Chapter 1. Introduction

Figure 1.1 Map showing study area and the geographical locations of some important landmark features such as major rivers, towns, lakes etc. The inset map shows location of the study area within India.

Figure 1.2 The Geological Map of the study area. A large part of the area is covered by Quaternary alluvium. Proterozoic rocks (mainly granitic) lie along the Aravalli foothills in the east and the upper Cretaceous Deccan Traps in the SW and SE corner. A small patch of Mesozoic sandstone is also seen towards the west. A sub-surface lithological section along AA' is shown in Figure 1.6.


Figure 1.4 Tectonic framework of the NGC region. Two major bounding faults, namely, the ECBBF and the WCBBF define the Cambay Basin. Several sympathetic faults parallel or orthogonal to the major faults also exist. Most thermal springs are seen to be located in the vicinity of known basement faults.

Figure 1.5 Map showing River drainage and surface elevation in the NGC region. The low lying belt linking LRK-NS-GC is less than 40 m in elevation and forms the zone of convergence for surface drainage from both the sides.

Figure 1.6 Sub-surface lithological cross-section along line AA' (in Figure 1.2) from Nayaka to Chadotar. The sandy layers forming aquifer horizons are seen to be laterally continuous and vertically interspersed with thin semi-permeable clay/silt layers that may not have lateral continuity over a large area. The uncertainty of continuity in view of large separation is indicated by (?). Tubewells tap all water bearing horizons up to their maximum depth.

Chapter 2. Theory

Figure 2.1 Radioactive decay series of Uranium and Thorium showing production of α particles (the helium nucleus) and the 222Rn. Note that 8, 7 and 6 helium atoms are produced in the decay chains of 238U, 235U and 232Th respectively. 222Rn is produced in the decay chain of 238U.

Figure 2.2 Global distribution of endemic fluorosis. Note that the most affected areas are in the arid/semiarid regions.

Figure 2.3 The linear regression line between δ18O and δD of global precipitation samples. Data are weighted average annual values for precipitation monitored at 219 stations of IAEA/WMO global network. Redrawn from Rozanski et al (1993).
Figure 2.4  Atmospheric mixing ratios of CFC-11, CFC-12 and CFC-113 for Northern and Southern Hemisphere (NH and SH) atmosphere. Redrawn from United States Geological Survey (URL: http://water.usgs.gov/lab/software/air_curve/).

Chapter 3. Experimental Procedures

Figure 3.1  Various tools and gadgets used for sampling of groundwater and soil air. 1 – Metallic rod; 2 – Hand operated suction pump; 3 – copper tube perforated at the bottom; 4 – Hammer; 5 – Three-way valve; 6 – Pinch cock; 7 & 8 – Metallic rod with a PVC tube tied on it for diverting groundwater flow from pump outlet; 9 – 1.2-litre soda-lime glass bottle; 10 – three layers of the aluminium seal; 11 – Hand operated crimping tool for aluminium seal; 12 – Bromo-butyl synthetic rubber stopper; 13 & 14 – Nylon ropes connected to mouth and base of the collection glass bottle for extraction of water from the desired depth of the water column in dug wells, lakes and streams; 15 – Heavy weight tied to the base of the glass bottle; 16 – The water collection glass bottle; 17 – Heavy weight tied to the mouth of the bottle. Weights (15 and 17) are meant to keep the bottle vertical while lowering or lifting and for reverting the bottle at the desired depth in the water column.

Figure 3.2  Residual helium concentrations on long term storage in soda-lime glass sampling bottles with bromobutyl rubber stopper and triple aluminium protection seal. Two separate sets of multiple samples were collected from two different sources. Individual samples were analysed subsequently at various intervals during a period of 20 months after the sample collection. The maximum observed loss of helium is given by the steepest line on this log-linear plot which corresponds to a loss of <0.15 % per day. The average loss, obtained by averaging the rates from the two best fit lines is, however, 0.075% per day.

Figure 3.3  Schematic diagram showing layout of (a) drawing of equilibrated air sample and (b) helium measurement through helium leak detector for water/air/gas samples.

Figure 3.4  (a) Comparison of measured and calculated dilution curves; and (b) the results of a set of six experiments undertaken for estimation of Henry's law constant for water-helium system. The experimental values are similar to the known value of 105.7 at 25°C (Weiss, 1971). These experiments validate the calibration of the helium measurements and the robustness of the analytical procedure.

Figure 3.5  (a) Picture showing a specially designed foldable stand with conical aluminium base which holds the high density PVC bag filled with 100 litre of water sample; The supernatant water is decanted by piercing the bag after the carbonate precipitates settle in the conical base of the bag; (b) Carbonate precipitates are transferred from PVC bag into 1.2-litre soda-lime glass bottle without exposure to atmosphere.

Figure 3.6  The groundwater sampling system for CFC analyses. (a) Relative position of 3-way valve and ampoule for flushing the ampoule with ultrapure nitrogen and filling with groundwater sample. (b) Relative...
position of 3-way valve and ampoule for evacuating the neck of ampoule and sealing it. (see the text for details).

Figure 3.7 A gas purification subsystem, purge and trap subsystem and the gas chromatograph are the major components of the Groundwater CFC Laboratory. A blow up of the purge and trap system is shown in Figure 3.8. Complete line drawing of the CFC analytical set up is shown in Figure 3.9.

Figure 3.8 Blow up of the Purge and Trap System showing its constituents. 1 – Vacuum gauge; 2 – Carrier gas injection port; 3 – Pressure gauge; 4 – Multi-port valve; 5 – Bubblers; 6 – Gas sampling loops; 7- Valco valves; 8 – Suction port; 9 – Water inlet port; 10 – Purge tower; 11 – CFC trap in Dewar flask; 12 – Switch for Valco valves; 13- heating tape; 14 – Drain collector.

Figure 3.9 Line drawing of the complete CFC analytical system.

Figure 3.10 Three different chromatograms for 2 ml injection of CFC standard. Two CFC species of interest (F-12 and F-11) are identifiable from known elution time but F-113 peak is barely visible though it also can be identified from its known retention time.

Figure 3.11 Three different chromatograms for 5 ml injection of CFC standard. Three CFC species of interest (F-12, F-11 and F-113) can be identified from their known retention time. Though identifiable, F-113 peak is small.

Figure 3.12 Three different chromatograms for 5 ml injection of CFC standard. Three CFC species of interest (F-12, F-11 and F-113) can be identified from their known retention time. Though identifiable, F-113 peak is small.

Figure 3.13 Peak area calibration curve for estimating CFC concentration in the injected gas sample. Concentration in the standard gas mixture used for calibration corresponds to: F-12 (4.834E-10 ml.ml^{-1}); F-11 (2.303E-10 ml.ml^{-1}); F-113 (7.3E-11 ml.ml^{-1}).

Chapter 4. Results and Discussions

Figure 4.1 Isoline map of He_{ex} in groundwater of the NGC region. The isoline of 5 ppmAEU He_{ex} runs almost along the WCBBF. Pockets of He_{ex} >50 ppmAEU overlap with pockets of high (>40°C) groundwater temperature (Figure 4.2). Sampling locations are indicated by dots. L, T and Z respectively indicate the locations of thermal springs at Lasundra, Tuwa and a tubewell in Zinzawadar.

Figure 4.2 Isoline map of groundwater temperature in the NGC region. Large areas on both east and west flanks of the Cambay basin show groundwater temperature >35°C. Temperatures >40°C are seen around thermal springs. Sampling locations are indicated by dots. L and T respectively indicate locations of thermal springs at Lasundra and Tuwa.

Figure 4.3 Groundwater temperature vs. He_{ex} in groundwater from NGC region.

Figure 4.4 Depth of the sampled wells (bgl) vs. He_{ex} in groundwater in NGC region.
Figure 4.5 Isoline map of the fluoride concentration in groundwater – NGC region. Patches of high fluoride concentration (>1.5 ppm) appear to be aligned around four lines (PP', QQ', RR' and SS') separated by areas with low fluoride. Acronyms: Ch – Chadotar; Ku – Kuwarva; Da – Dantiwada; Dh – Dharoi; Ka – Kadana; L – Lasundra; T – Tuwa.

Figure 4.6 (a) Depth of sampled wells (bgl) vs. fluoride concentration for all sampled wells. (b) Samples with fluoride concentration <1.5 ppm area removed from plot (a). Several aquifer depth zones with >1.5 ppm groundwater fluoride are identified within the Cambay basin.

Figure 4.7 A comparison of groundwater fluoride content and fluoride rich sub-aquifer depth zones tapped in selected five tubewells. The shallowest tubewell–A does not tap any of the fluoride rich sub-aquifer depth zones and has the lowest fluoride content in groundwater. Tubewell–B, tapping zones I and II, has the highest fluoride in groundwater. The deepest tubewell E, which taps sub-aquifers from depth zones –I and –II but does not tap zone–I, has comparatively lower fluoride content of 1.5 ppm.

Figure 4.8 Isoline map of EC of groundwater from study area. Areas of high EC overlap in general with areas of high fluoride shown in Fig. 4.5. Acronyms for the locations are: Da – Dantiwada; Dh – Dharoi; Ka – Kadana; L – Lasundra; T – Tuwa. The geographical co-variation of EC and fluoride along Lines 1-3 and SS' is shown in Figure 4.9.

Figure 4.9 Geographical co-variation of fluoride and EC of groundwater along the four lines (1, 2, 3 and SS' in Figure 4.8) in NGC region. Distances are measured from the western end of each line and the arrow marks the point of intersection of each of these lines with QQ'. It is seen that the two parameters co-vary in the Cambay basin and the central belt of high fluoride – high EC is flanked by relatively lower values on either side.

Figure 4.10 A scatter plot of fluoride concentration vs. EC in groundwater from the NGC region, showing absence of correlation between the two.

Figure 4.11 Variation in the amount of rainfall, dissolved fluoride and EC in the fortnightly accumulated precipitation samples at the dam sites of Dantiwada, Dharoi and Kadana. The locations of these dam sites within NGC region are shown in Figure 4.8.

Figure 4.12 Variation in the amount of rainfall, dissolved fluoride and EC in the fortnightly accumulated precipitation samples at the dam sites of Bhadar, Shetrunji and Ukai. The locations of these dam sites are shown in Figure 4.14.

Figure 4.13 Relationship between dissolved fluoride and EC in modern rainwater collected at the six dam sites in and around NGC region.

Figure 4.14 The highest and the average fluoride content at various dam sites and their relative latitudinal positions with reference to the NGC region.

Figure 4.15 δ¹⁸O vs. δD and δ¹⁸O vs. d-excess for precipitation (a and b) and for groundwater samples (c and d). The average values for
respective parameters in each figure are shown by big circle. In case of precipitation, the average value is amount weighted.

**Figure 4.16** Isoline map of (a) $\delta^{18}$O and (b) $\delta$-excess of groundwater from NGC region. Line QQ' representing the central linear belt of high fluoride (in Figure 4.5) and high EC (in Figure 4.8) is superposed for comparison.

**Figure 4.17** Isoline map of groundwater Radiocarbon ages, along with sampling locations. Sampling locations of an earlier study (Borole et al, 1979) are enclosed in an ellipse. Within the Cambay basin the groundwater $\Delta^{14}$C ages increase progressively towards the WCBBF, beyond which a limiting $\Delta^{14}$C age of $>35$ kaBP is observed. Dots indicate sampling locations. L, T and G respectively indicate the locations of thermal springs at Lasundra, Tuwa and a free flowing thermal artesian well at Gundl. The groundwater age gradient along BB' is shown in Figure 4.21.

**Figure 4.18** Isoline map of estimated $4\text{He}$ ages of groundwater from the NGC region (for helium release factor: $\Lambda_{\text{He}} = 1$). Isoline of 15 kaBP runs almost along the WCBBF. This isoline will correspond to the $4\text{He}$ age of $\sim 37$ kaBP for $\Lambda_{\text{He}} = 0.4$ (See Section 2.6.2). Dots indicate sampling locations. L, T and Z respectively indicate the locations of thermal springs at Lasundra, Tuwa, and the tubewell in Zinzawadar. The groundwater age gradient along BB' is shown in Figure 4.21.

**Figure 4.19** Iso-line map of groundwater $4\text{He}^{222}\text{Rn}$ ages in the NGC region for $\text{Th}/U = 7.1; \Lambda_{\text{He}}/\Lambda_{\text{He}} = 0.4; \rho = 2.6 \text{ g cm}^{-3}$ and $n = 20\%$. Samples with $>10$ ppmAEU 'excess He' and/or $>2000$ dpm/l $^{222}\text{Rn}$ were excluded during contouring. Dots indicate sampling locations. The groundwater age gradient along BB' is shown in Figure 4.21.

**Figure 4.20** A conceptual tectono-hydrothermal model to explain the origin and observed geographical distribution of Heex and high temperature of groundwater in NGC region. The set of braided fractures joining the major fault traces is indicative of migration of helium from micro-cracks into macro-fractures, eventually joining the conduits provided by the major fractures and faults. The joining-in fractures (indicated by an arrow with a circle at top) thus acts as the pathway for build-up of helium in deep groundwater. Another set of braided fractures emanating out of the major fault traces is indicative of pathway that the upward migrating helium follows through the overlying sedimentary cover leading to dispersion/diffusion. In both cases, the size of circles schematically depicts the changing helium concentration during upward migration of deeper fluids. The arrows leading to major faults depict the preferred pathways for migration of radiogenic helium derived from a large area. The thick arrows indicate the hydrothermal circulation along major faults, facilitated by high heat flux.

**Figure 4.21** Plot of groundwater age progression along line BB' (shown in Figure 4.17, Figure 4.18 and Figure 4.19) for comparing the age gradients for model $\Delta^{14}$C ages, $4\text{He}$ ages for $\Lambda_{\text{He}} = 1$ and $4\text{He}^{222}\text{Rn}$ ages both for $\Lambda_{\text{He}} = 1$ and $\Lambda_{\text{He}} = 0.4$. 