Groundwater in and Around Cambay Basin, Gujarat: Some Geochemical and Isotopic Investigations

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Introduction

This thesis is based on the geochemical and isotopic investigations of groundwater from North Gujarat-Cambay (NGC) region in the Western India. The NGC region is characterized by a unique combination of geological, hydrological, tectonic and climatic features, namely (i) two major deep seated faults (East Cambay Basin Bounding Fault; ECBBF and West Cambay Basin Bounding Fault; WCBBF) 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 (vii) significant mining of groundwater over the past few decades.

As a result of 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 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). 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.

Objectives

The objective of this study was to bridge the existing gap in the knowledge as discussed above by carrying out specific geochemical and isotopic investigations. This study aimed to (i) determine the distribution of helium and temperature of groundwater and relate the anomalies with the tectonic framework of the region; (ii) determine the distribution of various geochemical tracers that could help identify the origin of groundwater fluoride; (iii) determine the direction and rate of movement of groundwater in the regional aquifer system; and (iv) search for hydrological proxies of past climates.

Methodology

To achieve the above objectives, following methodology was adopted.

- A survey of dissolved helium and temperature of groundwater in the NGC region was undertaken to delineate areas with anomalies in these parameters and to understand their inter-relationship with the regional tectonics. 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.
- Groundwater dating was undertaken employing ^{14}C decay, ^{4}He accumulation and $^{4}He/^{222}Rn$ ratio methods to determine regional groundwater flow parameters. 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.
- 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.

Results and Conclusions

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

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} and high temperature of groundwater, no quantitative correlation is 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 of groundwater. 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 interpretation is also presented in the form of a conceptual tectono-hydrothermal model for the NGC region. In this 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.

Groundwater Fluoride

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 (ii) to the higher residence time of groundwater. Geographical distribution of dissolved fluoride in groundwater of NGC region and its radiometric age, however, reveals that areas of high fluoride concentrations (>1.5 ppm) are not related to residence time. It is observed that the areas of high fluoride and high EC (>2 mS) are aligned around four linear belts. Three of these linear belts are trending NNW-SSE and roughly parallel to recharge zone in the Aravalli foothills. These groundwater belts of high fluoride are separated by low fluoride groundwater, forming alternate bands of high and low fluoride in groundwater. The fourth linear belt is trending EW from the region of thermal springs (Tuwa and Lasundra) to the low lying area around Nalsarovar.

This 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 progressively corresponding to groundwater age. Instead, 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 within the Cambay Basin corresponds to groundwater ^{14}C age in the range 15-25 kaBP. 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. 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 are seen in the ionic concentration and stable isotopic composition of modern rainfall. The significant control of dry deposition is seen in the variation of fluoride and EC of fortnightly accumulated rain water samples. 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 high fluoride groundwater belt. The groundwater, with relatively low fluoride concentration, on either side of this belt suggests recharge during less arid climatic regime.

The eastern high fluoride belt located in the recharge area corresponds to the modern recharge. The existence of high fluoride groundwater pockets 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 western high fluoride belt 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 area and its subsequent infiltration into shallower aquifers.

The high fluoride and EC in the E-W belt, linking the regions of thermal springs 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 EW belt. 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 of salts in the stagnant water in the low lying convergence zone and its infiltration into groundwater.

Stable Isotopes of Oxygen and Hydrogen

The amount weighted average values for the modern rainfall in the NGC region are: $\delta^{18}O$ = –4.3 ± 2.1‰, δD = –33 ± 16‰ and *d*-excess =1.2 ± 4.8‰. This *d*-excess value and both the slope (7.6 ± 0.6) and the intercept (–2.9 ± 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 exhibit a range of variation in isotopic composition significantly narrower than that for precipitation and both $\delta^{18}O$ and δD are higher than that for modern precipitation. The average value of *d*-excess of all groundwater samples (–4.5 ± 11‰) is 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 from the geographical distribution of $\delta^{18}O$ and *d*-excess that groundwater around a linear belt within Cambay Basin 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 $\delta^{18}O$, the groundwater around this belt within Cambay Basin represents relatively increased evaporation (indicative of enhanced aridity) either during rainfall or during groundwater recharge compared to groundwater on either side of this belt. The ^{14}C age of the confined groundwater around this belt 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.

The isotopic characteristics of thermal waters indicate a trend towards isotopic equilibrium between ^{18}O depleted meteoric water and ^{18}O enriched rocks at higher temperatures.

Groundwater 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. 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 farther 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 groundwater 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. From hydro-geological considerations, it seems that the confinement of the regional aquifers in the NGC region becomes effective near the 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. 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.

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. Except for pockets of anomalous groundwater helium concentrations, the ^4He ages are in close agreement with the ^{14}C ages 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, the groundwater flow entrains insignificant amount of helium and therefore, groundwater ^4He ages are almost unaffected by the deep crustal ^4He flux.

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

Important Contributions of this Study

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.

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.

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.

Origin of High Fluoride in Groundwater from NGC Region

The high fluoride concentration in groundwater of NGC region around the E-W line 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. 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; (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 within Cambay Basin 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.

Palaeo-climatic Imprints in Groundwater from NGC Region

The confined groundwater around a belt within Cambay Basin 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 are 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 liner belt within Cambay Basin, indicate its recharge during enhanced aridity around LGM.