is about 1100 km² or 11 x10⁵ hectares, it may be calculated that per hectare application of K is only about 12 kg, which is not much and under normal circumstances is likely to get fixed and held by soils in the area. Anomalous values of K, particularly, in samples 22 (264 mg/l) and 25 (203 mg/l) collected in November, 2005 suggest lack of their fixation. It has been suggested by Simonis (1981) that the highest K – fixation occurs in soils with higher clay content. By increasing the clay content from <10% to >20% the amount of K that could be fixed increases about three fold. May be it is a coincidence that samples 22 and 25 are from the southern part of the area collected from close to the eastern bank of EYC. The southern part has a 32 to 35 m thickness of clay only (Figures-4.2 and 4.6). That these high values of K are related to lack of fixation is also suggested by the fact that these two samples give K values of 102 and 4 mg/l in the pre-monsoon period of 2006 implying partial and
complete fixation, respectively. The example of these two samples (samples 22 and 25) probably gives an idea about the upper limit of the time involved in the transport of chemical signatures.

9.8 ANTHROPOGENIC IMPACTS ON GROUNDWATER CHEMISTRY

Possible impacts of fertilizer application and irrigation have been discussed above. These non-point source human activities seem to influence the chemistry of shallow groundwater in a limited but discernible way. The role of point-source impacts, for example, landfills, underground septic/sewage disposal pits, sewage lines and effluents from various industries (Figure-9.1) has, evidently, a much larger role in determining the chemical quality of shallow groundwater.

Landfills and garbage dumps may be responsible for generating CO₂ as a result of the decomposition of organic matter, which may find its way to the groundwater level in solution with infiltrating water. Samples of such groundwater may be characterized by excess HCO₃⁻, over and above that consumed with various ionic species. Such waste and refuse dumps occur in urban areas and by the side of river discharges. This is suggested by the occurrence of samples with high HCO₃⁻ content (5, 6, 12 and 17 of post-monsoon 2005) in the vicinity of townships of Baraut and Sarai and at river banks (samples 21, 22, 41 and 49 of pre-monsoon 2006). As discussed in a later section, HCO₃⁻ may also be contributed from industrial sources, particularly, sugar and textile units.

Another significant point-source anthropogenic pollution is through septic/sewage disposal pits and leakages from sewage lines. It is very well established now that under such a scenario Na, Cl and NO₃⁻ may be directly added to groundwater. It is difficult to segregate the effect of this possible source of pollution on Na and Cl concentrations which are already anomalously high. Nitrate values of > 50 mg/l in some samples may as well be related to application of fertilizers rather than contamination by sewage discharges.
The role of the most significant of point-sources of pollution, i.e. industrial effluents may now be evaluated. The study area is considerably industrialized owing to its proximity to big markets and consumption centers at Delhi, Meerut, Muzzafarnagar and parts of Haryana state. Major industrial centers are at Ramala, Malakpur, Baraut, Sarai, Baghpat, Chaprauli and Khekra, which have soap, textile, sugar, gur, medicines, shoes, iron goods and antimony industries (Figure-9.1). Textile-related industries consist of Khadi, handloom, yarn and cotton cloth manufacturing units. Ramala sugar factory
and medicines, gur and iron goods industries at Baraut are located in the northeastern part of the area. Malakpur sugar factory and cotton and gur industries at Chaprauli are located in the northwestern part. In the central part, soap, khadi yarn and gur units are located at Sarai on the eastern side of EYC, whereas located on its western side are sugar, gur, khadi and leather industries. In the southern part, the industrial center at Khekra has gur, handloom and antimony industries (Figure-9.1).

To evaluate the effects of above mentioned industries on the chemistry of groundwater, it is important to understand succinctly the chemical constituents of the wastes and effluents generated by these industries.

9.8.1 Soap Manufacturing

The soap manufacturing unit employs the process of saponification of fats and oils. Fats and oils are heated with alkalis as a result of which soap is formed and water is released. Both NaOH and KOH are used, the former for hard soaps and the latter for soft soaps (liquid soaps and shaving creams). The water generated as a result of heating of triglyceride or fatty acids with alkalis is charged with Na and/or K and is discharged as an effluent (www.wikipedia.com). Soap manufacturing units are centered around Sarai. Samples 3, 4, 5 and 6 are from the area around and the highest Na value of 382 mg/l in the post-monsoon season 2005 is recorded in one of these samples. It is difficult to say that this anomalous Na concentration may be related to soap industry because lower values are recorded in these samples in pre-monsoon 2006 period. The possibility of periodic discharge of effluents may, however, be not ruled out. May be that the effluents are discharged during the monsoon period for better dissipation and they show their effect on groundwater chemistry in post-monsoon period. The observation that K values are relatively low, however, is consistent with the fact that only hard soaps are manufactured in the area.

9.8.2 Textiles Related Industries

Textiles industry has been condemned as being one of the world’s worst offenders in terms of pollution of both surface water bodies and groundwater. It require as many as
2000 chemicals, both organic and inorganic, to act as dyes in different stages and as transfer agents (www.wikipedia.com). Most well known pollutant from Textile industry is CI which has its application for bleaching. Formaldehyde (HCHO), an organic compound, is another major component of discharge from this industry, which on decomposition could give rise to HCO₃ through the process involving dissolution of CO₂ released during its decomposition (www.oecotextiles.com). Release of Ca (a constituent of bleaching compounds), Mg (component of dyes and transfer agent) and CI (bleach) to surface and groundwater bodies have been related to textile industry by Geetha et al. (2008).

With this background, it may be speculated that Ca, Mg, CI and HCO₃, may have been derived partially from khadi, handloom and cotton cloth and yarn industries located at Chaprauli, Baghpat and Khekra on the western and Sarai on the eastern side of EYC. Chloride is a necessary component of textile-related chemicals. Moreover, it is likely to remain in solution, once entered, by virtue of its conservative chemical characters. It may therefore be used to trace the effect of textile industries on groundwater chemistry.

There is clear indication of relative abundance of CI in the vicinity of Sarai which has khadi and yarn industries. Four samples (3, 4, 5 and 6) from this area have high CI values averaging 130 to 140 mg/l in both pre-and post monsoon samples, the highest value of 207 mg/l reported from Sarai itself. Baghpat, with khadi manufacturing unit, records 220 mg/l CI in November, 2005. There is a mutual contradiction in distribution of CI values at Sarai and Baghpat though. While the former records a lower value of 68 mg/l in November, 2005, the value in June, 2006 swells to 207 mg/l; the reverse is true for the latter, which records the high value in November, 2005 (post-monsoon period). The reason for this anomaly is not well understood and may probably have to do with hydrological parameters and/or differences in chemicals used in khadi and yarn units. That CI values at Sarai and Baghpat are related to Khadi and yarn industries is also suggested by the fact that relatively low CI values are recorded at Khekra, where raw (unfinished and not chemically dyed and treated) handloom cloth is woven.

It may be speculated, therefore, that textile industries have contributed CI and may be some HCO₃ and Mg too. Magnesium is being mentioned here as it has relatively
high and more or less consistent values in the study area and its entry in to groundwater systems has been recorded in some other areas of textile industries (Geetha et al. 2008).

9.8.3. Sugar and Gur Industries

More than 50% of the total land available for agricultural purposes is under sugarcane cultivation and consequently sugar factories and gur manufacturing units constitute the most thriving industrial activity in the area. Major sugar industries are located at Ramala, east of EYC in the northeastern part and Malkapur and Baghpat, west of EYC. There are numerous gur making units in the area of which the major ones are centered around Chaprauli, Baraut, Sarai and Khekra (Figure-9.1).

That SO$_4$ is of anthropogenic origin is clearly indicated by its abnormally high average values of 175 to 188 mg/l (the highest values being 457 and 394 mg/l, respectively, in the two sampling seasons). Such high values could neither be expected as a result of water-rock interaction nor oxidation of sulphides. Dissolution of some sulphate mineral is ruled out in the light of available geological and subsurface information. Under such a situation it is logical to infer that the bulk of SO$_4$ is of anthropogenic origin and as seen in the later section it’s most potential source is sugar and gur industry.

Sulphur is used in elemental or compound form in sugar industries (Umar et al. 2006), which on oxidation gives rise to SO$_4$. More or less the same process with some variations is employed in the sugar industry. Sugarcane juice is heated with CO$_2$ and milk of lime [Ca (OH)$_2$] to boiling point. Carbon dioxide travels through the juice and forms CaCO$_3$ which collects non-sugar debris consisting of fats, gums and waxes from the juice and segregates these from the juice. Another effect of mixing [Ca (OH)$_2$] is that the pH is adjusted at about 7 to prevent the formation of glucose and fructose. In the next stage SO$_2$ generated from S or some of its compounds is bubbled through the juice before evaporation so as to bleach color forming impurities to nearly colorless. Further refining needs mixing of phosphoric acid (H$_3$PO$_4$) and [Ca (OH)$_2$] to form calcium phosphate. Calcium phosphate further entraps some impurities and then floats to top to be separated. It is very relevant to note here that some producers add sodium hydrogen sulphate during the final stage of boiling. This releases SO$_2$ in to the juice and lightens the color of the
final product (www.wikipedia.com). In most of the gur manufacturing units this process is in vogue to make the gur look very light colored.

Thus the separates from the juice during various stages of the evaporation of juice consist of sulphates of Na and Ca, phosphate of Ca and some CaCO3 and [Ca (OH)2]. These separates, floats and slag, as per the requirements of Pollution Control Authorities, are required to be treated for their harmful contents in Effluent Treatment Plants (ETP) and then discharged. Contrary to this the practice in vogue is that all the discarded material from sugar industry is disposed off in the open field taking it to have manure value. Agriculture return water and infiltrating rainwater carries water soluble components from this disposed off waste to groundwater causing addition of Na, Ca, P, SO4 and CO3/HCO3. Data available on a sugar mill’s untreated effluents in Bhadravathi Taluk in the state of Karnataka (Shivappa et al. 2007) gives an idea about the potential of these discharges for polluting groundwater resources. The effluents have, on an average, a TDS value of 2516 mg/l. Calcium, Mg and Na values are 364. 151 and 254 mg/l, respectively, and SO4 concentration averages at 540 mg/l.

In the light of the discussion above, there is hardly any doubt that the bulk of SO4 in groundwater in the study area has its origin in sugar and gur industries. Sodium also is derived from this industry, mainly from gur manufacturing units, which use Na-H- SO4 for getting rid of impurities from the juice and making the finished product look light colored. Baraut, where many gur and raw sugar making units are clustered, has Na and SO4 contents of 398 and 394 mg/l, respectively, as recorded in June, 2006. High values of these ions are also recorded at Baghpat and Sarai. At Mawai Kalan (sample 5), just east of Sarai, Na and SO4 contents of 382 and 305 mg/l, respectively, in November, 2005. This is not only an indication of Na and SO4 added to the system from gur manufacturing units but also of transport of chemical signatures in the direction of groundwater movement.

There is an anomaly and that is in respect of distribution of Ca. In the light of the discussion above, sugar industry should have contributed Ca to groundwater. However, it does not appear to be so and the groundwater in the area is, in general, Ca-deficient. Distribution of Ca in the area is some what enigmatic. For example, sample 41 at
Barnawa has Ca value of 101 mg/l in November, 2005, which declines to 6 mg/l in June, 2006. It seems that two factors have facilitated the dissipation of Na more than Ca. First, the prevalent use of Na hydrogen sulphate in sugar technology in the area than calcium compounds and its use in gur units have resulted in the observed pattern. Secondly, relative dispersion of Na and Ca may depend on relative solubility of their compounds present in factory wastes.

The effects of sugar and gur industries on groundwater chemistry are more pronounced in pre-monsoon samples than those of the post-monsoon period. This is because sugarcane crushing season starts in October and November and the peak of the industry is in the months of January and February. The effects are transmitted to groundwater in three to six months time.

9.8.4 Miscellaneous Industries

Medicines, iron goods, shoes and some antimony-based industries are also based in the area, the first two being at Baraut on the left bank of EYC. Not much information is available on the kinds of medicines made and chemicals used at Baraut. Iron goods industry here is practically confined to the manufacturing of wheel rims for automobiles. The groundwater collected from Baraut (sample 12) has some peculiarities, such as, very high TDS value of > 1300 to >1800 mg/l and the highest values for Na and SO₄ of 398 and 394 mg/l, respectively in the samples collected in June, 2006. Concentration of Cl and Mg is also abnormally high for the same lot of samples at 318 and 88 mg/l, respectively. Sodium and SO₄ may be speculated to be related partially to pharmaceuticals due to common use of Na and S in medicines (www.wikipedia.com). Chloride and Mg may have derived from iron goods manufacturing, the former being part of the acid (HCl) cleaning of metals (removing oxide coats), and the latter involved in making alloy and chemical treatment. On the other hand, abundance of both Mg and Cl in nearly equimolar proportions suggests use of MgCl₂ in some of the industries in the area. Chemical signature of the abundance of Na and SO₄ in Baraut sample extends eastward to samples 11, 10 and 9 and this is consistent with the inferred easterly flow of groundwater.
Leather treatment and shoe manufacturing units normally use NaCl and dilute H₂SO₄ for various processes from treatment of raw leather to its finishing (District Statistical Report of Unnao, 2003). Chloride values as high as 213 to 805 mg/l and very high SO₄ values are reported in the leather-belt of Kanpur and Unnao districts of Uttar Pradesh (http://cgwb.gov.in/nr/hydro/dist30.pdf). High Cl and SO₄ values at Baghpat may therefore suggest some influence of the local leather industry.

District Statistical Report records the existence of stibnite-based industry at Khekra details of which are not available. Whatever may be the case, stibnite (Sb₂S₃) may yield SO₄ ions on oxidation.

9.9 TRACE METALS

Leather works and dying units are known to contribute Zn, Pb, Cu, Cr and Mn. Textiles industry, similarly, may contribute Cu, Pb, Cr and As. The area is characterized by the presence of Cr and Al in quantities far above the permissible limits of these metals in groundwater. Chromium may be getting in to the system from textile-related industries in the area. As far as Al is concerned, its source is rather enigmatic.

9.10 EXTENT OF VERTICAL INFLUENCE OF POLLUTION

It has been established unequivocally that groundwater in the top aquifer is severely affected by deterioration of the chemical quality and this is mainly the consequence of anthropogenic influences rather than natural processes. The aspect that needs to be looked in to is that how far these effects of quality degradation on account of pollution have been transported vertically to the underlying aquifers.

This study has remained more or less confined to the first aquifer which extends to 126 m bgl. The data, however, are available on the quality of groundwater in deeper aquifers encountered in exploratory wells drilled by Central Ground Water Board (Khan, 2004). Available data is reproduced in Table-9.2. Average chemical composition of the shallow groundwater (aquifer 1) and that of wells tapping the shallow aquifer at Daha (location 44) and Barnawa (location 41) is also given. Deeper exploratory wells drilled at
these two locations have encountered aquifers II (130 to 260 m) and III (275 to 425 m), respectively.

Groundwater in aquifers II and III is of pristine quality and it is very encouraging to note that aquifer II has not yet been affected by the deterioration in the chemical quality as witnessed in the top aquifer. This is in spite of the fact that the northeastern part of the area, where Daha is located, is relatively more polluted because of the contribution from the highly polluted river Krishni and the sugar factory at Ramala. Thus, the influence of pollution does not seem to have descended to the underlying aquifer at least in the northeastern part of the area. Difference in the chemistry of shallow groundwater at Daha is so very distinct from that of the aquifer II (Table-9.2) that it practically demonstrates the extent to which pollution has affected aquifer I. Chemistry of aquifers II and III demonstrates acquisition of solutes through water-rock interaction. In comparison, chemistry of samples 44 and 41 from Daha and Barnawa, respectively, shows the influence of pollution superimposed over the chemical signatures imparted by water-rock interaction.

<table>
<thead>
<tr>
<th>Major Ions (mg/l)</th>
<th>Average Shallow Aquifer*</th>
<th>Average Daha Sample 44*</th>
<th>Aquifer II Daha (Near 44)^</th>
<th>Average Barnawa Sample 41*</th>
<th>Aquifer III Barnawa (Near 41)^</th>
<th>Aquifer IV Ganganagar^</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO₃</td>
<td>523</td>
<td>450</td>
<td>183</td>
<td>700</td>
<td>256</td>
<td>189</td>
</tr>
<tr>
<td>Cl</td>
<td>78</td>
<td>85</td>
<td>18</td>
<td>140</td>
<td>21</td>
<td>1980</td>
</tr>
<tr>
<td>SO₄</td>
<td>182</td>
<td>130</td>
<td>50</td>
<td>170</td>
<td>38</td>
<td>8</td>
</tr>
<tr>
<td>Na</td>
<td>197</td>
<td>210</td>
<td>83</td>
<td>320</td>
<td>120</td>
<td>1150</td>
</tr>
<tr>
<td>K</td>
<td>20</td>
<td>8</td>
<td>1</td>
<td>22</td>
<td>1</td>
<td>44</td>
</tr>
<tr>
<td>Ca</td>
<td>31</td>
<td>17</td>
<td>4</td>
<td>55</td>
<td>8</td>
<td>16</td>
</tr>
<tr>
<td>Mg</td>
<td>49</td>
<td>42</td>
<td>11</td>
<td>34</td>
<td>5</td>
<td>19</td>
</tr>
</tbody>
</table>

* Average value for post- and pre-monsoon collections in 2005 and 2006
^ Khan (2004)

Aquifer IV (625 to 675 m) has been intersected outside the study area just east of river Hindon. It has preponderance of Na-Cl, which together account for >3000 mg/l of the total dissolved solids. There is clear evidence of the occurrence of a saline water body
in the area. It is not clear at this stage whether the saline water body itself has been
intersected or the groundwater encountered is a mixture of two deep groundwater bodies
of contrasting chemical compositions, one being dilute like that in aquifer III and the
other being a brine like liquid. In the latter scenario the saline water may be more like
brine which has been encountered at Mubarakpur and Nuh in Haryana and is used for salt
extraction (official website of CGWB). It is also not clear whether aquifer IV extends
westwards in the study area or not and there is no evidence for either of the two
situations. Logically, in view of similar geological and hydrological conditions, aquifer
IV should underlie the area of study.

9.11 POSSIBLE TIME SCALE OF CHEMICAL CHANGES

It needs to be understood as to how much time is involved in getting the chemical
changes registered. There are two ways this problem could be addressed to. One way is
by monitoring the chemical changes and the other by estimating the velocity of the
movement of groundwater. If changes imparted by pollution related factors are taken in
to consideration, which are of prime importance from the point of view of solute
acquisition in the study area, they would depend on two parameters, depth to water table
and vertical permeability. First the pollution effects are to be transmitted to the
groundwater level then transported laterally in prevailing groundwater movement
direction.

Chemical evidence for time involved in pollution-related changes getting
registered are there but these are confusing and often in mutual contradiction. As a matter
of fact, it is to be expected so as pollution is a uncontrolled process difficult to be
quantified. Some speculations based on the chemical data are:

- Sample 25 records K value of 203 mg/l in November, 2005. As fertilizer is
  applied in October prior to sowing of wheat an implication may be that within a
  period of a month the effects could be registered on groundwater chemistry.
- The same sample records a K value of 4 mg/l six months later. This may point to
  the upper time limit of fixation of K.
• The peak of the sugarcane industry is in the months of January and February. The pollution effects caused by it are transmitted to groundwater in three to six months time to get registered in pre-monsoon samples.

• Baraut, where many gur and raw sugar making units are clustered, has Na and SO$_4$ contents of 398 and 394 mg/l, respectively, as recorded in June, 2006. High values of these ions are also recorded at Baghpat and Sarai.

• Using Cl values for post-monsoon 2005 and pre-monsoon 2006 samples, such as, 3, 5, 12, 25, 40 and 41, it may be estimated that in the 6 months period nearly total flushing takes place in some parts of the area and one composition gives way to the other.

An attempt is made here to estimate the velocity of groundwater movement in the area using Darcy’s law. For the average gradient of the area of .00162 m/m, porosity values of 0.30 and 0.35 and hydraulic conductivity values of 20 and 25 m$^3$/day, the velocity of the lateral movement of groundwater comes to 9.2 to 11.6 m/day or about 10 m/day. This implies that groundwater would cover a distance of 1 km in 3 to 4 months time. This gives an approximate idea about the time involved in lateral transport of pollution and is more or less of the same order as speculated from chemical data.

9.12 CONCEPTUAL MODEL

A conceptual model of the study area is presented in Figure-9.2. It shows the four aquifers that have been encountered. The system between rivers Yamuna and Hindon receives a recharge of 350 MCM per annum. This recharge consists of contributions from dissolution of saline soils, fertilizers and various pollutants and contaminants. There are evidence that soap, textile-related, sugar, gur and other industries contribute Na, Ca, Cl, HCO$_3$ and SO$_4$ to the groundwater.
In addition a further 150 MCM is added to the groundwater system as a result of seepages from the Eastern Yamuna Canal. There is chemical evidence that the bulk of this canal seepage goes to the west. Yamuna shows, in general, effluent behavior, for
which there is chemical evidence too in the form of Cl mass balance. Chemical evidence shows that Hindon is effluent in its northern part, beyond that it is influent.

Groundwater moves in the top aquifer at an average velocity of 10 m/day. The movement is westward west of EYC and, in general, eastward on the eastern side of EYC. There are some variations in groundwater movement direction in the eastern side particularly along the right bank of river Hindon. EYC acts as a nearly perfect groundwater divide. The effects of pollution are propagated from one place to other in non-uniform way and there are indications that within a period of 3 to 6 months one chemical quality of groundwater is taken over by the other.

The chemistry of shallow groundwater does not follow any defined trend and wells with contrasting chemical characters occur side by side or the same well shows markedly different chemistries in post- and pre-monsoon seasons. Such characteristics suggest relative lack of lateral hydraulic continuity in the shallow aquifer. This, in turn, results in precluding the stirring of groundwater. This is what is reflected in the form of each well having its own short term chemical characteristics and hardly any signatures which could be considered valid over a long period of time.

Chemistry of aquifers II and III is consistent with the water-rock interaction being the most abundant mechanism for the acquisition of solutes. Water from aquifer II may be ascending to aquifer I bringing about dilution which is chemically indistinguishable. The other way round may also be happening but the chemical composition of aquifer II (TDS = 350 mg/l and Cl = 18 mg/l) indicates that if at all aquifer I is in hydraulic continuity with the underlying aquifer II, it is only on a trivial scale. TDS in aquifer III is about 450 mg/l, 100 mg/l higher than that of aquifer II, which reflects enhanced water-rock interaction. These two aquifers may be in vertical hydraulic continuity of one another.

Aquifer IV has been identified just to the east of the study area across river Hindon. In all likelihood, this aquifer may be extending westward towards river Yamuna. Chemical characteristics of this aquifer are unique in being saline. It is not clear whether the observed salinity is in situ or it is the effect of mixing of water from two aquifers of contrasting chemical characteristics. Water in this aquifer is at a temperature of 52°C,
which is consistent with the normal thermal gradient of 30°C/km over the ambient temperature of 25 to 30°C.

The groundwater system in the area bounded by rivers Yamuna and Hindon is under tremendous stress as against a recharge of about 500 MCM per annum the discharge is about 700 MCM. It is to be conserved at all cost and attempts should be made to ameliorate its chemical degradation because aquifers II and III have been inferred to have relatively low yielding potentials.

9.13 INFERENCES

Some inferences, arrived at after synthesizing the data, are listed below:

• Chemical data show no obvious relationship with inferred relative permeability. Similarly, there are no chemical expression of inferred groundwater troughs and mounds.

• Regularly alternating irrigation by sodic water in the dry season and rainwater during monsoon may induce cycles of precipitation and dissolution of salts and resultant increase and decrease in concentration levels of Na and Ca. Some of the high Na values particularly in the northeastern part are due to cation exchange as a result groundwater-clay interaction. Acquisition of Na ions by this process, however, is relatively insignificant.

• Observed large variations in Ca may at least partially be related to alternating dissolution and precipitation of carbonates during successive winter and summer seasons.

• There is chemical evidence indicating that the bulk of about 150 MCM (per annum) water entering the groundwater system as canal seepage, affects the western part more than the eastern. Mass balance equation shows that this mixing of groundwater and canal seepage has to be in a ratio of 0.95:0.05.

• The saline water body encountered at a depth of >600 m in the area to the east of Hindon may extend to the area of study but could not be contributing to the shallow aquifer as suggested by the paucity of Na-Cl in samples from the area.
The closed box model suggests that recharge tends to ameliorate the concentration levels of solutes in the groundwater but additions of chemical species through uncontrolled anthropogenic processes keep on deteriorating the quality.

It may be calculated that even if 1 mm of saline soil layer is dissolved in infiltrating water, 47,000 tons of Na$_2$CO$_3$ would be dissolved which would yield 20400 tons of Na and 54080 tons of bicarbonate ions to the groundwater. So, saline source could serve as a periodical/seasonal source of Na and HCO$_3$ in the groundwater. On the other hand, per hectare application of K is only about 12 kg, which is not much and under normal circumstances is likely to get fixed and held by soils in the area. Infiltration of K, applied as fertilizer, to groundwater level probably takes about a month. It could get fixed up/equilibrate at the most in 6 months.

Textile industries have contributed Cl and may be some HCO$_3$ and Mg. Bicarbonate could also come as a result of the dissolution of CO$_2$ generated due to the decay of organic matter in garbage dumps.

Discards and separates from sugar and gur industries consist of sulphates of Na and Ca, phosphate of Ca and some CaCO$_3$ and [Ca (OH)$_2$]. There is hardly any doubt that the bulk of SO$_4$ and Na in groundwater in the study area have their origin in sugar and gur industries. This is because of the use of Na-H-SO$_4$ for getting rid of impurities and to bleach the final product. Prevalent use of Na-H-SO$_4$ compared to calcium compounds and relative dispersion of Na and Ca depending on relative solubility of their compounds has resulted in the observed trend of lesser addition of the latter to the groundwater as a pollutant. The effects of sugar and gur industries on groundwater chemistry are transmitted in three to six months time.

Chromium may be getting in to the system from textile-related industries in the area. As far as Al is concerned, its source is rather enigmatic.

Groundwater in aquifers II and III is of pristine quality and it is very encouraging to note that aquifer II has not yet been affected by the deterioration in the chemical quality as witnessed in the top aquifer.
- Aquifer IV comprising saline water may or may not extend to the study area. Logically, in view of geological and hydrological conditions, it should underlie the area of study.
- The velocity of the lateral movement of groundwater comes to 9.2 to 11.6 m/day or about 10 m/day. This implies that groundwater would cover a distance of 1 km in 3 to 4 months time. This gives an approximate idea of the time involved in lateral transport of pollution and is more or less of the same order as speculated from chemical data.