Chapter 5. Summary and Conclusions

In this chapter, results from various geochemical and isotopic investigations of groundwater in the North Gujarat Cambay (NGC) region of Gujarat State in Western India, undertaken as part of this study are summarized and major conclusions that have significantly improved understanding of the geo-hydrological processes in the NGC region and may also contribute to the science of hydrology are highlighted.

It may be recalled that the NGC region is characterized by a unique combination of geological, hydrological, tectonic and climatic features, namely (i) two major deep seated faults defining the Cambay Graben and several sympathetic faults parallel and orthogonal to these; (ii) more than 3 km thick sedimentary succession forming a regional aquifer system in the upper part; (iii) higher than average geothermal heat flow; (iv) intermittent seismicity; (v) emergence of thermal springs; (vi) arid climate with high rate of evapotranspiration; and (v) significant mining of groundwater over the past few decades.

As a result of the extensive groundwater mining, the piezometric levels have declined - by >3 m/yr during the last couple of decades. During the same period, progressive increase in groundwater fluoride concentrations with time and associated endemic fluorosis has been observed. In general, high fluoride in groundwater of the region has been associated with long residence time of the mined groundwater or subsurface injection of thermal waters. Very high amounts of dissolved helium and high groundwater temperatures from some parts of the NGC region were reported earlier (Datta et al, 1980) but, their inter-relationship as well as their possible relationship with basement faults in the region was not understood in terms of tectonic framework and geothermal regime of the NGC region. The Late Quaternary sedimentary record of the region is indicative of increased aridity around Last Glacial Maxima (LGM; ~20 kaBP) (Prasad and Gupta, 1999; Pandarinath et al, 1999b; Wasson et al, 1983; Juyal et al, 2003). However, no palaeoclimatic imprints were reported in hydrological studies.

Based on general topography, geology, lithologs of the drilled tubewells and the water level/ piezometric level data, the area of the foothills of the Aravalli Mountains in the NE was considered as the recharge area of the regional aquifer system with groundwater moving westwards towards the low lying tract linking Little Rann of Kachchh (LRK) – Nalsarovar (NS) – Gulf of Cambay (GC). However, this inference of groundwater recharge and movement, from conventional methods needed to be reinforced and substantiated by determining the age of groundwater by employing radiometric dating methods.

The objective of this study was to generate data for bridging the gap in the knowledge.

To achieve the above objectives, following methodology was adopted.

- Groundwater dating was undertaken employing ^{14}C decay, ^{4}He accumulation and $^{4}He/^{222}Rn$ ratio methods. Laboratory and field procedures for carbonate precipitation (for ^{14}C method) and water sample collection, storage and analyses for other groundwater dating methods were developed and standardized.
- A survey of dissolved helium and temperature of groundwater in the NGC region was undertaken. Simple procedures were developed and standardized for (i) sample collection and storage, and (ii) measurement of helium concentrations in soil-gas and groundwater using commercially available helium leak detector.
- A survey of dissolved groundwater fluoride and electrical conductivity (EC) was undertaken to identify areas of high concentration of fluoride, and to understand its origin. Dissolved fluoride and EC of modern rainfall were also measured to understand the role of dry deposition and/ or amount of rain in controlling the fluoride and EC of rainwater.
- Oxygen and hydrogen isotope ratios ($\delta^{18}O$ and δD) in thermal springs and groundwater samples were measured to identify the possible signatures of the past aridity and to identify the source of thermal spring water. Isotopic analyses of modern precipitation were also carried out to provide a reference for interpretation of the groundwater data.
- A groundwater CFC laboratory was set up as part of this study. Field and laboratory procedures for sample collection, storage, extraction of dissolved CFCs and injection for gas chromatographic analyses were standardized.

Important observations from the above investigations and conclusions drawn are summarized in the following.

5.1 Groundwater Helium and Temperature

Areas of high values of excess helium (He_{ex} >15 ppm AEU) in groundwater are generally associated with areas of high values of groundwater temperatures (>35 °C). Such areas are found to (i) lie along the major basement faults (ECBBF and WCBBF) on both flanks of the Cambay Graben; (ii) overlie sympathetic faults parallel or orthogonal to major faults; and (iii) overlie regions of thermal springs. Despite this geographical correlation between high He_{ex} (see Figure 4.1) and high temperature (see Figure 4.2) of groundwater, no quantitative correlation was seen between the two. Interpretation of such a high value of dissolved helium in groundwater pockets in terms of *in situ* accumulation would imply a long residence time (>100 kaBP) in aquifer. Such a long residence time of groundwater particularly in the recharge area and the observed inliers of old ground waters away from recharge area are not compatible with the hydrogeology and the ^{14}C age (see Figure 4.17). Evidence of near surface uranium mineralization was also not found from ^{222}Rn activity measurements and has also not been reported in any other study from this region ruling out the possibility of near surface uranium mineralization as the source for the observed He_{ex}. It is, therefore, inferred that observed high He_{ex} in certain groundwater pockets is due to injection from deeper sources that derive helium from much larger aquifer/rock volumes.

In this scheme of interpretation, deep subsurface faults provide pathways for upward migration of deeper fluids with high helium concentration and high temperature. Lack of quantitative relationship between He_{ex} and temperature, however, indicates that many localized sources with their varying helium concentration and fluid temperature may be involved in transferring helium and/ or heat from deeper levels to shallower aquifers.

This scheme of interpretation is also presented in the form of a conceptual tectono-hydrothermal model for the NGC region (see Figure 4.20). In this conceptual model, the radiogenic helium produced in a large volume of rocks within or below the basement migrates through micro-cracks into braided and interconnected fractures and dissolves in deep fluids/groundwater. Such deep fluids could either be of lower crust/ upper mantle origin or originate through downward migration of meteoric water from other locations using the pathways provided by deep fractures and fissures. This could result in setting up of a hydrothermal circulation along the deep seated fractures and fissures. The extent to which these deep fluids may have high concentration of helium is governed by interconnectedness of micro-cracks and fractures and the temperature is governed by the depth up to which any particular hydrothermal circulation cell penetrates.

5.2 Fluoride in Groundwater

Based on the understanding that dissolved salt content of groundwater is to some extent related to leaching from the aquifer matrix, the high fluoride concentration in ground waters of NGC region was earlier believed to be related (i) either to the relatively high concentration of fluoride bearing minerals in certain sub-aquifer zones or to the higher residence time (Patel, 1986). Geographical distribution of dissolved fluoride in groundwater of NGC region, however, reveals that areas of high fluoride concentrations (>1.5 ppm) are not related to residence time. Instead, it is observed that the areas of high fluoride and high EC (>2 mS) are aligned around four lines PP', QQ', RR' and SS' (see Figure 4.5 and Figure 4.8) with the central belt around QQ' having groundwater of higher residence time on the western side and lower residence time on its eastern side.

Within the Cambay Basin in the high fluoride belt around the QQ', certain sub-aquifer zones appeared to have high (>1.5 ppm) groundwater fluoride (see Figure 4.6). Based on investigation of 5 tube wells tapping these high fluoride depth zones within a small region, it appears that if a particular well taps the identified high fluoride depth zone, its water shows high concentration. However, this hypothesis could not be confirmed for other areas within this belt or in other parts of the NGC regional aquifer system due to limited availability of tube wells with suitable conditions for investigation. Instead, the fluoride distribution in the NGC region is explained based on a hydrological model comprising a recharge area in the foothills of the Aravalli Mountains, grading into the confined aquifer south westwards towards LRK-NS-GC belt and general disposition of this semi-arid region to enhanced groundwater fluoride concentration. The groundwater in this aquifer system moves through the confined aquifer with the chemical characteristics acquired in the recharge area but progressively aging as it moves away from the recharge area.

The groundwater ages (using ^{14}C, ^{4}He and $^{4}He/^{222}Rn$ methods) progressively increase away from recharge area but the dissolved fluoride concentration does not increase correspondingly. Instead, as mentioned earlier, alternating bands of high and low fluoride concentration in groundwater from confined aquifers are observed. This observation suggests the possibility of an additional control on fluoride concentration in groundwater of NGC region.

The confined groundwater in the central high fluoride groundwater belt (QQ') within the Cambay Basin corresponds to groundwater ^{14}C age in the range 15-25 kaBP (Figure 4.17). The period around 20 kaBP, corresponding to the Last Glacial Maxima (LGM) is known to be a period of enhanced aridity in the NGC region (Prasad and Gupta, 1999; Pandarinath et al, 1999b; Wasson et al, 1983; Juyal et al, 2003). The enhanced aridity is generally associated with (i) increased evaporation; (ii) decreased rainfall; and (iii) increased dry deposition. Some imprints of evaporation and dry deposition even in the present climate were seen in the ionic concentration (Section 4.1.4) and stable isotopic composition (Section 4.1.5) of modern rainfall. The significant control of dry deposition is seen in the variation of fluoride and EC of fortnightly accumulated rain water samples (Figure 4.11). It is, therefore, inferred that groundwater recharged around LGM in the Aravalli foothills during the period of enhanced aridity has since traveled to its present position within Cambay Basin and corresponds to the central (QQ') high fluoride groundwater belt. The groundwater, with relatively low fluoride concentration, on either side of QQ' suggests recharge during less arid climatic regime.

The eastern (RR') high fluoride belt (see Figure 4.5) located in the recharge area corresponds to the modern recharge. The existence of high fluoride groundwater pockets around RR' in the recharge area is an indication that even under the present geo-environmental conditions, groundwater recharged to the regional aquifer system is predisposed to a certain degree of high fluoride content due to combination of (i) leaching; (ii) dry deposition and evaporation prior to recharge; and (iii) increased rock-water interaction at higher temperatures during hydrothermal circulation (as evidenced in thermal springs).

The line PP' (see Figure 4.5) overlies a low lying LRK-NS-GC tract which is the convergence zone for surface and subsurface drainage. The very high level of groundwater fluoride concentration in this belt is possibly due to evaporative enrichment of salts in the stagnant water in the topographically low lying convergence zone and its infiltration into shallower aquifers. Deep groundwater in this low lying tract may have been recharged during a past arid climate phase (^{14}C age >35 kaBP; ^{4}He age 45-110 kaBP depending on helium release factor).

The high fluoride and EC in the E-W belt (SS'), linking the regions of thermal springs (Tuwa and Lasundra) to the low lying area around Nalsarovar, can be attributed to additional source (hydrothermal fluids with relatively high concentration of ions including fluoride) steadily venting into the groundwater in the recharge area of the confined aquifers around Tuwa and Lasundra throughout the Late Quaternary period and the steady movement of the mixed groundwater in the regional aquifer system. The fluoride contribution by the hydrothermal fluids is so prominent and steady that imprints of the wet/arid excursions in climate are not visible along SS'. Instead a continuous belt of higher fluoride (>1.5 ppm) and high EC (>2 mS) is seen.

It is, therefore, concluded that the high fluoride in groundwater of NGC region is not governed by its residence time in the aquifer but arises from a combination of (i) predisposition of this semi-arid region to high groundwater fluoride resulting from mineral assemblage in surface soils and aquifer matrix aided by general aridity, in particular the enhanced aridity around LGM; (ii) injection of hydrothermal fluids into groundwater; and

(iii) evaporative enrichment in the low lying convergence zone and infiltration into groundwater.

5.3 Isotopes of Oxygen and Hydrogen in Groundwater and Precipitation

The amount weighted average values for the modern rainfall in the NGC region are: $\delta^{18}O = -4.3 \pm 2.1‰$, $\delta D = -33 \pm 16‰$ and *d*-excess $=1.2 \pm 4.8‰$. This *d*-excess value and both the slope (7.6 ± 0.6) and the intercept ($-2.9 \pm 2.2‰$) of the local meteoric water line (LMWL) are lower than the average values of global meteoric water line (GMWL) and are interpreted as isotopic imprints of evaporation from falling raindrops under the present semi-arid climatic regime.

The groundwater samples from the NGC region exhibit a range of variation significantly narrower than that for precipitation and both $\delta^{18}O$ and δD are higher than that for modern precipitation (Figure 4.15). The average value of *d*-excess of all groundwater samples ($-4.5 \pm 11‰$) is also lower than that of precipitation samples. These isotopic characteristics for groundwater in the NGC region indicate mixing of rain water from different events in the soil and additional evaporation during the infiltration process confirming the predisposition of the region to evaporation, prior to groundwater recharge.

It is also seen (Figure 4.16) from the geographical distribution of $\delta^{18}O$ and *d*-excess that groundwater around a linear belt (QQ') is characterized by relatively lower values of *d*-excess and higher values of $\delta^{18}O$. Since evaporation of water results in low values of *d*-excess and higher $\delta^{18}O$ (see Section 2.4), the groundwater around QQ' represents relatively increased evaporation (indicative of enhanced aridity) either during rainfall or during groundwater recharge compared to that on either side of this belt. As mentioned earlier (see Section 5.2), the ^{14}C age of the confined groundwater around QQ' has been estimated to be in the range 15-25 kaBP corresponding to the known arid phase in the past. Taking a holistic view of the data, i.e., 15-25 kaBP groundwater age, its lowered *d*-excess and higher $\delta^{18}O$, it is concluded that groundwater recharged in the Aravalli foothills around LGM with signatures of enhanced aridity has since traveled to its present position. This corroborates enhanced aridity in the past as one of the important causes for the occurrence of enhanced fluoride and EC of groundwater around QQ'.

As mentioned above (see Section 5.2) , the geothermal waters in the NGC region too have high fluoride and EC, and higher values of these geochemical parameters around the line SS' were ascribed to continuous admixture of geothermal waters (in the region around Tuwa and Lasundra thermal springs) to the recharged groundwater. The isotopic exchange during interaction of geothermal waters and silicate rocks at elevated temperatures is known to impart a characteristic shift in the values of $\delta^{18}O$, δD and *d*-excess (see Section 4.2.3). The isotopic exchange with silicate rocks at elevated temperatures results in increase in $\delta^{18}O$, decrease of δD and a corresponding decrease in the *d*-excess values of thermal waters. In the NGC region two areas of significantly high groundwater temperature (>40°C) have been identified. These are: (i) the thermal springs at Lasundra and Tuwa on the eastern flank; and (ii) thermal artesian wells on the western flank of Cambay Basin. The thermal springs are seen to be slightly enriched in ^{18}O and lowered in *d*-excess (average $\delta^{18}O = -1.4 \pm 0.4$ ‰; *d*-excess = -4.1 ± 3.2‰ for 6 samples) compared to ground waters in the surrounding region. On the other hand, thermal artesian wells do not have much different isotopic composition (average $\delta^{18}O = -2.4 \pm 1.0$ ‰; *d*-excess = -6.5 ± 7.3‰ for 8 samples) compared to the other groundwater samples in NGC region. Statistically, these average values are indistinguishable from the average groundwater values for the entire NGC region, but local enrichment of ^{18}O and lowering of *d*-excess in the areas with thermal waters is seen in Figure 4.16.

The enrichment of ^{18}O in the thermal springs/ artesian wells is also associated with high concentration of dissolved helium. Similar enrichment of ^{18}O and lowering of *d*-excess around QQ', however, is not associated with high helium or high temperature and shows age corresponding to LGM and therefore, attributed to past climatic shift. The geothermal waters with enriched ^{18}O and low *d*-excess, on the other hand correspond to modern (on eastern flank) to >45 kaBP age (on western flank).

Thus, isotopic evidence of water-rock interaction in geothermal waters of the NGC region is indicated, though not very strong. It is, therefore, inferred that the $\delta^{18}O$ in thermal springs at Tuwa and Lasundra is perhaps a trend towards isotopic equilibrium between ^{18}O depleted meteoric water and ^{18}O enriched rocks at higher temperatures.

5.4 Groundwater Dating

5.4.1 ^{14}C Dating

It is observed that the succession of sand/ silty-clay layers forming multilayered aquifer system is nearly parallel to the regional inclination of ground surface and the sampled tube wells tap almost the same set of water bearing formations across the NGC region (Figure 1.6). The groundwater in these nearly parallel layers of confined aquifers is recharged largely from the sediment-rock contact zone in the foot hills of Aravalli Mountains, and after the confinement becomes effective, moves with approximately the same velocity. This geohydrological model of the regional aquifer system appears to be justified because, the unconfined aquifers in the regions of Cambay Basin and westwards are almost completely dried up (as evident from several dried up and abandoned dug wells). Since the tubewells tap all the water bearing horizons intercepted within their maximum depth, these are treated as pumping a single aquifer unit, within which the ^{14}C ages progressively increase in the flow direction. The estimated groundwater ^{14}C ages progressively increase from <2 kaBP in the ENE (along Aravalli foothills) to >35 kaBP in the WSW direction towards the low-lying tract linking LRK-NS-GC (Figure 4.17).

From hydro-geological considerations (see Section 1.2), it seems that the confinement of the regional aquifers in the NGC region becomes effective near the ECBBF. The ^{14}C age of the groundwater starts progressively increasing from ~2 kaBP westwards of ECBBF. Within the Cambay Basin, the age isolines are nearly parallel to each other and the horizontal distance between the successive 5 kaBP isolines is nearly constant giving a regional flow velocity in the range 2.5 – 3.5 m a^{-1} under the prevailing average hydraulic gradient of 1 in 2000 (GWRDC, unpublished data). West of WCBBF, the ^{14}C ages increase rapidly, roughly in agreement with the distribution of transmissivity of the aquifers obtained from the pump test data, progressively decreasing from ~1000 m^2 d^{-1} east of the ECBBF to <200 m^2 d^{-1} west of the WCBBF (GWRDC, unpublished data).

5.4.2 ^{4}He Dating

It is seen that the 5 ppmAEU He_{ex} isoline runs nearly along the WCBBF and corresponds to ^4He age of ~15 kaBP for helium release factor Λ_{He} = 1, and ~37 kaBP for Λ_{He} = 0.4 (Figure 4.1 and Figure 4.18). Except for pockets of anomalous groundwater helium concentrations, the ^4He ages (Figure 4.18) are in close agreement with the ^{14}C ages (Figure 4.17) for Λ_{He} = 0.4 when no crustal flux is considered. Ignoring the crustal flux is justified because the sampled wells up to the WCBBF in the in the NGC region tap shallow depth compared to total depth (~3 km) of the Cambay basin and hence are free from the crustal influence. For transmissivity values (~200 m^2d^{-1} – 1000 m^2d^{-1}) of the aquifers and crustal helium flux of 3.0 x 10^{-8} cm^3STPHe $cm^{-2}y^{-1}$ for sedimentary basin (Takahata and Sano, 2000), the groundwater flow entrains insignificant amount of helium and therefore, groundwater ^4He ages are almost unaffected by the deep crustal ^4He flux.

5.4.3 ^{4}He /^{222}Rn Dating

A gradual $^4He/^{222}Rn$ age progression from the recharge area towards the WCBBF is observed in the major part of the study area (Figure 4.19), similar to that for ^{14}C ages (Figure 4.17) and ^4He ages (Figure 4.18).

5.5 Important Contributions

In the forgoing, main inferences from various geochemical and isotopic investigations of this study were summarised. The major contributions of this study, are enumerated in the following.

5.5.1 A Geo-hydrological Model of Aquifer System in NGC Region

The regional aquifer system of NGC region comprises a sequence of unconfined and confined sub-aquifers. The recharge area of the confined aquifers lies in the foot hills of the Aravalli Mountains in the east. The confinement of aquifers becomes effective only towards west of the ECBBF. Beyond the region of effective confinement, the groundwater in the aquifer system preserves the geochemical and isotopic characteristics acquired at the time of recharge in the recharge area. The groundwater ages progressively increase in the general flow direction nearly along WSW up to the low lying tract of the LRK-NS-GC, which is also a zone of convergence with groundwater flow from its both the sides.

However, in certain pockets overlying the intersecting basement faults, deeper crustal fluids do get injected into the aquifer system and significantly alter some of the geochemical properties of the groundwater of the region.

5.5.2 A Conceptual Tectono-hydrothermal Model of NGC Region

Deeper crustal fluids injected into the groundwater of NGC region have been shown to affect temperature, dissolved helium, water isotopes, fluoride and EC of groundwater in certain pockets. The localization of these pockets along intersecting deep seated basement faults on the two flanks of the Cambay basin is conceptualised in the form of a tectono-hydrothermal model of the NGC region.

This tectono-hydrothermal model (Figure 4.20) involves hydrothermal circulation of water of meteoric origin into deeper crustal layers, its interaction with deeper fluids and its return flow back to shallow depths, either into groundwater or as thermal springs. The faults and fractures provide the pathways for (i) downward percolation of shallow groundwater (of meteoric origin) as also (ii) for the upward migration of return flow with changed geochemical properties due to interaction with deeper fluids. In this manner the hydrothermal circulation imprints its signatures on geochemical properties of groundwater localised over regions of deep seated faults and fractures on both flanks of the Cambay basin where the basement is at relatively shallow depth. The geochemical properties include enhanced helium (produced in large volume of rocks within or below the basement), enhanced temperature (resulting from geothermal gradient ~60°C km^{-1}

during hydrothermal circulation), and enhanced fluoride as also EC and some isotopic characters (acquired from rock-water interaction at elevated temperature). In this model the sedimentary cover overlying the basement rocks acts to diffuse the upward migrating plume of deeper fluids because of the primary porosity of the granular fabric. Whereas, the secondary porosity due to fractures and fissures in the crystalline basement restricts the location of upward migrating plumes. This explains the localization of various anomalies observed on both the flanks and their absence over the Cambay basin between the ECBBF and the WCBBF.

The temperature and geochemical as well as isotopic properties of injected plume depends on interconnectedness of micro-cracks and fractures and the depth of penetration of a hydrothermal circulation cell from where the deeper fluids rise. These factors will locally affect the temperature, geochemical and isotopic characteristic of individual hydrothermal cells. This explains absence of statistical correlation between anomalous helium and temperature of groundwater even while a significant geographical correlation exists between the two.

5.5.3 Origin of High Fluoride in Groundwater from NGC Region

The high fluoride concentration in groundwater of NGC region around the E-W line SS' (Figure 4.5) is explained by a continuous injection throughout Late Quaternary of hydrothermal fluids from around the thermal springs of Lasundra and Tuwa and the groundwater flow in the regional aquifer as governed by hydraulic gradient from the recharge area in the Aravalli foothills towards the Nalsarovar in low lying LRK-NS-GC tract. This mechanism, however, does not explain the observed distribution of enhanced groundwater fluoride around the three nearly NNW-SSE parallel lines PP', QQ' and RR'. This distribution is explained by: (i) predisposition of this semi-arid region to high groundwater fluoride arising from mineral assemblage in surface soils and in aquifer matrix, aided by general aridity particularly in the recharge area around RR'; (ii) enhanced aridity around the LGM leading to recharge of groundwater enriched in fluoride resulting from enhanced evaporation as well as dry deposition and flow of this groundwater to its present location around QQ' during the past 20 ± 5 kaBP; and (iii) evaporative enrichment of stagnant surface water in the low lying LRK-NS-GC convergence zone and infiltration of a part of it into groundwater.

5.5.4 Palaeo-climatic Imprints in Groundwater from NGC Region

As mentioned above, groundwater around the belt QQ' within Cambay Basin corresponds to ^{14}C ages around LGM (20 ± 5 kaBP) which is known to be a period of enhanced aridity in the palaeoclimatic history of the NGC region. The confined groundwater in this belt has characteristic geochemical (high fluoride and high EC) and isotopic (high $\delta^{18}O$ and low *d*-excess) signatures that are different from signatures of these parameters on either side. The alternating bands of groundwater with distinguishable geochemical and isotopic properties can only be explained as imprints of the past climate alternating between arid and humid phase, which modifies the geochemical and isotopic properties of the water infiltrating from the recharge area (Aravalli foothills) of the confined aquifer. The groundwater recharged during different climatic regime flows subsequently in the confined regional aquifer system giving rise to observed alternating bands of groundwater with distinctly different chemical properties. Thus, groundwater around the belt QQ' within Cambay Basin, indicate its recharge during enhanced aridity around LGM.

In addition to the important contributions, as mentioned above, it has also been possible, as a result of this study, to identify areas of future research that will reduce uncertainties in the present understanding of geohydrological processes. This is elaborated in Chapter 6.