CHAPTER 4

EXPERIMENTAL METHODS

4.1 Ambient Gamma level

The ambient gamma exposure in the environs of granite and sand quarrying regions of Chitradurga, Shimoga, Chikmagalur and Hassan districts was measured using an environmental radiation dosimeter ER 709 (Section 3.1). The instrument has the sensitivity of 1 $\mu$R h$^{-1}$ and was calibrated using $^{137}$Cs standard source.

The measurements were made 1 m above the ground level, and the area chosen were of both disturbed and undisturbed nature. Due to the random nature of radioactive decay, the radiation exposure rate changes rapidly in time. In order to average out the exposure level, about 10-15 readings were recorded at each location in a given area. This was repeated at many other locations within a given area in order to obtain a representative value for that region. The geometric mean of all the values was calculated so as to reduce small-scale variation of the exposure rate within the site. The dosimeter readings obtained in $\mu$R h$^{-1}$ were converted into dose rate using the conversion factor $1\mu$Rh$^{-1} = 10$ nGy h$^{-1}$.
4.2 Sample Collection

Samples from various selected sites situated in and around Malnad biosphere were collected in order to measure individual activity of radionuclides in them. In the present study, 31 locations were covered in the Chitradurga district. 10 locations each from Shimoga, Chikmagalur and Hassan districts were covered in the present study. The environmental samples studied were both from Hydrosphere and Bio-sphere, namely, soil, granites, rocks, minerals, and water from openwells and borewells. The procedure adopted in collecting the samples was as follows.

4.2.1 Soil

Soil analysis for the presence of radionuclides is very important as the major part of radiation dose received by man either directly or indirectly is due to this medium. The sampling sites selected were undisturbed, open fields away from public roads and buildings. At each region, 5-7 spots were chosen for grab sampling. A pit of 30 x 30 x 15 cm was dug in each spot and the whole soil was collected. The soil obtained from similar other spots were thoroughly mixed and about 5 kg of the resulting composite soil was brought to the laboratory in a sealed polythene bag. The informations about sample
description, area of sampling, code, date and time of sampling were noted on the samples and in the sample register.

4.2.2 Granite and mineral samples

Granite, Copper ore, Gold ore, Silver ore and Iron ore samples were collected from different sampling stations. Each sample was washed in distilled water and dried in an oven at 110°C to ensure that moisture was completely removed. The samples were crushed, homogenized and sieved through a 200 mesh, which is the optimum size enriched for heavy minerals. Weighted samples were placed in polyethylene bottles. The bottles were completely sealed for 4 weeks to reach secular equilibrium, where the rate of decay of the daughters equals to that of the parent. This step is necessary to ensure that radon gas confined within the volume and the daughters will also remain in the sample. Later on these samples were subjected for gamma spectrometry studies.

Minerals were collected from various mining areas initially by studying some of their physical properties and later were confirmed at Mines and Geology Department. The following tests were conducted for the macroscopic identification of minerals.
**Streak test:** Grinding a small amount of a mineral into a powder on a porcelain streak plate and observing the colour of the powder.

**Hardness test using Mohs scale of mineral hardness:** As, all minerals will fall somewhere along the Mohs scale, based on their ability to scratch any mineral with a number lower than theirs and their inability to scratch any mineral with a number higher than theirs.

**Lustre:** It refers to the absorption, reflection, or refraction of light by the surface of a mineral.

### 4.2.3 Water

**Openwell and Borewell waters:** Water samples from Openwells and borewells were collected from all the 38 sampling locations. About 40 litres of water were collected from each sampling location and acidified with 11M HCl to avoid adsorption of radionuclides on the walls of the container (IAEA, 1990).

### 4.2.4 Water samples for $^{222}$Rn

About 100ml of water was collected in air tight bottles with minimal sample aeration. A bottle with small opening was preferred because it prevents an air bubble from forming inside the collected sample. Bottles were gently and completely filled so that zero head space was present. They
were actually overfilled to obtain a representative sample and to minimize any $^{222}\text{Rn}$ losses during collection. It was expected that open wells were actively pumping before and during the sample collection. All the borewells selected in the present study are manually operated ones. In case of bore wells the stagnant water from the well casing was pumped out before a representative sample was collected. At the well head sampling port a clear plastic hose was inserted into the spigot and a slow and steady flow of water was obtained. Care was taken to see that no air bubbles were present inside the container and also to avoid aeration during sampling process, which might lead to outgassing. After collection, the samples were brought to the laboratory immediately with least loss of time and analysed.

4.3 Sample Processing

All the samples were carefully processed by using the standard procedures (EML 1983, IAEA/RCA 1989, Iyengar et al 1990) before taking them up for individual radionuclides activity concentration measurement. The procedures adopted for processing are given in the following sections.

4.3.1 Soil Samples

The soil samples were mixed thoroughly in the laboratory and extraneous matter like plant materials, pebbles, etc., were removed. The
samples were dried overnight in an oven at 110°C, and then cooled. Part of the sample was separated and sieved through 2 mm mesh sieve and was used for radiochemical estimation of $^{210}$Po, $^{210}$Pb and for the estimation of primordial radionuclides by gamma spectrometry.

Soil can be considered to be a composite of clay (<2 microns), silt (2 - 63 microns) and sand fractions (63 - 2000 microns). In order to determine the enrichment of radionuclides in these fractions, the dried soil was gently crushed in a mortar to separate the smaller fractions that are stuck to larger grains. The crushed soil was then passed through ISI grade sieves to obtain the grain size fractions of < 63 microns, 63 -106 microns and 106 -2000 microns. 500 g of the composite soil was treated with 5 litres of distilled water and kept overnight to ensure the complete separation of these fractions from the above method. It was then wet sieved through the above sieves and then dried (Surbeck et al 1988). Each fraction was weighed, from which the percentage of each fraction was found. It was found that the results obtained from both these method are in good agreement within the experimental errors. The mass of fresh sample, dried sample and ash were recorded in respect of all the samples.
4.3.2 Granite and mineral samples

Granite, Copper ore, Gold ore, Silver ore and Iron ore samples were collected from different sampling stations. Each sample was washed in distilled water and dried in an oven at 110°C to ensure that moisture was completely removed. The samples were crushed, homogenized and sieved through a 200-mesh, which is the optimum size enriched for heavy minerals. Weighted samples were placed in polyethylene bottles. The bottles were completely sealed for 4 weeks to reach secular equilibrium, where the rate of decay of the daughters equals to that of the parent. This step is necessary to ensure that radon gas confined within the volume and the daughters will also remain in the sample. Later on these samples were subjected for gamma spectrometry studies.

4.3.3 Water

Many methods like Liquid Scintillation cell (LSC) (Dillon et al 1991; Hightower and Watson, 1995; Barnett et al 1995; Sohrabi et al 1998; Otwoma and Mustapha, 1998; William Field and Burton Kross, 1998), Gamma ray spectrometry using NaI(Tl) detector (Farrai and Sanni,1992), HPGe detector using merinelli beaker (Capra et al 1991), Cerenkov counting method (Al-Misri and Blackman,1999) and the emanometry method (Strain
and Watson 1979) are available for the measurement of $^{222}$Rn in water. But among all these the simplest and accurate method is the emanometry method. Therefore, in the present investigations the concentration of $^{222}$Rn dissolved in water was estimated by the emanometry method. About 60-75 ml of water has to be first transferred to a bubbler by vacuum transferred without any air space using bubbler tubing. An evacuated scintillation cell is connected to the top end of the bubbler and the tap is slowly opened. Effervescence is seen in the bubbler indicating the partial disruption of dissolved air. Now the tap at the bottom of the bubbler is opened slowly and carefully, so that vigorous effervescence results. Since both taps of the bubbler are open, room air with only background radon enters the bubbler through the side of the capillary, brakes up into tiny bubbles due to the sintered disc and carries with it the radon dissolved in water in to the scintillation cell. The automatic ceasing of effervescence signals the end of sampling. Usually it takes about 2-3 minutes. Trials have shown that radon is quantitatively carried into the scintillation cell in a single transfer run, which is counted in an alpha counter after coupling the scintillation cell to the photo multiplier assembly.

The emanometry method was used in the measurement of $^{222}$Rn concentration in water samples. The method involved transfer of water
sample into radon bubbler by vacuum transfer technique and later transferring dissolved $^{222}\text{Rn}$ in the water into a pre-evacuated and background counted scintillation cell. The scintillation cell was stored for 180 minutes to allow $^{222}\text{Rn}$ to attain equilibrium with its daughters and then it was coupled to photomultiplier and alpha-counting assembly to calculate $^{222}\text{Rn}$ activity. The emanometry setup was calibrated at BARC, Mumbai and the average efficiency of scintillation cells used in the present study was found to be 74%.

4.4 Activity of Radionuclides

4.4.1 Activity of $^{226}\text{Ra}$, $^{232}\text{Th}$ and $^{40}\text{K}$ in soil, granites and mineral samples

In order to estimate the activity of $^{226}\text{Ra}$, $^{232}\text{Th}$ and $^{40}\text{K}$ in soil samples, a High Pure Germanium (HPGe) detector was used. The analysis was based on the identification and measurement of photopeak of specific gamma energy and abundance. To obtain low background and hence to increase the detectable limit, the detector was properly shielded. About 250 to 300 g of the oven dried, sieved soil, granite and mineral samples were filled in plastic bottles provided with inner and outer lids. The lids were tightly screwed so
as to avoid leakage of radon gas from the sample. This set up was kept for a minimum period of one month to allow radioactive equilibrium between 226Ra with its progeny. The activity was then estimated using gamma spectrometry using HPGe detector coupled to 16K MCA. The gamma spectrometer was calibrated using the standard sources 133Ba, 65Zn, 22Na and 60Co. The efficiency of the spectrometer for various gamma energies were determined using uranium thorium and standards.

Gamma spectrum of each sample was accumulated over a period of 25000 sec to accumulate significant counts. Following criterion were considered while selecting the gamma lines for measuring the photopeak area to represent a particular nuclide.

1. The photopeak corresponding to specific gamma energy under consideration must have relatively high efficiency.

2. There should be no nearby energy peaks that may cause interference.

3. The selected photopeak must have sufficient gamma abundance.

Due to these reasons gamma line of energy 609 keV (214Bi) having gamma abundance of 46.1% was used as a surrogate for estimating the activity of 226Ra. If the 186 keV gamma line of 226Ra were selected, its
photon intensity being only 3.3% and there would be possibility of interference by the line at 185.7 keV of $^{235}$U. For the same reasons the 911 keV ($^{228}$Ac) gamma line with intensity of 27.7% was used to represent the $^{232}$Th activity and 1460.8 keV gamma line of abundance 10.7% was used to represent the $^{40}$K activity. However, to ascertain the equilibrium of $^{232}$Th series nuclides, the photopeaks 238.6 keV ($^{212}$Pb), 338.4 keV ($^{208}$Tl), 583.2 keV ($^{208}$Tl), 911 keV ($^{228}$Ac) and 2614 keV ($^{208}$Tl) were also selected. The 295 keV ($^{214}$Bi), 353 keV ($^{214}$Pb) and 609 keV ($^{214}$Bi) were recorded to ensure equilibrium of $^{238}$U series nuclides.

The area under the photopeaks of gamma energy as explained above, were determined, from which the activity of $^{226}$Ra, $^{232}$Th and $^{40}$K were calculated using the relation (IAEA/RCA 1989)

$$A = \left\{ S \pm SD \right\} \frac{100 \times 100 \times 1000}{\varepsilon \times G \times W} \ldots 4.1$$

Where,

- $A$ = Activity in Bq kg$^{-1}$
- $S$ = Net sample count rate under the photopeak (s$^{-1}$).
- $SD$ = Standard deviation = $(C_s / T_s^2 + C_b / T_b^2)^{\frac{1}{2}}$

$C_s$ and $C_b$ are the sample and background counts respectively, $T_s$ and $T_b$ are the sample and background counting periods respectively(s).
\( \varepsilon \) = Efficiency of the detector for corresponding gamma energy (\%)

\( W \) = Mass of the dry sample taken for analysis (g)

\( G \) = Gamma abundance of the photopeak under consideration. (\%)

### 4.4.2 Activity of \(^{210}\text{Po}\) in soil

\(^{210}\text{Po}\) is volatile. Processing of the samples at high temperature is likely to lead to loss of polonium. So wet ashing of environmental samples was carried at a temperature of 90\(^\circ\)C for the radiochemical separation of \(^{210}\text{Po}\). Initially the radionuclides were leached from the sample using nitric acid. After obtaining the white residue the sample was treated with 10 ml of concentrated hydrochloric acid and evaporated to near dryness. This procedure was repeated 5 to 6 times so as to bring the sample into HCl medium. Finally the residue was treated with 400 ml of 0.5N hydrochloric acid and stirred. If any turbidity occurs the solution was filtered through Whatman 42 filter paper. The solution was used for the analysis of \(^{210}\text{Po}\) by electrochemical displacement method.

### 4.4.3 Spontaneous deposition of \(^{210}\text{Po}\)

The sample solution was kept on a magnetic stirrer provided with heating arrangement. The temperature of the solution was maintained between 90\(^\circ\)C to 95\(^\circ\)C. About 100 mg of ascorbic acid was added to the
solution to reduce ferric ions in the solution to ferrous ions which otherwise would interfere in the $^{210}$Po deposition. A clean, brightly polished and background counted (on both sides) silver disc (0.1 cm thick and 3.5 cm dia) was suspended into the solution. The solution was then stirred using the magnetic stirrer for a period of 6 hours. Distilled water was added in small dose occasionally to maintain the level of solution as well as to wash $^{210}$Po sticking to the beaker and glass rod. At the end of the plating period, the disc was removed, washed with distilled water, ethyl alcohol and dried under IR lamp. It was then counted both sides for alpha activity in an alpha counting system (Photograph). The $^{210}$Po activity was calculated using the relation.

$$A = \{S \pm SD\} \frac{100 \times 100 \times 1000 \times (100 - M)}{\varepsilon \times E' \times W \times 100} \quad \ldots \text{4.2}$$

Where,

$A =$ Activity in Bq kg$^{-1}$

$S =$ Background subtracted sample counts per sec

$SD =$ Standard deviation $= (C_s / T_s^2 + C_b / T_b^2)^{\frac{1}{2}}$

$C_s$ and $C_b$ are the sample and background counts respectively, $T_s$ and $T_b$ are the sample and background counting periods respectively (s).

$\varepsilon =$ Efficiency of the alpha counting system (%) 

$W =$ Mass of the dry sample taken for analysis in g
$M = \text{ Moisture content in the sample (\%)}$

$E_p = \text{ plating efficiency (\%)}$

The plating efficiency of the Po was determined through Po standard of known activity spiked in the sample. The sample was brought to solution form using radiochemical procedures as explained above. The Po in the solution was plated on a silver planchet and the percentage of recovery was calculated using the alpha counts obtained. This check was done for 5 samples and the overall plating efficiency was found to be 95%.

To determine plating efficiency, five soil samples were spiked with yield tracers of known activity. The yield tracer used in the present study was $^{208}\text{Po} \ (E_a = 5.15\text{MeV})$ tracer. $^{208}\text{Po}$ tracer was procured from BARC, Mumbai. The spiked sample was brought to solution form using radiochemical procedures explained in the chapter 4. The $^{210}\text{Po}$ was spontaneously deposited on a rotating silver planchet. The silver planchet was counted using alpha spectrometer. The spectra showed two singlet peaks, at 5.15 and 5.3 MeV which are the characteristic alpha particle energies of $^{208}\text{Po}$- tracer and $^{210}\text{Po}$ respectively. The net peak areas were calculated. The chemical yield was calculated from the net peak area of the tracer.
4.4.4 Activity of $^{210}\text{Pb}$ in environmental samples

The principle adopted in estimating $^{210}\text{Pb}$ was through back calculation method. In this method, the sample solution after extracting Po, was kept for a period of 6 to 8 months to allow the growth of $^{210}\text{Po}$ from $^{210}\text{Pb}$ (Iyengar et al 1990). The sample solution was then subjected to electrochemical displacement to know the $^{210}\text{Po}$ activity, from which the $^{210}\text{Pb}$ was estimated by using the build up factor for $^{210}\text{Po}$ from $^{210}\text{Pb}$ during the sample storage period. This is one of the easiest methods but requires the complete removal of $^{210}\text{Po}$ from the sample solution during first plating. This was ensured by replating polonium on silver planchet soon after first plating. The counts thus obtained were insignificant which confirms the complete removal of Po from the sample solution during the first plating itself.

4.4.5 Activity of $^{222}\text{Rn}$ in Water

After processing the water samples for $^{222}\text{Rn}$ activity as explained in (4.3.3), the concentration of dissolved radon in water is found by,

$$Rn(W) = \frac{6.97 \times 10^{-3} \times D}{V \times E e^{-\lambda t} \times e^{-\mu t} \times (1 - e^{-\lambda t})} Bql^{-1} \quad \text{...4.3}$$
Where,

D = Gross alpha counts above background

V = Volume of water in Radon bubbler (ml)

E = Efficiency of the Scintillation cell

$\lambda$ = Decay constant of radon ($2.098 \times 10^{-6} \text{sec}^{-1}$)

T = Counting delay (T $> 1000 \text{sec}$)

t = Counting duration (s)

$\theta$ = Delay between water sampling and de-emanation of radon from water to scintillation cell (s)

The minimum detectable radon concentration (MDRC) is a function of the cell background and the counting duration. The typical background observed is about 0.5 cpm. For such a background the MDRC would be $10.7 \times 10^{-3}$ Bql$^{-1}$ if the counting duration were 10 minutes.
Fig: 4.1(a) Scintillation cell. (b) Radon bubbler.