ESTIMATION OF DIETARY INGESTION INTAKE OF THORIUM FOR INHABITANTS OF HIGH BACKGROUND RADIATION AREA OF SOUTHERN INDIA

By

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Recommendations of the Viva Voce Committee

As members of the Viva Voce Committee, we certify that we have read the dissertation prepared by **Sathyapriya R Sreejith** entitled "**Estimation of Dietary Ingestion Intake of Thorium for Inhabitants of High Background Radiation Areas of Southern India**" and recommend that it may be accepted as fulfilling the thesis requirement for the award of Degree of Doctor of Philosophy.

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DECLARATION

I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree / diploma at this or any other Institution / University.

(Sathyapriya R Sreejith)

List of Publications arising from the thesis

Journal

1. "*Estimation of thorium intake due to consumption of vegetables by inhabitants of high background radiation area by INAA*", Sathyapriya R.S., Kamesh V., Prabhath R.K., Madhu Nair, Acharya R., Rao, D.D.. Journal of Radioanalytical and Nuclear Chemistry, 2012, 294 (3), 387-390.
2. "*Assessment of annual intake of thorium from animal origin food consumed by population residing in thorium rich area of Southern India*" Sathyapriya R.S., Prabhath R K., Acharya R., Rao D.D, Journal of Radioanalytical and Nuclear Chemistry, 2017, 312(2), 405–41.
3. "*Choosing an appropriate method for measurement of ^{232}Th in environmental samples"* Sathyapriya R S, Rao D D, Prabhath R K., Radiation Protection and Environment; 2017, 40, 90-94.

Conference

1. "*Thorium intake due to consumption of locally grown vegetables by inhabitants of High radiation background areas using INAA*". R.S. Sathyapriya**,** Suma Nair, V. Kamesh, R K Prabhath, Madhu Nair, K.D Arunachalam, R. Acharya and S. Bhati. Proceedings of fourth International Symposium on Nuclear Analytical Chemistry (NAC-IV). 2010, BARC, Mumbai.

2. "*Evaluation of natural radionuclides in dietary intake in high background radiation area, Tamilnadu, India*" Kantha Deivi Arunachalam, Sathyapriya R Sreejith, Kamesh Visvanathan Baskaran, International Conference on Radiation Biology:Nanotechnology, Imaging Science and Stem Cell Research in radiation Oncology, International Conference on Radiobiology (ICRB-2010), 2010, Chennai.
3. "*Determination of low concentration Thorium in diet samples by INAA using high flux, Dhruva research Reactor*", Sathyapriya R.S., Jagadeesan K C., Acharya R., Rao D.D. Proceedings of second international conference on New frontiers in chemistry – from fundamentals to applications, New Frontiers in Chemistry-from Fundamentals to Applications" (NFCFA 2017), 2017, BITS K K Birla Campus, Goa.

(Sathyapriya R Sreejith)

Dedicated

to

My Family

For their endless love, support

and encouragement

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Environmental chemistry and bio-kinetic studies became my topic of interest in the early career in BARC, India. The quest for analysis of very low level concentration of radionuclide in environmental and biological samples introduced me to the powerful Neutron Activation Analysis (NAA) technique. This led me to come in contact with my guide ***Dr. Raghunath Acharya****, an expert in NAA and nuclear analytical techniques. The planning cum formulation of this work was initiated with his guidance. It has been a privilege to work in his research group and I have received firm support and encouragement throughout. With his guidance planning, execution, experimental, data reporting and interpretation works were done meticulously. I would like to express my deepest gratitude to my supervisor for his unwavering support and mentorship throughout this thesis work.*

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Sathyapriya R Sreejith

Contents

Synopsis

Estimation of dietary ingestion intake of thorium for inhabitants of high background radiation area of Southern India

Primordial radionuclides are present in human habitats that represent the main source of chronic radiation exposure to member of public. Humans get exposed to natural radiation externally from cosmic rays and terrestrial radiation and receive internal exposure primarily due to inhalation and ingestion of radionuclides of terrestrial origin. According to the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) [1] the highest contribution to human exposure is from natural background radiation from Naturally Occurring Radioactive Material (NORM) and the worldwide average annual effective dose per capita is 2.4 mSv, out of which 0.29 mSv is from ingestion of radionuclides of terrestrial origin. In some parts of the world, the average annual effective dose due to natural radioactivity is significantly higher than the global average. Some coastal towns of India namely, Chatrapur, Chavara, Manavalakurichi, Ullal etc. are well known High Background Radiation Areas (HBRA) [2,3]. The high background radiation is due to presence of thorium rich monazite mineral in the beach sands. Southwest coastal belt from Manavalakurichi–Kadiapattinam–Midalam in Tamilnadu, India have large placer deposits of monazite mineral in the beach sands. Monazite in this area contains 8-10% of thorium oxide and 0.35% uranium oxide along with other minerals and rare earths. People residing in this area are likely to have internal exposure due to dietary ingestion of radionuclides from thorium series. Thorium is the parent radionuclide of 4n series with a very long half-life (1.39×10^{10} y) and low specific activity (4.1 kBq g^{-1}). Humans are chronically exposed to thorium mainly through the ingestion of food

and drinking water and to a lesser extent through inhalation. Thus, it is important to have reliable information on the intake of thorium, i.e., to study the incorporation of thorium via dietary intake and the resulting internal radiation dose to the public.

In India, several studies have been performed to measure the dietary intakes of ^{228,226}Ra, ^{210} Po, ^{210}Pb but information on dietary intake of ^{232}Th is scarce [4,5]. The investigation on dietary intake will also serve as baseline study to evaluate the impact of any human activity that may result in technologically enhanced naturally occurring radioactive material (TENORM) and also as an input parameter for the biokinetic and epidemiological studies to be conducted in these areas. In view of these aspects, present thesis work is focused on estimation of thorium using sensitive techniques like INAA (Instrumental Neutron Activation Analysis) and ICP MS (Inductively Coupled Plasma Mass Spectrometry) in dietary components, total diet, drinking water and urine. The thorium concentration thus estimated was used for establishing the age dependent daily dietary intake and the corresponding annual effective dose. The thesis is divided into six chapters, details of which are briefly given here.

Chapter 1: Introduction

This chapter gives the introduction, need and motivation for the present studies. Internal intakes of radionuclides occur through either or all modes, inhalation, ingestion, dermal absorption and direct injection through a wound. Ingestion intake of thorium is the scarcely investigated pathway due to the difficulties encountered in the quantification of very low concentration of ^{232}Th in food and drinking water [4]. Daily intake of ^{232}Th through diet was estimated for adults in few countries including India, but the studies were conducted for population residing in Normal Background Radiation Areas (NBRA) and were restricted to urban population. There are regions in

India along the coastal belt of Kerala, Tamilnadu, Andhra Pradesh and Orissa where the background radiation levels are high due to large placer deposits of monazite mineral in the beach sand. The population residing in these areas is likely to have a higher intake of radionuclides from thorium series from ingestion pathway compared to normal background radiation area. Hence it is important and also essential to assess the internal dose due to ingestion of NORM. Radionuclides (^{228,226}Ra, ^{40}K and ^{210}Po) dietary intake other than ^{232}Th in the study area has been well investigated and reported [5, 6]. Paucity on information on the concentration of ^{232}Th in dietary material, led to conduct this research.

When radionuclides are ingested through food and drinking water, it traverses through gastrointestinal tract and part of it gets absorbed, primarily from the small intestine and finds its way into the blood and lymphatic system and the rest is excreted in the feces. The thorium that gets absorbed into blood is distributed and deposited in different organs/tissues. About 70% of the thorium that enters the blood gets deposited in bone resulting in a long term retention in the body causing internal exposure [7]. Moreover, for monitoring absorption pattern of radionuclides, reliable knowledge of the daily intake and their metabolic behavior is essential. The results of the studies will enable us to generate more useful information on intake of thorium which will serve as an important input parameter for validating thorium biokinetic model and especially the Gut Absorption Fraction, F_A.

As the concentration of thorium in environmental, food and excreta mainly urine is in very low level, highly sensitive INAA and ICP MS techniques were standardized and used for quantification of thorium in environmental and biological samples. The objectives of the work include, determination of ^{232}Th concentration in various food

material, total diet and drinking water consumed by the inhabitants of the study area and evaluating the daily intake and the subsequent annual effective ingestion dose to ^{232}Th oral intake. The outcome of the research will also supplement in addressing the possible concerns of inhabitants of HBRA where mining activities are undertaken.

Chapter 2: Literature Survey

This chapter is a review on the existing literature relevant to the present work. It contains the concept of basic radiation exposure to human describing different types of exposure pathways and the global exposure levels. Radionuclides can enter the food chain via terrestrial or aquatic pathway. The dietary intake varies from region to region and the main source being the geographic variation that results in differences in concentration of NORM in soil and also the uptake varies for plant species. Review of literature dealing with studies on the NORM concentration in dietary items both from normal and HBRA is discussed. Large information is available on dietary intake and its corresponding annual intake for uranium, radium and polonium isotopes while scarce data is available for ^{232}Th intake by ingestion. A brief discussion on the chemical and physical properties of thorium, its behavior in the environment and its industrial application is presented. The behavior of thorium in human and its biokinetic model provided by ICRP is also discussed. Various radiometric and non-radiometric techniques used for quantification of thorium in environmental and biological matrices is elaborated and compared.

Chapter 3: Research Methodology and Experimental

Experimental details, sampling location (villages) and sampling collection techniques are described in this chapter. The sampling locations were selected based on the ground radiometric survey conducted along a 45 km costal belt of Southern

Tamilnadu. Market basket study (MBS) and Duplicate Portion study (DPS) methods were used for sample collection from the study area. Samples like cereals, pulses, vegetables, fruits, flesh food etc., were purchased from farmer's market. Milk samples were collected from milk vendors from the selected villages. The sample processing and pretreatment methods adopted are elaborated for the individual food groups. The freeze dried vegetation samples were irradiated in *CIRUS* reactor for one day in self-server facility. As the reactor was decommissioned, the samples were irradiated for 7 d in tray rod facility at *Dhruva*. Long irradiation period of the sample caused the samples and the packing material to melt. Hence the freeze dried samples were ashed, packed in 25μm thick Al foil and irradiated for 2-3 d at *Dhruva*. ^{232}Th in the samples were quantified by measuring the delayed gamma–rays of energy 311.6 keV of ^{233}Pa daughter product of ^{232}Th (half-life of 27.1d) using high resolution gamma ray spectrometry with HPGe detector coupled with 8k MCA (Multichannel Analyzer). The accuracy of the INAA method was established using standard reference materials (SRMs) procured from NIST (Spinach leaves, orchard leaves, Apple leaves and Tomato leaves). The ^{232}Th concentration was determined using relative method of NAA and the results of Th concentration are in good agreement (within ±5% in most of the cases). ICP MS was used for quantifying thorium in drinking water and urine. The daily consumption (g d^{-1}) data provided by National Nutrition Monitoring Bureau (NNMB) for each food group was used for evaluating the daily intake using MBS method. For DPS method, 24 h diet samples actually consumed was collected from individual households The estimated thorium intake (Bq y^{-1}) and the dose coefficient factor (Sv y^{-1}) provided by ICRP was used for assessing the internal dose received by

the inhabitants of the study area. For estimating the age dependent dietary intake by the population the 24 h dietary records collected for the various age groups was used.

Results and discussion

Chapter 4: Dietary intake of thorium using MBS method

Thorium(Th) is generally present in very low concentration in diet and drinking water. The individual food items collected from the local markets of the study area was processed and Th concentration was determined using relative INAA. The concentration in the samples varied from 0.3 ± 0.04 to 136.1 ± 12.6 μg kg^{-1}_{fresh}. The highest concentration was found in curated fish with a mean concentration of 107.1 ± 26.1 μg kg^{-1}_{fresh}.Variation in ^{232}Th concentration among different food vegetables was large. This variation may be attributed to the difference in selective absorption by the plants. ^{232}Th in cereals, green leafy vegetable, milk and flesh food was high compared to the concentration of samples obtained from an urban region in India [8]. Daily intakes of ^{232}Th for adult members of the population were evaluated from the consumption of food items such as, Rice from 1.1-4.7, Pulses and legumes from 0.1 to 0.5; green leafy vegetables from 0.6 to 0.9; other vegetables from 0.1 to 1.4; roots and tubers from 0.5 to 4.3; fruits from 0.3- 1.1; fish from 0.5 to 1.8; curated fish from 13.2 to 18.2; flesh food (meat, beef and chicken), from 0.1 to 0.3; and milk from 0.7 to 1.2 mBq d^{-1}. Though the Th concentrations in rice were less, they contributed significantly to the daily intake due to higher daily consumption rate. In children below 3y, milk contributed about 32 % to the annual intake. The total annual internal dose resulting from ingestion of ^{232}Th in these food groups was 3.4 μSv y^{-1} for male adult population.

Chapter 5: Dietary intake using Duplicate Portion Study Method

The breakfast, lunch, dinner and beverages, (excluding water) consumed by the people in 24 h were collected from four villages (Putteti, Thengapattinam, Manvalakurichi and Idindakarai). The 24 h dietary record was also collected from different age group members in the selected households. The ^{232}Th in the duplicate diet was estimated using INAA. The concentration varied from 6.1 ± 0.1 to 31.3 ± 1.1 μg kg^{-1}_{fresh}. It was also observed that the diet samples collected from households from village that showed higher ground radiometric dose had slightly higher concentration of ^{232}Th. This can be attributed to the cooking practices and eating habits adopted by the population. The annual intake was estimated using the concentration of ^{232}Th and the total quantity of the diet consumed by the individual. The annual intake for adult population varied from 15.1 ± 1.2 to 86.8 ± 7.8 Bq y^{-1}. Using the daily food consumption obtained using 24 h diet record obtained for different age group; the daily ingestion intake of thorium was evaluated for three different age groups. The average annual effective ingestion dose to the adult using DPS was 7.7 μSv y^{-1}.

The ^{232}Th was estimated in drinking water using Nu Attom HR- SF-ICP MS. The concentration in the samples ranged between 2.4 ± 0.1 and 18.3 ± 0.7 ng L^{-1}. The average annual effective dose of ^{232}Th from drinking water was estimated to be 13.6 nSv y^{-1}. It was observed that water consumption contributed to a very small part of the annual internal dose.

Chapter 6: Conclusions and Future Outlook

1) INAA method using high flux reactor neutrons was optimized for determination of trace concentrations of ^{232}Th in various food items and duplicate diet from thorium rich area of Southern India

2) ICP-MS method was utilized for sub-trace Th concentrations in drinking water and urine samples from same area.
3) Methods were validated by determining Th in (certified) reference materials.
4) Age dependent average annual intake and effective ingestion dose values were evaluated using MBS and DPS method. Major contributors to dietary ^{232}Th intakes in the study group were found to be marine products and the lowest contribution was from fruits and vegetables.
5) It is observed from the study that though the intake is slightly higher compared to another study conducted for evaluation of daily intake by an urban population, the contribution to total annual dose to the individual is insignificant from ingestion intake.
6) Another interesting observation is that annual effective dose evaluated using DPS method was higher than that evaluated using MBS. This indicates that DPS is a preferred method for realistic biokinetic studies and MBS method gives us the indication of individual major contributor to the dose.
7) The results of this study will supplement to background data on terrestrial radioisotopes in this region and will also provide to evaluate the gut absorption fraction of thorium for Indian population.
8) Due to lack of adequate data on ^{232}Th concentration in individual dietary components from normal background areas of India, our results couldn't be compared. Hence it was thus important to estimate ^{232}Th concentration in dietary component from different normal background areas of India, which will be treated as the base / literature value.

9) As the contribution to the total dose by ingestion pathway is very less, it can be concluded that the mining activities in the study area hasn't influenced the ingestion dose.

10) The evaluated ingestion intake of Th from food and diet will be helpful to assess the gut absorption fraction $F_{A.}$

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List of Abbreviations

AMAD-Activity Median Aerodynamic Diameter

CIRUS -Canadian-Indian Reactor Uranium System

DCF-Dose Conversion Factor

DD-Duplicate Diet

DPS-Duplicate Portion Study

FWHM-Full width at Half Maximum

GPS-Geographical Positioning System

HPGe -High Purity Germanium

MBS - Market Basket Study

IAEA - International Atomic Energy Agency

ICP MS- Inductively Couples Plasma Mass Spectrometer

ICRP-International Commission for Radiological Protection

NAA-Neutron Activation Analysis

NNMB- National Nutrition Monitoring Bureau

MCA-Multichannel analyser

NORM- Naturally Occurring Radioactive Materials

NIST-National Institute of standards and Technology

HBRA-High Background Radiation Area

NBRA-Normal Background Radiation Area

REE- Rare Earth Element

SRM- Standard Reference Material

WHO-World Health Organization

UNSCEAR-United Nations Scientific Committee on the Effects of Atomic Radiation

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Naturally occurring radionuclides are the major sources of radiation exposure to human being. Radionuclides of natural origin enter the human body via inhalation or ingestion and are retained in the body causing a source of long term internal exposure. Radionuclides are present in food at different concentration depending on radioactivity contents in soil, its chemical form, mobility in soil and uptake capacity of the plant. In India, there are some areas where the concentrations of thorium in the soil are elevated. South west coastal belts of Tamilnadu have large deposits of monazite minerals in the beach sands. The inhabitants of these areas get chronically exposed to the radioactivity from radionuclides from the decay series of thorium. A little work has been carried out on internal exposure from thorium intake via ingestion to the population residing in this area. There is also a growing concern among the inhabitants of the region for the mining activity taking place in this area, which needs to be addressed to.

1.2 Radiation exposure to humans

Members of public get chronically exposed to radiation both from naturally occurring radioactive material (NORM) and man-made radionuclides. Ingestion and inhalation are two important pathways in which these radionuclides get entry into the human body. Gamma emitting radionuclides in the ^{238}U and ^{232}Th decay series and from ^{40}K contribute significantly to external exposure. Radionuclides of terrestrial origin belonging to the uranium series such as ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra,^{210}Pb and ^{210}Po, and the thorium series such as ^{232}Th, ^{228}Th, ^{228}Ra, ^{212}Po, ^{212}Pb and ^{40}K are important in internal dose assessment point of view. These radionuclides are transferred and cycled to various environmental compartments through natural processes in the ecosystem

and find their route into human food chains. According to reports of United Nations Scientific Committee on Effects of Atomic Radiation (UNSCEAR), ingestion intake are the major contributors to internal exposure from terrestrial radionuclides and inhalation intake was very less [1, 9]. Hence, internal exposure needs to be evaluated from the intake of these radionuclides in food and water for population residing in all parts of the country covering both rural and urban regions. Thorium is the parent radionuclide of thorium decay chain and it has higher crustal abundance than uranium. It has many industrial application and is likely to get incorporated into human system by means of ingestion. Once it is in the human body, thorium accumulates in lungs, liver, and skeleton. The principal site of deposition of thorium in the body is the skeleton (70%). Thorium also gets deposited in the liver (4%), other soft tissue (16%), gonads (~1%) and the remaining activity (10%) is promptly excreted out in urine via the bladder [7].

Evaluation of metabolic behavior like absorption into blood and retention in the human body and subsequent assessment of internal dose of any radionuclide requires detailed information of its intake by means of drinking water and dietary components. In the study area where the background radiation levels are high due to presence of large monazite deposits, the ingestion rate of radionuclides from thorium series and uranium series namely ^{228,226}Ra, ^{210}Po, has been studied but there is no study related to ^{232}Th ingestion intake for the inhabitants. The ^{232}Th concentration in a few food items like milk, banana and fish collected from the study area has been reported by other researchers but they have used gamma ray spectrometry considering a secular equilibrium between ^{232}Th and its progenies. It has been observed that the use of gamma ray spectrometry results in overestimation of ingestion intake value.

1.3 High background radiation area of India

Naturally occurring radionuclides like uranium (^{238}U) and thorium (^{232}Th) are present universally except for a few places where they are concentrated as minerals and these regions are called High Background Radiation Areas (HBRA). HBRA are present in many parts of the world such as Guarapari in Brazil [10], Yangjiang in China[11], and Ramsar in Iran[12]. The coastal towns such as Chavara, Manavalakurichi, Bimilipattinam[13] and Chhatrapur [14] are reported to be the HBRA in India. ^{238}U and ^{232}Th concentration of ~ 0.35% and ~ 9%, respectively, in monazite are found in these regions. The presence of monazite deposits on the coastal areas of Kerala and Tamil Nadu is due to the combined effect of weathering of rocks, rivers and stream flow, morphological features of the river basins and their interaction with the sea. Distribution of the heavy minerals in the beach sector of the study region is due to above mentioned reasons [15].

1.4 Behavior of radionuclides in the environment

In terrestrial and aquatic ecosystems, naturally occurring radionuclides called as naturally occurring radioactive material (NORM) are transferred from the site of origin by air emissions, leaching, by dissolving in runoff waters, uptake by plants from soil, transfer to animals and, finally, from the food chain to human being. The concentration of thorium, uranium and its progeny products in natural water are influenced by the chemical and physical characteristics of the aquifer, geological formation involved and the oxidation states. The mobility of the radionuclides in the environment and its uptake by the plants depend on the parameters like pH, redox potential, ionic strength, availability of inorganic and organic ligands, presence of microorganisms and the interaction of solved and sorbed complexes.

Radium is an alkaline earth element and behaves like other alkaline-earth metals. Thus in environmental matrices, radium co-precipitates with barium to form mixed sulphate phase. In nature, all the alkaline earths are found only in +2 oxidation state. Radium is a water soluble and mobile element. It is easily transferred from rocks, soil or sediments into the environment. It is often concentrated in the ground water.

Uranous (U^{4+}) and uranyl (U^{6+}) valence states of uranium are stable in geologic environments. Hexavalent U compounds are more soluble than tetravalent uranium as uranium in U^{6+} occurs as the uranyl ion UO_2^{2+}. There is a disequilibrium between the parent isotope and its progenies as there is a separation between the parent and the radionuclide progenies when the rocks are exposed to weathering and water circulation.

Thorium compounds are more stable in the +4 oxidation state in aqueous systems. Thorium as ThO_2 due to its low solubility occurs mostly as suspended particles or sorbed onto sediments in water. Above pH 2-3, Th in +4 state (Th^{4+}) undergoes hydrolysis in aqueous solutions. At near neutral pH, Th gets sorbed to clay minerals and humic acid. Thorium ions in water also forms $Th(OH)_4$ precipitate or hydroxyl complexes at pH above 5, which get adsorbed by particulate matter in water. Thorium also form soluble complexes with carbonate, humic materials or other ligands in the water [16]. Among the NORM, the order of mobility in terrestrial and aquatic environment observed was Radium >Uranium> Thorium [16].

In an isolated equilibrium, the naturally occurring U-series or Th series radionuclides are in secular equilibrium, but natural processes disturb this equilibrium due to the differences in the chemical properties of the parent and the progenies. As isotopes of U, Th and Ra has different solid – liquid distribution coefficients (K_d), the mobility in

different matrices and plant uptake are different and hence, there is a disequilibrium in the environment [17]. In monazite rich soil, ^{232}Th is expected to exist in secular equilibrium with its daughter products. But natural processes and mining activity often disturb the equilibrium in the soil.

In view of all above discussed factors, transfer as well as uptake of radium is more compared to thorium and hence there is disequilibrium between the parent and the progenies in food items.

1.5 Radioactivity in air, soil and food

Gross alpha and beta measurement are most primitive and simplest radioanalytical procedures that are used widely for radioactivity measurements in radioecology and environmental monitoring studies. Another radiometric technique that is often used is gamma-ray spectrometry. ^{220}Rn and ^{222}Rn are two important radionuclides from thorium and uranium series that are constantly emanating from the ground due to the ubiquitous presence of ^{232}Th and ^{238}U in soil. These radionuclides can accumulate in enclosed structure and is a main source of internal exposure via inhalation causing considerable dose to the lungs. There are large number of reported work carried out in this field by many investigators in different parts of the world to evaluate the dose from radon to human from external and internal pathway [18–24].

The study area has a higher concentration of ^{232}Th in the soil resulting in higher rate of emanation of radon. In a work conducted by Devajayanthi, in the study area, radon and thoron concentration in the dwelling were measured using twin cup SSNDT (LR-115-II) detectors. The annual effective dose due to inhalation of radon and thoron varied from 1.12 to 4.32 mSv y^{-1}. The external radiation dose, evaluated using TLD using CaF_2 as TL phosphor, was varied from 1.23 to 4.23 mSv y^{-1} [25].

For estimating the external exposure due to outdoor occupation, it is necessary to measure the natural radioactivity levels in the soils. There are widespread research that has been carried out by many groups to measure the radioactivity in the soil and sand samples in the HBRA of India [15, 26–28]. In a work carried out by Devajayanthi et al.,^{226}Ra, ^{232}Th and ^{40}K were measured in soil samples collected from different villages in the Midalam-Manavalakurichi stretch by gamma ray spectrometry using the peaks of 1764 keV of ^{214}Bi, 2614.5 keV of ^{208}Tl and 1464 keV respectively. ^{226}Ra and ^{232}Th in the soil varied from 18.9 to 260.5 and 534.5 to 2961 Bq kg^{-1} respectively [29]. The gross alpha and beta activity was also calculated. The gross alpha activity of beach soil ranged from 8496 to 18350 Bq kg^{-1} [29] . In another work carried out by Esaiselvan to measure the gross alpha activity in the soil, have reported that the soil activity ranged from 1600 to 12000 Bq kg^{-1} [30].

Intake of water is an important route of internal exposure to human being. Naturally occurring radionuclides from ^{232}Th and ^{238}U series in the drinking water contributes to internal exposure. The concentration and existence of natural radionuclides in drinking water depends on the geological environment like the aquifer rock type and geolithology.

As the dose coefficient (Sv Bq^{-1}) given by ICRP is different for different radionuclides, for example the dose coefficient for adult of ^{238}U, ^{226}Ra, ^{210}Po, ^{232}Th are 4.5×10^{-8}, 2.8×10^{-7}, 2.1×10^{-6} and 2.3×10^{-7} Sv Bq^{-1} respectively, determination of concentration of each radionuclide separately is essential for assessing the effective dose.

Determination of radionuclides in drinking water has been carried out in many countries in the past [31–35]. In India, works has been carried out for determination of

^{226,228}Ra, ^{210}Po, ^{210}Pb and total uranium by many investigators [36–39]. Devajayanthi et al., have determined the gross beta and alpha activity in the drinking water and ^{228}Ra, ^{238}U and ^{40}K by gamma ray spectrometry. The radionuclides in water was pre-concentrated with $BaSO_4$ precipitate and counted in a ZnS (Ag) counter for gross alpha activity in the drinking water and ^{232}Th was determined using NaI(Tl) detector by measuring 2.614 MeV gamma line of ^{208}Tl. The gross alpha activity ranged from 0.07 to 0.28 Bq L^{-1} and ^{232}Th activity using gamma ray spectrometry varied from 0.32 to 0.77 Bq l^{-1} [29]. The estimated ^{232}Th thorium in the water was much higher than the values reported by other workers around the world who had used alpha spectrometry, Neutron Activation Analysis (NAA) or Inductively Coupled Plasma Mass Spectrometry (ICP MS). The reason being, ^{232}Th has a lesser mobility than its progenies, so there exists a disequilibrium between the parent and the daughters. Using gamma ray spectrometry for measuring ^{232}Th activity in water, we are only measuring the activity of ^{228}Ra and not ^{232}Th. Hence gamma ray spectrometry measurement often results in overestimation and should not be used for quantifying ^{232}Th in water or food material.

Another important pathway for internal intake of radionuclide by members of public is ingestion of foodstuff. These food products are mainly of plant or animal origin. The radionuclides can enter into the food chain both from soil and water. Hence it is important to quantify radionuclides in dietary components consumed by the members of public. Dietary intakes of ^{238,234}U, ^{232,230,228}Th, ^{228,226}Ra ,^{210}Pb and ^{210}Po and ^{226}Ra have been evaluated by many investigators using various techniques [8, 40–45]. In a study carried out in the southwest coastal regions of Tamilnadu, $^{226,\ 228}$Ra, ^{228}Th, ^{40}K in typical south Indian foods such as milk, fish, rice, tapioca, banana, mango, guava,

tomato etc., was evaluated using gamma ray spectrometry. The concentration of ^{228}Ra and ^{228}Th ranged from 0.08 to 5.42 and from 0.14 to 34.3 Bq kg^{-1}_{fresh} respectively [5]. ^{210}Po was also measured in the food samples and reported, whereas no comprehensive study has been carried out on intake of ^{232}Th for population residing in the region of interest.

1.6 Objective of the study

The general objective of this research was to establish the ingestion intake of ^{232}Th and estimation of internal dose from ^{232}Th dietary intake for population residing in the HBRA regions of south west coast of Tamilnadu. Internal effective dose has been calculated for other radionuclides both by inhalation and ingestion pathway but no work has been reported upon the dietary intake of ^{232}Th for the study group. Due to the difficulties in estimation of ^{232}Th in the biological matrices, information on ^{232}Th in dietary item and drinking water is rare worldwide and is absent in the study area. An accurate, sensitive and reliable nuclear analytical technique known as instrumental neutron activation analysis (INAA) and non-radiometric method ICP MS is used to estimate the ^{232}Th in foodstuff and water consumed by the inhabitant.

The objective of the present study is aimed:

(a) to measure ^{232}Th in diet, dietary components and drinking water consumed by the population; in order to have complete study on the ingestion intake and append to the previous research carried out on ingestion intake of other radionuclides from thorium series (^{228}Ra and^{228}Th) and Uranium Series (^{238,234}U, ^{226}Ra, ^{210}Pb and ^{210}Po);

(b) to provide information on the background of natural radioactivity concentration and to contribute in this way to the creation of databases that can be used to evaluate the impact, for instance, of mining process,

(c) to calculate the annual intake of the ^{232}Th by ingestion of foodstuffs consumed by children and adults and

(d) to estimate the annual effective dose from ^{232}Th from ingestion pathway thereby adding to the existing data on external, inhalation and ingestion dose from other radionuclides from uranium and thorium decay series.

1.7 Significance of the study

For realistic dose assessment, clear understanding of biokinetic behavior of thorium is important. The regions in the study area have large deposits of monazite and other minerals. ^{232}Th is the main element and there is a paucity of information on its dietary intake by the population. The outcome of the study will serve as baseline information for any epidemiological studies to be carried out in the study area. Sand containing minerals (monazite, illeminite, zirconite etc.) are being mined from the region for separation of rare earths and thorium. There is a growing concern among the population that the mining in the region will cause health effects. The results of the study will help to confirm that mining activities don't contribute to any increase in the concentration of radionuclides in the food chain.

For a large country like India, to meet the growing energy needs, it is important to look upon solar and non-conventional renewable energy sources. In this scenario, nuclear energy is a sustainable option and in Indian Nuclear Power Programme (INPP), thorium has a very important role in view of large thorium reserves in the form of monazite deposits along the coastal regions compared to the limited uranium reserve [46]. Hence there is a growing interest in our country to use this reservoir which will result in more mining, milling and separation activities in the country. More workers may likely get exposed to thorium and its progenies in the following

years to come. Using the daily excretion in urine, it is possible to assess the extent of exposure of subjects to thorium and the related risk provided biokinetic factors like absorption fraction from gastrointestinal tract or respiratory tract, its distribution, retention is available. Information on daily dietary intake is one of the important input parameter for evaluating the absorption fraction from gastrointestinal tract. Hence, information on daily dietary intakes of ^{232}Th is important in the development of realistic biokinetic model for Indian population.

CHAPTER 2

LITERATURE SURVEY

2.1 Radioactivity in the environment

Members of public get exposed to radiation from sources of natural and man-made origin. Cosmic rays cause external exposure whereas the radionuclides of terrestrial and cosmic origin can cause both internal and external exposure.

The radionuclides in our environment can be classified as

i) *Natural radionuclides* which are formed from high-energy cosmic ray particles incident on the earth's atmosphere (cosmo-genic) and those that are part of the natural decay chains (Thorium, Uranium) and singly occurring long lived radionuclides like ^{40}K and ^{87}Rb that are omnipresent in earth crust.

ii) *Man-made or anthropogenic radionuclides* that are formed from modern techniques.

The largest contribution to exposure is from natural background radiation. UNSCEAR has estimated an annual per capita dose of 2.4 mSv [1]. The main sources of human exposure to radiation are cosmic rays, cosmogenic radiation, and terrestrial radiation. A significant contribution to the natural exposure of people is due to radon gas, which emanates from the soil and concentrates in dwellings. Natural radiation levels vary from place to place and depend on the geophysical and chemical factors. Radiation exposure for medical purposes is the second largest contribution to exposures of individuals worldwide. Series of nuclear test conducted between 1958-1962 also resulted in radiation exposure of the world's population due to the release of large amounts of radioactive materials directly into the atmosphere. Atmospheric nuclear testing involves large scale release of anthropogenic radionuclides into the environment, contributing about 0.005 mSv in a year.

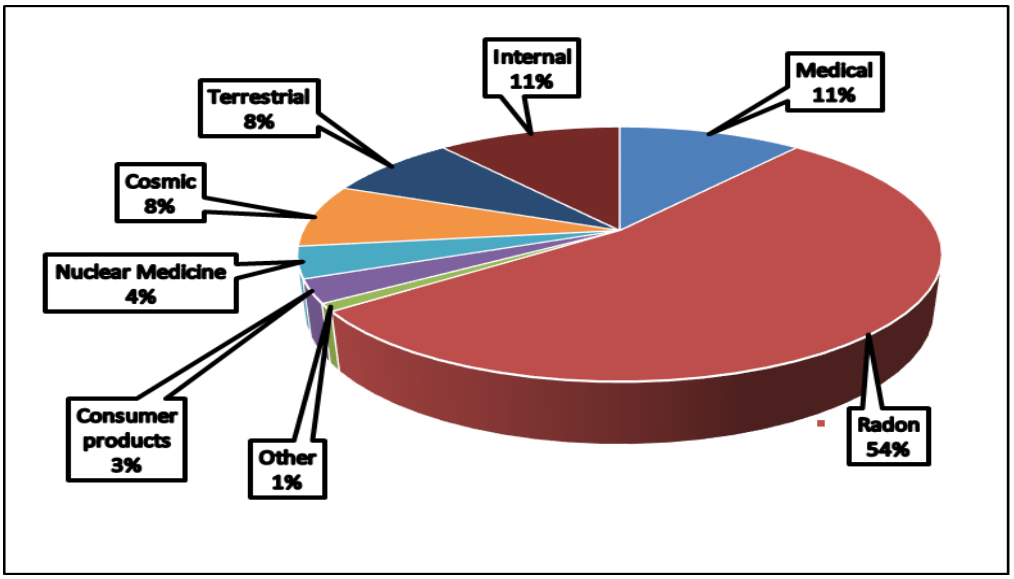


Figure 2-1: Average radiation dose from natural and man-made sources

2.1.1 Naturally occurring radionuclides

2.1.1.1 Cosmogenic radionuclides

Cosmogenic nuclides are produced from spallation of atoms in the atmosphere by cosmic rays. These are light radionuclides with low atomic number and half-lives ranging from minutes to 2.5×10^6 y (Table 2-1). They are transferred to the earth's surface by precipitation and gravitational settling. Of the 22 identified cosmogenic nuclides only four (^{3}H, ^{7}Be, ^{14}C, ^{22}Na) are significant from the perspective of doses to humans.

2.1.1.2 Terrestrial Radionuclides:

Primordial radionuclides were produced at the origin of our solar system (^{40}K, ^{87}Rb, ^{238}U, ^{235}U, ^{232}Th) and still exist because of their long half-life. ^{238}U, ^{235}U and ^{232}Th are the mother nuclides of the three radioactive decay chains (4n+2, 4n+3 and 4n series), which generate most of the important natural radionuclides also known as naturally occurring radioactive material (NORM) and each series ends up in a stable lead isotope.

Table 2-1: Cosmogenic radionuclides

Element	Isotope	Half-life	Decay Mode
Hydrogen	^{3}H	12.33 y	β (100%)
Beryllium	^{7}Be ^{10}Be	53.29 d 1.51×10^{6} y	EC (100%) β (100%)
Carbon	^{14}C	5730 y	β (100%)
Sodium	^{22}Na	2.602 y	EC (100%)
Aluminium	^{26}Al	7.41×10^{5} y	EC (100%)
Silicon	^{32}Si	172 y	β (100%)
Phosphorus	^{32}P ^{35}P	14.26 d 25.34 d	β (100%) β (100%)
Sulphur	^{35}S	87.51 d	β (100%)
Chlorine	^{36}Cl	3.01×10^{5} y	EC (1.9%), β (100%)
Argon	^{37}Ar ^{39}Ar	35.04 d 269 y	EC (100%) β (100%)
Krypton	^{81}Kr	2.29×10^{5} y	EC (100%)

2.1.1.2.1 Potassium 40 (^{40}K) and Rubidium 87 (^{87}Rb)

Natural potassium comprises three isotopes (^{39}K, ^{40}K, ^{41}K) where ^{40}K is the only radioactive isotope. ^{40}K has a long half-life of 1.26×10^{9} y with an isotopic abundance of 0.012% of naturally occurring potassium. ^{40}K undergoes beta decay (E_{max} 1.314 MeV, 89%) to form stable ^{40}Ca, 11% undergoes decay by positron emission and emitting a characteristic photon of 1.46 MeV energy. Potassium is a lithophile element and is uniformly distributed in rocks. Potassium is soluble under most conditions and during weathering; it gets easily mobilized into solution.

^{85}Rb and ^{87}Rb are two isotopes of rubidium and only ^{87}Rb is radioactive and undergoes beta decay with a half-life of 4.8×10^{10} y with an elemental abundance of 27.8%. ^{87}Rb emits beta particles with E_{max} of 292 keV (E_{avg} of ~79 keV).

2.1.1.2.2 ^{238}U series

^{238}U is the parent radionuclide of 4n +2 series and the important ones are ^{230}Th, ^{226}Ra, ^{222}Rn, ^{210}Po and ^{210}Pb. Decay characteristics of ^{238}U series radionuclides are given in Table 2-2.

Table 2-2: Decay characteristics of ^{238}U series radionuclides

Nuclide	Half life	Major radiation energies(MeV)		
		Alpha	Beta	gamma
^{238}U	4.5×10^9 y	4.15(23%) 4.19(77%)	-	-
^{234}Th	24.1 d	-	0.103 (19%) 0.191(81%)	0.063(3.5%) 0.093(4%)
^{234}Pa	6.7h	-	0.53 (66%) 1.13(13%)	0.10(50%) 0.70(24%) 0.90(70%)
^{234}U	2.48×10^5 y	4.72(28%) 4.77(72%)	-	0.053(0.2%)
^{230}Th	7.52×10^4 y	4.62(24%) 4.68(76%)	-	0.068(0.7%) 0.142(0.07%)
^{226}Ra	1602 y	4.6(5.5%) 4.78(94.5%)		0.186(4%)
^{222}Rn	3.825d	5.49(~100%)	-	0.510(0.07%)
^{218}Po	3.05m	6.11(100%)	0.33(100%)	-
^{214}Pb	26.8m	-	1.03(6%)	0.295(19%) 0.352(36%)
^{214}Bi	19.7m	5.61(100%)	3.26(100%)	0.609(47%) 1.120(17%) 1.764(17%)
^{214}Po	164μs	7.83(100%)	-	0.799(0.014%)
^{210}Tl	1.32m		2.3(100%)	0.296(80%) 0.795(100%)
^{210}Pb	22y		0.017(85%)	0.047(4%)
^{210}Bi	5.02d	4.93(60%) 4.89(34%) 4.59(5%)	1.155(100%)	
^{210}Po	138.2d	5.3(100%)	-	0.803(0.0011%)
^{206}Tl	4.19m		1.52 (100%)	-
^{206}Po	stable			

^{238}U is the most abundant isotope (99.27%) of natural uranium with a half-life of 4.5×10^9 y. ^{222}Rn formed from the decay of ^{226}Ra, diffuses from soil to the atmosphere and its concentration decreases monotonously with height. ^{222}Rn has a half-life of 3.82 d and decays to the short-lived radon daughters which attach to airborne particles and deposit as dry and wet deposition. The decay products following ^{214}Po are moderately long-lived radionuclides such as ^{210}Pb ,^{210}Bi ,^{210}Po. The daughter radionuclides would

achieve secular equilibrium in an isolated system. However, natural processes can separate the radionuclides in decay chains because of differences in chemical and physical properties.

2.1.1.2.3 ^{235}U Decay Series

The series, also called the actinium series, begins with its longest lived nuclide ^{235}U and ends with the stable ^{207}Pb. The actinium 4n + 3 series is summarized in Table 2-3. ^{235}U has a half-life of 7.1 x 10^8 y. ^{235}U decays to beta emitting ^{231}Th with half-life of 26.6 h. The subsequent daughter products ^{231}Pa ($T_{1/2}$ = 3.43 × 10^4 y) is a long lived alpha emitter. The other daughter nuclides are very short lived.

2.1.1.2.4 Thorium Series

The decay chain of ^{232}Th includes 6 alphas and 4 beta decays, with associated gamma de-excitation of nuclei. ^{232}Th is the longest lived naturally occurring radionuclide with half-life of 1.4 × 10^{10} y and emits alpha (4.01 and 3.95 MeV). This series has three subseries. ^{228}Ra subseries radionuclides include ^{228}Ac, ^{228}Th and ^{224}Ra. The daughter product, ^{228}Ra is the longest lived intermediate in ^{232}Th series with half-life of 5.76 y and decays to ^{228}Ac. ^{228}Ac has a half-life of 6.13 h and decays with emission of beta and gamma rays. The gamma energies of ^{228}Ac are often used for measuring ^{228}Ra activity. The nuclear characteristics are given in Table 2-4. ^{224}Ra decays to ^{220}Rn and heads the subsequent subseries. ^{220}Rn and its decay products are all very short lived, the longest half-life being that of ^{212}Pb with half-life, 10.64 h. The daughter product ^{208}Tl emits 2.62 MeV gamma rays that can cause significant external exposure dose if high concentration of ^{228}Ra is present.

Table 2-3: Decay characteristics of ^{235}U series

Nuclide	Half life	Major radiation energies(MeV)		
		Alpha	Beta	gamma
^{235}U	7.13 × 10^8y	4.36 (18%) 4.39 (57%) 4.1-4.6 (8%)	-	0.143 (11%) 0.185 (54%) 0.204 (5%)
^{231}Th	25.6h		0.300(100%)	0.026 (2%) 0.084 (10%)
^{231}Pa	3.43 × 10^4y	5.01 (<20%) 4.99 (25%) 4.94 (23%)	-	0.27 (6%) 0.29 (6%)
^{227}Ac	22y	4.95 (48.7%) 4.94 (36.1%) 4.87 (6.9%)	-	0.070 (0.08%)
^{227}Th	18.17d	5.76 (21%) 5.98 (24%) 6.04 (23%)	-	0.050 (8%) 0.237 (15%) 0.31 (8%)
^{223}Fr	21m	5.34 (0.005%)	1.15 (100%)	0.050 (40%) 0.080 (13%) 0.234 (4%)
^{223}Ra	11.68d	5.61 (26%) 5.71 (53.7%) 5.75 (9.1%)	-	0.149 (10%) 0.270 (10%) 0.33 (6%)
^{219}Rn	3.92s	6.42 (8%) 6.55 (11%) 6.82 (81%)	-	0.272 (9%) 0.401 (5%)
^{215}Po	1.83ms	7.38 (100%)	-	-
^{211}Pb	36.1m	-	0.95 (1.4%) 0.53 (5.5%) 1.36 (92.4%)	0.405 (3.4%) 0.427 (1.8%) 0.832 (3.4%)
^{211}Bi	2.16m	6.28 (17%) 6.62 (83%)	0.60 (0.28%)	0.351 (14%)
^{211}Po	0.52s	7.43 (99%)	-	0.570 (0.5%) 0.90 (0.5%)
^{207}Tl	4.79m	-	1.44 (100%)	0.897 (0.16%)
^{207}Pb	stable			

Table 2-4:Decay characteristics of ^{232}Th series

Nuclide	Half life	Major radiation energies(MeV)		
		Alpha	**Beta**	**gamma**
^{232}Th	1.39 × 10^{10}y	3.95 (24%) 4.01 (76%)	-	
^{228}Ra	5.75 y	-	0.055(100%)	
^{228}Ac	6.13 h	-	2.11 (100 %)	0.34 (15 %) 0.908 (25%) 0.96 (20%)
^{228}Th	1.913y	5.34 (28%) 5.42 (71%)	-	0.084 (1.6%) 0.214 (0.3%)
^{224}Ra	3.64d	5.45 (5.5%) 5.68 (94.5%)	-	0.241 (3.7%)
^{220}Rn	55.6s	6.3 (~100%)	1.15 (100%)	0.55 (0.07%)
^{216}Po	0.145s	6.78 (100%)	-	-
^{212}Pb	10.64h	-	0.580 (100%)	0.239 (47%) 0.300 (3.2%)
^{212}Bi	60.5m	6.05 (70%) 6.09 (30%)	2.25 (100%)	0.040 (2%) 0.727 (7%) 1.620 (1.8%)
^{212}Po	304 ns	8.78 (100%)	-	-
^{208}Tl	3.1m	-	1.8 (100 %)	.511 (23%) 0.583 (86%) 0.860 (12%) 1.620(100%)
^{208}Pb	Stable			

2.1.2 Man-made radionuclides

Anthropogenic (man-made) radionuclides are created by human activities. There are about over 1300 artificial radionuclides produced either by nuclear reactions or particle accelerator [47]. In the second half of the 20th century, the background from the anthropogenic radionuclides started to increase due to nuclear weapon tests, nuclear accidents, mining and milling operations of uranium ores, nuclear fuel fabrication processes, reprocessing of spent fuel, operations of nuclear reactors, nuclear medicine, and from storage of nuclear wastes. Between 1945 and 1980, over 500 nuclear tests that injected radioactive debris into the atmosphere were conducted around the world [48]. ^{3}H, ^{14}C, ^{131}I, ^{90}Sr and ^{137}Cs are few very important

radionuclides produced in nuclear detonations. Nuclear reactor accidents involved release of short term single source of radioactive materials to the atmosphere. ^{90}Sr, ^{134}Cs, ^{137}Cs, ^{85}Kr, ^{95}Zr, ^{239}Pu, ^{131}I, ^{129}I etc. are few radionuclides released during nuclear reactor accidents along with highly radioactive fuel fragments.

Table 2-5: Average annual Effective dose from Natural and Man-made Source

Source	**Average annual dose per person**
Natural background	2.4 mSv
Medical diagnostics	0.4 mSv
Nuclear weapon tests	0.005 mSv
Chernobyl accident	0.002 mSv
Nuclear fuel cycle	0.0002 mSv

Radionuclides can be transported into the human body through inhalation, as well as through the food chain. The average annual dose per person from various sources was estimated by UNSCEAR and is shown in the Table 2-5 [9].

2.2 Geochemical properties of important elements from Th series

2.2.1 Radium

Radium exhibits only the +2 oxidation state in solution, and its chemistry resembles that of barium. Radium forms water-soluble chloride, bromide, and nitrate salts. The phosphate, carbonate, selenite, fluoride, and oxalate salts of radium are slightly soluble in water, whereas radium sulfate is relatively insoluble in water ($K_{sp} = 4.25 \times 10^{-11}$ at 20° C). $RaCl_2$ and $Ra(NO_3)_2$ are highly soluble than $RaSO_4$. Radium does not form discrete minerals but can precipitate with many minerals, including calcium carbonate, hydrous ferric oxides, and barite ($BaSO_4$). Radium can be sorbed by clay minerals, colloidal silicic acid, manganese oxides, and organic matter. Although radium (unlike uranium) has only a single valence state, the dissolution or precipitation of sorbing phases, such as barite and ferric hydrous oxides, under

changing oxidation-reduction conditions can influence its mobility. Groundwater is low in sulfate but high in ionic strength, calcium, and barium resulting in conduciveness to the transport of radium.

2.2.2 Thorium

In nature, thorium occurs as ^{232}Th with 100% abundance though the shorter lived ^{234}Th (24.1 d half-life) and ^{230}Th (7.54×10^4 y half-life) in the ^{238}U chain; ^{228}Th (1.9 y half-life) in the ^{232}Th chain; and ^{231}Th (1.06 d half-life) in the ^{235}U chain are present. Natural thorium has a specific activity of 4.07 MBq kg^{-1}. Thorium is more abundant than uranium in the earth crust. Thorium is commonly present in the +4 oxidation state, which is mostly immobile. Though fractionation occurs for both thorium and uranium during igneous processes, uranium is more mobile as uranium oxidizes to U^{6+} to form the very soluble, uranyl $(UO_2)^{2+}$ ion. Thorium remains in the refractory solid form and are hence often transported as distinct grains of various minerals. Sandstones contain about 2 ppm Th, beach sands contain 10 ppm, and limestone has about 2 ppm. Monazite is the common ore mineral of thorium that occurs in igneous rocks. Thorium has the tendency to substitute with elements of similar size and charge, such as U, Zr, Ce and other rare earth. Thorium shows a strong affinity for phosphorous, hence in most minerals, thorium always has greater phosphate content. Like U, Th also has a high affinity for inorganic ligands, like fluoride, phosphate, hydroxide and sulfate, hence increasing its mobility especially at pH between 2 and 8. Th also forms organic ligand with humic acid [49, 50].

Thorium forms highly insoluble hydrated oxide precipitate at near neutral pH and they also co precipitate with hydrated ferric oxides. This helps in mobility or removal of

thorium from the minerals. The dissolution rate of thorium bearing mineral is very low, hence thorium concentrations in natural waters are generally low [51].

2.3 High Background Radiation Area (HBRA)

There are regions around the world where the natural background radiation levels are high with potential public annual effective dose from external and internal exposures higher than 1 mSv y^{-1} dose limit set for members of public due to operation of nuclear facilities. Accordingly, High Background Radiation Area (HBRA) is defined as "an area or a complex of dwellings where the sum of exposures from cosmic radiation and natural radioactivity in soil, indoor and outdoor air, water, food, etc. lead to higher/chronic exposure situations from external and internal exposures that results in an annual effective dose to the public above a defined level" [52]. Based on the annual effective doses of the inhabitants, HBRA have been classified accordingly into four levels: low, annual effective dose below 5 mSv y^{-1} (or about twice the global average of 2.4 mSvy^{-1} reported by UNSCEAR, 2000); medium (5-20 mSv y^{-1}), high (20-50 mSv y^{-1}); and very high (>50 mSv y^{-1}) [53, 54]. The geology and geochemistry of the rocks and minerals have the greatest influence in determining where the high natural radiation shows up.

2.3.1 Iran

In Iran, Ramsar is a well-known HBRA. The higher levels of radiation in these regions are due enhanced concentration of ^{226}Ra and its decay products, which were brought to the earth's surface by hot springs. Subsurface geological activity causes the heating up of the ground water and when this hot water passes through relatively young and uraniferous igneous rock, radium is dissolved from the rocks into the hot ground water. A dose of about 260 mSv y^{-1} is received by the population residing in

this area [12]. According to Sohrabi et al., absorbed dose rates in the air outdoors ranged from 0.08 to 20 μGy h^{-1} and some hot spots in northern region showed higher values up to 100 μGy h^{-1}.[55]. He has also reported the soil concentration in the range of 15 – 120 Bq kg^{-1} for ^{232}Th, 20 – 3.8 × 10^4 Bq kg^{-1} for ^{226}Ra and 235 – 634 Bq kg^{-1} for ^{40}K. Another spring, in Hormozg in south of Iran also had higher levels of radiation. Dabbagh et al., has measured a maximum effective dose of 42 mSv y^{-1} around the spring and the highest activity concentration of ^{226}Ra, ^{232}Th and ^{40}K in the mineral spring was 34 Bq l^{-1}, 2.52 Bq $l^{-1}$and 11.80 Bq l^{-1} respectively [56].

2.3.2 Brazil

The radioactivity originated from the mountains rich in zirconites and monazites along the coast. The coastal region in this area showed radiation dose as high as 130 μSv h^{-1} in few places. Guarapari, a village in Brazil, with population of about 12,000 inhabitants has high concentration of monazite in the local soil. The naturally occurring ^{226}Ra, ^{214}Pb, ^{232}Th, and ^{40}K in beach sands ranged from 6.0 to 4100, 6.0 to 3600, 20 to 57,000 and 73 to 3000 Bq kg^{-1} respectively [57].

2.3.3 China

Two regions namely, Donganling and Tongyou, in Yangjiang County, are well known HBRA in china, with more than 80,000 inhabitants. The annual effective dose is estimated to be 6.4 mSv (640 mrem) [9, 11]. The mean of the natural radionuclides ^{238}U, ^{232}Th, ^{226}Ra and ^{40}K in soil of the well-known HBRA in China from Guangdong province was reported to be 140, 187, 134 and 680 Bq kg^{-1} [58, 59].

2.3.4 India

In India, there are a monazite placer deposits along its coastal line like Ullal and Mangalore beaches in Karnataka, Chavara, Neendakara, Vizhinjam-Kovalam, etc., in

Kerala, Midalam- Manavalakurichi- Muttom coastal stretch, Kalpakkam, etc., in Tamilnadu, Bhimunipatnam, Konda- Kandivaiasa- Mukumpeta in Andhra Pradesh, and Chhatrapur Sanaeka- sangi- Gopalpur and Puri in Orissa [60]. A typical composition of monazite contains 3-10% of thorium oxide, less than 0.5% of uranium oxide and 60-65% of rare earth oxide of which 20% is Cerium oxide[61]. Indian monazite has an average Th content of about 9-10% as Oxide [62].

Beach sand mineral deposits containing the mineral Monazite along the coastal tracts in parts of Odisha, Andhra Pradesh, Tamil Nadu and Kerala was established by Minerals Directorate for Exploration and Research (AMD), an unit of DAE. The state-wise resources of in-situ monazite established by AMD are as follows (Table 2-6) [63]:

Table 2-6: Monazite resources in India

State	Monazite (MillonTonne)
Odisha	2.41
Andhra Pradesh	3.72
Tamil Nadu	2.46
Kerala	1.90
West Bengal	1.22
Jharkhand	0.22
Total	11.93

In India, Monazite occurs as placer deposits along the coastal shore. Mechanical concentration of mineral particles from weathered mineral debris resulted in formation of placer deposits. This placer deposits can show up in beaches, rivers, dunes and offshore areas. Placer deposit minerals have high density and are resistant to chemical breakdown. Crystalline rocks are the primary source for placer formation. Suitable weathering environment helps in liberation of the minerals from the source rocks. The movement and final destination are dependent on the natural process like running water, wind [64]. Additionally, the coastal hydrodynamics helps the terrestrial processes (geomorphology of the area, climate, and drainage pattern in the rocks,

geotectonic) in formation of beach placer deposits. When heavy minerals gets deposited on the beach, by means of processes like wind action in the upper part of the beach, the minerals get eroded and further form heavy mineral rich coastal dune deposits [65]. Beach placers forms the important source for mineral deposits like ilmenite, rutile, zircon, monazite and garnet. India has large placer deposits along its coast. Due to the high concentration of thorium rich monazite mineral in these regions, epidemiological, radiobiological and dosimetry studies is important.

2.4 The human radiation exposure

Humans and all living beings are exposed to ionizing radiation from cosmic rays, terrestrial radionuclides in soil, building material, air, water, food and in humans itself (Fig 2-2). The contribution from manmade radionuclides is minuscule when compared to natural radiation.

Exposure to radiation from natural and artificial sources are classified into two categories (Table 2-7)

1) *External exposure* from extra-terrestrial radiation i.e., cosmic radiation, and radiation of terrestrial origin and man manmade radionuclides.
2) *Internal exposure* involving naturally occurring radionuclides and man-made radionuclides entering the human via inhalation and ingestion.

2.4.1 External Exposure

The *external exposure* is primarily from gamma radiation arising from the decay of cosmic radiation, decay of naturally occurring and man-made radionuclides. The three important contributors to the terrestrial radiation are ^{40}K, radionuclides from thorium and uranium series. Radionuclides present in the top 20 cm soil contributes maximum to the external dose. Fig 2.2 shows the various exposure pathways.

Table 2-7: Estimated Annual Effective Dose and contribution(%) from natural sources to Indian Population and its comparison with global average [66]**.**

Source of Radiation	India		World	
	mSv y^{-1}	**%**	**mSv y^{-1}**	**%**
External Exposure				
Cosmic Radiation	0.355	15.4	0.380	15.5
Terrestrial Radiation	0.379	16.5	0.48	19.6
Internal Exposure				
Cosmogenic (inhalation)	0.015	0.65	0.010	0.41
Radon and Thoron(Inhalation)	1.235	53.7	1.275	51.9
Terrestrial(Ingestion)	0.315	13.7	0.310	12.6
Total	2.299	100	2.455	100

2.4.2 Internal Exposure

Ingestion and *inhalation* are two primary routes for *internal exposure* from the intake of terrestrial radionuclides. Inhalation dose is due to the presence of dust particles in air containing radionuclides of the ^{238}U and ^{232}Th decay chains and the short-lived decay products of radon. The ingestion pathway via the intake of foods may be a potential contributor to radiological dose if elevated levels of radioactivity are present in the environment. Unlike external exposure which causes dose only during exposure period, radionuclides that are inhaled or ingested can result in a dose in the subsequent years depending upon the biological half-life of the ingested radionuclides.

2.4.2.1 Inhalation Intake

The radionuclides released from the earth crust get attached with dust particles. When human beings breathe this air, radionuclides (gaseous and particulates) find their way into the human system via respiratory tract. The deposition, clearance in respiratory tract and its subsequent absorption into blood of the inhaled radionuclide depends on the amount, solubility, size, chemical composition, tendency to attach to aerosol etc.

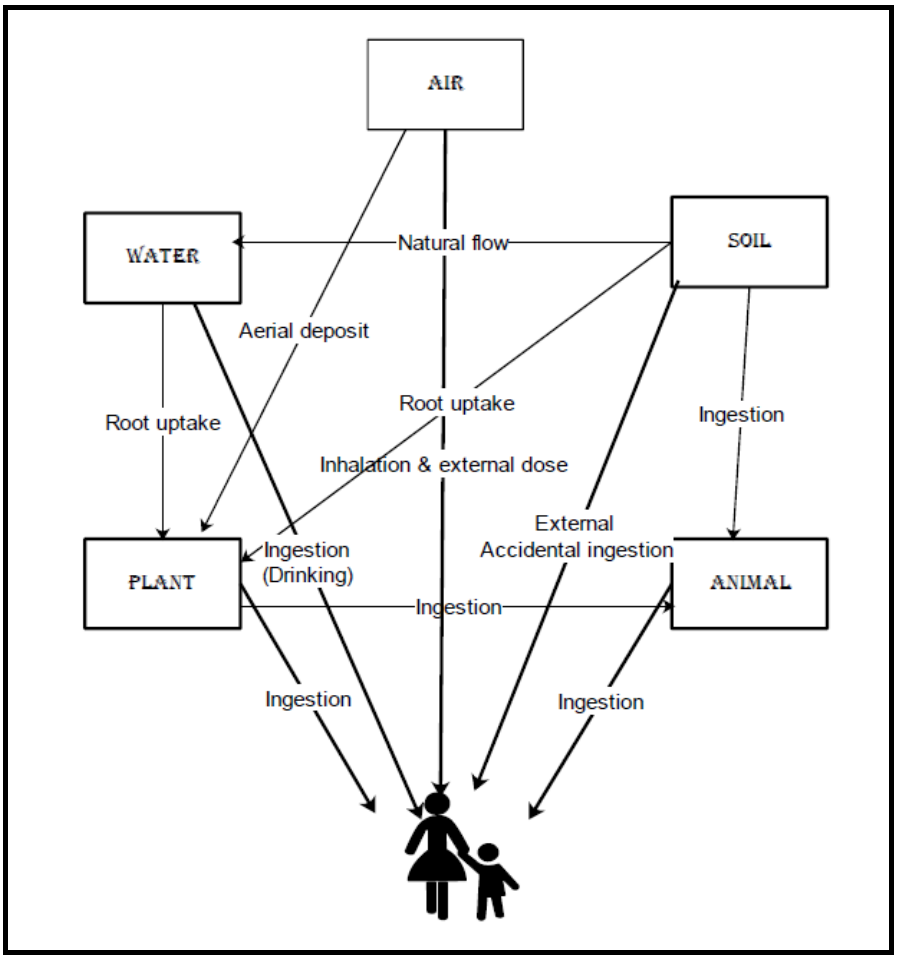


Figure 2-2: Human exposure pathway to radiation

The main cause of inhalation dose from terrestrial radionuclides is the radon and its short lived decay products. Indoor radiation exposure in a building is mainly due to the external gamma radiation from the primary radionuclides present in the construction materials and due to inhalation of ^{222}Rn, ^{220}Rn and their progenies.

2.4.2.2 Ingestion Intake

NORM is present in the soil, rocks, underground water, oceans and the atmosphere. Anthropogenic radionuclides resulted from use of nuclear weapons, the use of radionuclides in nuclear medicine and accidental releases from nuclear facilities also contributed to internal exposure. Ingestion pathways include drinking water, ingestion of water while bathing, ingestion of agricultural products (leafy vegetables, other

vegetables, meat, and milk etc.), ingestion of aquatic foods (fish and shellfish), ingestion of water or sediment while participating in aquatic recreational activities (swimming, boating, or shoreline use), and ingestion of soil. Ingestion of radionuclides through food is an important route for long term internal radiation does to various organs of the body. *It is important to monitor the activity concentration of radionuclides in food consumed by all living beings.*

Many studies have been conducted to evaluate the ingestion intake dose due to intake of NORM around the world both in normal background radiation area (NBRA) and HBRA. Human habitats in HBRA of India are likely to get exposed to higher level of radiation both by external and internal pathways and needs to be studied extensively. In this work, internal exposure to human from ^{232}Th for a group of population residing in a HBRA of southern India via ingestion is evaluated.

2.5 Radionuclides in food chain

Radionuclide can enter food chain either through *terrestrial environment* or *aquatic environment*. The aquatic pathway covers the radionuclides deposits in oceans, rivers and lakes. The terrestrial pathway deals with radionuclide deposits in soil and air. The radionuclide deposited on the plant or taken up by the plants can be consumed directly by human or first ingested by animals and then by the ingestion of contaminated animal products (dairy or meat). The accumulation of radionuclides by the plants depends on many factors and even in animals, certain tissues tend to accumulate more of selected radionuclides than others. The relevant incorporation of the radionuclides in the milk is usually due to the ingestion of contaminated pasture. This transfer process is often called the *pasture-cow-milk* exposure route.

2.5.1 Terrestrial Pathways

Mobility and potential transfer of radionuclides to the food chain are dependent on parameters such as their chemical form, environmental redox condition, difference in mineralogy and hydrogeology. The radionuclide concentration in food varies depending on the climate, soil type, agricultural practices, the background levels in soil and its transportation from soil to other systems like plants, animals, food and humans.

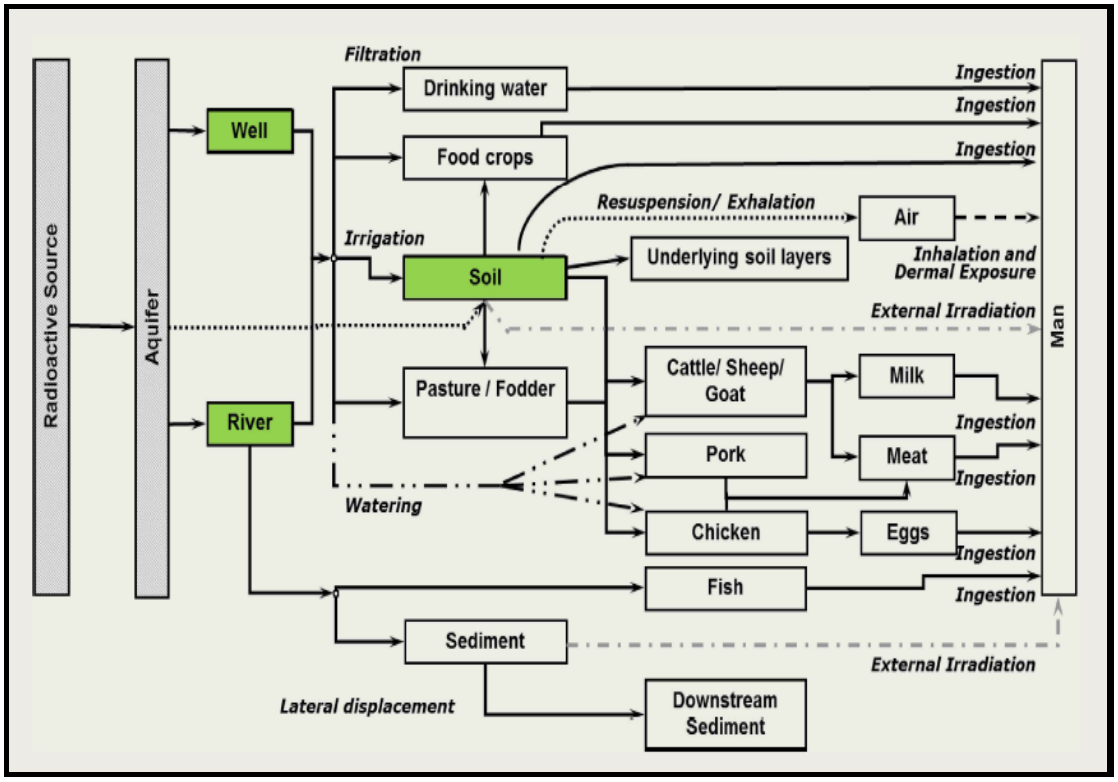


Figure 2-3: Schematic overview of the radionuclide exposure pathways to man by aquatic and terrestrial route[69]

The Fig 2-3 outlines the migration of radionuclides from soil and water to humans. Hegazy et al., in their study on uranium and thorium uptake by plants have indicated that the ability of plants to accumulate uranium and thorium in their edible portions depends on soil characteristics and properties such as clay content, pH, minerals, fertilizers and organic matter contents [67]. Radionuclides can enter plants through

root uptake, atmospheric deposition or re-suspension from the soil. Foliar absorption of radionuclides by plants that occur due to deposition of radionuclides carried by the air or rain on the leaves is an important path of radiation exposure to man and animal. Santos et al., have reported the presence of thorium and uranium in the aerosol particles, returning as rain droplets to the terrestrial and aquatic grounds is an important pathway for entry of radionuclide from grass to cow and into the milk [68]. The external contamination of plants can be transferred to the ground surface and may enter the soil by washing from the contaminated plant or the plant parts itself. Plants are capable of absorbing radionuclides from water or soil in the same way as other minerals are absorbed from their roots. The ability of absorption of radionuclide from soil is called the transfer factor (TF). TF is defined as the ratio between the activities of a radionuclide within a plant (fresh weight) to the activity of the radionuclide in soil (dry weight).

Several studies have been undertaken on various foodstuffs (e.g. vegetables cereals, tubers, herbs, etc.) to evaluate the transfer factor of naturally occurring radio-nuclides [17, 70–72]. The uptake of radionuclides by plants vary widely with plant species resulting in varying concentrations in food products [73]. As observed by Al Masari et al., the concentration of radionuclide in the plant material is high when the concentration is high in the soil [74]. The accumulated radionuclides in the plant will be consumed by either humans or animals [17, 70, 75]. NORM migrates from plants to animals through fodder, main source of food for cows, goats and chicken [76]. When human consume meat and other animal products containing the radionuclides, are indirectly exposed to internal radiation. A dynamic model for assessing the transfer of radionuclides in a food-chain was developed and applied to assess the

radiological impact on the Loire river, where 14 nuclear power plants situated on five different sites is operational by Ciffory et al., [77]. They have concluded that there is an need for improving evaluation of the deposition of radionuclides in bed sediments and subsequent external exposure and aerial contamination pathways of consumable vegetables.

2.5.2 Aquatic Pathway

Another important pathway for entry of radionuclides into food chains is the aquatic route. A radionuclide exists in water in a truly dissolved state or in an un-dissolved state such as a colloid or sorbed to particulate matter. The fate and mobility of thorium in environmental media are governed by its chemical and biological behaviors. Thorium discharged as ThO_2 into surface waters from mining, milling and processing are mostly present as suspended particles [78]. At pH >5, soluble thorium ions in water hydrolyses to form $Th(OH)_4$ precipitate or hydroxy complexes which gets adsorbed on the particulate matter in water [79]. Resuspension and mixing of this complexes in water decides the migration of the sorbed thorium in water. Concentration of dissolved thorium in waters may also increase due to formation of soluble complexes with carbonate, humic materials or other ligands in the water [80].

The migration of natural radionuclide in the aquatic system involves the phenomena of water turbulence. Radionuclides in the sediment surface is transported due to this turbulence to a larger distance before they are lost from the water column by sedimentation process. The radionuclides are then taken up by the aquatic microbes, planktons, plants and animals [81].

The main route for intake of radionuclide by fish are by foraging, oral intake of water and by accidental ingestion of sediments that has radionuclide adsorbed onto it [82].

Biological factors may also influence the degree of radionuclide uptake and distribution among various tissues and organs in fish.

Poston et al, have also indicated that though foraging and drinking water are the primary route for ingestion by fish, internal exposure can also occur through absorption across epithelial cells of the skin [82]. Fisher et al., has observed that certain marine organism accumulate higher concentrations of radionuclides [83]. Similar observation was reported by other workers also [45, 84]. Concentrations of natural radionuclides in marine organism groups have been compared by Brown et al for European aquatic environment and have indicated in the report that the highest concentrations in marine organisms are observed for ^{40}K and ^{210}Po [85, 86]. Absorption from GI tract is higher for marine fish compared to fresh water fish [87].

Certain marine organisms acts as first order biological indicators of radiation pollutant, Mussels is one such indicator [88, 89].

2.6 Literature review on ingestion Intake of Naturally Occurring Radioactive Material (NORM)

Natural radionuclides exist universally in the environment and contribute significantly to external and internal doses to the population. NORM like ^{238}U, ^{234}U, ^{232}Th, ^{230}Th, ^{228}Ra, ^{226}Ra,^{210}Pb and ^{210}Po are of particular importance. These radionuclides enter the human system mainly through ingestion and contribution via inhalation is minimal [1]. So lot of work has been carried out worldwide and also in India to evaluate the annual effective dose from intake of food and water. The ingestion intake depends on the dietary composition and its concentrations in food. Concentration of the NORM in the diet can be evaluated using *Market Basket Study (MBS) Method or Duplicate Portion Study (DPS) Method*. In MBS method, concentration of radionuclide is estimated in

individual food component and its daily consumption rate obtained from National Nutrition Survey reports available for the study group is used to evaluate the intake. Where as in DPS method, the duplicate portion of the total diet that is consumed by the individual is collected in actual and radionuclide concentration is estimated to evaluate the internal dose.

2.6.1 Studies worldwide for NORM ingestion intake

There have been several studies for estimation of NORM concentrations in foodstuffs from NBRA, such as those for ^{238}U [45, 90–93], ^{226}Ra [32, 41, 90, 94–101], ^{232}Th [90, 92, 97–99, 102], ^{210}Pb [39, 103–105] and ^{210}Po [37, 86, 106–109]. Cumhur Canbazog˘lu et al., have evaluated the concentration of ^{226}Ra, ^{232}Th and ^{40}K in vegetable and fruits consumed by Turkish population using gamma spectrometry [97]. The average activity concentrations in vegetables was calculated as 0.64 ± 0.26 Bq kg^{-1} for ^{226}Ra, 0.65 ± 0.14 Bq kg^{-1} for ^{232}Th, 13.98 ± 1.22 Bq kg^{-1} for ^{40}K, and 0.54 ± 0.04 Bq kg^{-1} for ^{137}Cs. The average activity concentrations in fruits were 1.52 ± 0.34, 0.98 ± 0.23, 18.66 ± 1.13 and 0.59 ± 0.16 Bq kg^{-1}, respectively for ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs.

Extensive work has been carried out to evaluate the concentration of NORM in dietary component collected from Poland. ^{238}U, ^{234}U, ^{232}Th,^{230}Th, ^{228}Th, ^{226}Ra was estimated in food stuffs and drinking water samples collected in the Walberzych region of Poland using alpha spectrometry. The average concentration of ^{238}U, ^{234}U, ^{232}Th,^{230}Th, ^{228}Th, ^{226}Ra in milk was 2.56, 3.69, 1.19,1.15, 2.64 and 9.95 mBq kg^{-1}_{fresh} respectively. Daily intake with food and water for the adult population was: ^{238}U - 17.7 ± 0.81, ^{234}U - 30.2 ± 1.40, ^{230}Th - 5.86 ± 0.38, ^{232}Th - 3.38 ± 0.29, ^{228}Th - 11.8 ± 1.21 and ^{226}Ra - 56.6 ± 6.2 mBq d^{-1} respectively [94]. In a work carried out by Fisenne et al., NORM

was estimated in the New York city diet, USA. They have reported that the highest contribution to daily intake was from ^{226}Ra [90].

In a recent study conducted by a Chinese group, the activity concentration of ^{238}U, ^{228}Ra, ^{226}Ra, ^{40}K and ^{137}Cs in different foodstuff groups was estimated and have reported that the highest radionuclide concentration was found in seafood, followed by poultry, tea and freshwater product [110]. They have also observed that total annual committed effective dose in Chinese men accounts for ~0.43 mSv, 43% higher than the world reference value. The dose by ingestion is about two orders of magnitude higher than that by inhalation.

Jing Chen attempted a study on dose to children from intakes of various radionuclides (except radon) by ingestion relative to adults by considering six different age groups (viz., 0–1, 1–2, 2–7, 7–12, 12–17, and adult >17 years) for Canadian populations [111]. The ingestion exposure dose is mostly related to ^{238}U and ^{232}Th decay series as well as ^{40}K through drinking and eating [90, 92].

2.6.2 Ingestion Studies in India.

The concentration of radionuclide in food materials depends on various environmental and biological factors. The geological environment and agricultural practices are different for various region. The dietary habits are also different and vary from region to region even within India. Hence it is important to have region specific data on the radionuclide concentration to evaluate the ingestion intake dose. India is a big country both in territory and with diversified population and includes quite different economic development level, life style and food culture. In India, there are many reports that gives the radionuclide concentration in various food samples [3, 87, 112–120].

Extensive work has been carried out to evaluate ^{210}Po in various matrices. Natural radionuclides ^{210}Po activity in food of plant origin such as cereals, pulses, vegetables and food of animal origin such fish, crab, prawn, chicken, egg etc. were determined in and around Kalpakkam by Kannan et al. The ^{210}Po activity levels in all the dietary components (excluding milk and drinking water) ranged widely from ⩽10 to 1,22,641 mBq kg^{-1}_{fresh}, the minimum in vegetables and maximum in the edible portions (muscle) of crab samples [3].

In another study conducted by Shivakumar, ^{210}Po in cereals, pulses, animal origin food, vegetables and spices collected from Gudalore (India) was estimated. The activity concentration of ^{210}Po in cereals varied from 124 to 604 mBq kg^{-1}_{fresh}. Raw rice has the highest mean activity of 604 ± 61 mBq kg^{-1}_{fresh} in cereals. Leafy vegetables had the highest ^{210}Po activity concentration (662-7336 mBq kg^{-1}_{fresh}) and followed by tuber vegetables (390-1269 mBq kg^{-1}_{fresh}) and then by other vegetables (75-595 mBq kg^{-1}_{fresh}) among the plant origin food items. Among animal products fish showed the highest ^{210}Po activity concentration 964 mBq kg^{-1}_{fresh} [121]. ^{210}Po was estimated in the edible muscle and soft tissue of 15 different marine species (fish, crab, prawn and bivalve) collected from Trans-Thane Creek area (Trombay) and Thane by Misra et al, and the ^{210}Po activity ranged from 0.18 to 10.9 mBq kg^{-1}_{fresh} [122]. In another study by Prabhath et al., ^{210}Po was evaluated in commercially available infant food using alpha spectrometry. The ^{210}Po concentration in the samples was in the range of 80 to 230 mBq kg^{-1}_{fresh} [123].

Isotopes of radium namely ^{226}Ra and ^{228}Ra was also estimated in many food materials. More data on ^{226}Ra and ^{228}Ra concentration in marine organism is available compared to vegetation or fruit items. In a study conducted by Raj et al., ^{226}Ra and ^{228}Ra in

marine organism collected along the western coast of India was evaluated using gamma ray spectrometry and ^{226}Ra activity was found to be in the range of 0.07–0.736 Bq kg^{-1}_{fresh} and ^{228}Ra in the range of 0.082–2.5 Bq kg^{-1}_{fresh}.

The mean concentrations of ^{226}Ra in duplicate diet samples collected from population residing around uranium mining complex, Jaduguda, Jharkhand, India was estimated using emanometric method and was found to vary from 0.06 to 0.18 Bq kg^{-1}_{fresh} [124]. Radium isotopes were estimated using gamma spectrometry by Patra et al., in food samples collected from Vishakhapatnam, Andhra Pradesh. The activity concentrations of ^{226}Ra was 1.78 ± 0.67 Bq kg^{-1}_{fresh} in milk, 1.94 ± 1.20 Bq kg^{-1}_{fresh} in eggs, 5.06 ± 1.35 Bq kg^{-1}_{fresh} in fruits and 0.79 ± 0.59 Bq kg^{-1}_{fresh} in fish.

Isotopes of uranium were estimated in food and water samples by many researchers in India. The daily intake of uranium (^{238}U) by an urban (Mumbai) Indian adult population was estimated by the analysis of a duplicate diet, drinking water, and air samples using NAA by Dang et al. The uranium intake through food was 6.9 mBq d^{-1} [125].

Giri et al., have estimated total uranium in vegetable samples consumed by population residing in mining area using fluorimetry technique. The concentration of uranium ranged between 0.017–0.213 Bq kg^{-1}_{fresh} [109]. Extensive work for estimation of drinking water sample is reported [116, 126–128].

Due to the difficulty in estimation of ^{232}Th in food and biological matrices, data on intake of ^{232}Th is scarce. Dang et al., have estimated ^{232}Th content in various food material collected from Mumbai, India by NAA [8].

Daily dietary intake of two naturally occurring long-lived radionuclides, ^{232}Th and ^{238}U, were estimated for the adult population living in a number of Asian countries

and reported by Iyengar et al. The median for daily intake of ^{232}Th ranged between 0.6 and 14.4 mBq and daily intake of ^{238}U ranged between 6.7 and 62.5 mBq. The annual committed effective doses to Asian population from the dietary intake of ^{232}Th and ^{238}U were calculated to be 0.34 and 0.20 μSv, respectively.

In another study conducted by Jha et al., in food item cultivated and consumed by tribal population residing around the proposed uranium mine in north eastern part of India, ^{232}Th in leafy vegetables ranged from 26.2 to 48.8 mBq kg^{-1}_{fresh}, in cereals from 5.3 to 16.1 mBq kg^{-1}_{fresh}, in roots and tubers from 4.8 to 81.4 mBq kg^{-1}_{fresh} and in other vegetables from 1.6 to 16.9 Bq kg^{-1}_{fresh} [120].

In another study, ^{232}Th concentration was evaluated in plant origin food samples collected from Cohin, Kerala using INAA. The highest concentration was found in roots and tubers [129]. Though data on ingestion intake of NORM is extensively available, very little is known about ingestion intake of ^{232}Th.

Hence it is important to focus on generating more baseline data on ^{232}Th intake for Indian population of various regions.

2.7 Radiation Dose to Inhabitants of HBRA from NORM

2.7.1 External Radiation Exposure:

A study on radiation exposures to the populations living in the HBRA of the monazite-bearing region in Kerala, India was conducted by Chougoankar et al. using thermo-luminescent dosimeters (TLD). The external radiation dose varied from 1.95 to 9.73 mSv y^{-1}[20]**.**

External radiation exposure and effective dose received by residents of 10 villages belonging to Natural High Background Radiation Areas (NHBRA) of coastal regions of Kanyakumari District, Tamilnadu in India were studied by using TLD. External

gamma doses were also measured inside and outside the houses using a scintillation survey meter. The annual effective dose (external) was estimated between 1.22 to 4.73 mSv y^{-1} and 1.23 to 4.23 mSv y^{-1} using scintillometer and TLD respectively [25].

In another study conducted by Esaiselvan et al., external doses using scintillometer and TLD (TLDs were exposed for one year, on a quarterly basis, inside the house at a height of 3 meters and about 1 meter away from the walls) were measured. They have reported the external exposure to vary from 1.95 to 4.45 mSv y^{-1} [30].

Gamma ray spectrometric measurements was carried out for the natural radioactivity levels due to ^{226}Ra, ^{232}Th and ^{40}K in beach sand samples around the coast of Kanyakumari district by Sarojini and the annual effective dose ranged from 0.94 to 2.23 mSv y^{-1} [130].

2.7.2 Internal Radiation exposure:

2.7.2.1 Inhalation:

Inhalation exposure to the general public was estimated from collection and analysis of air samples. Air sample particles were collected on glass fiber filter paper using vacuum pump of suitable flow rate. Activity deposited on the filter paper was measured using gamma spectrometry. Passive measurements using Solid State Nuclear Track Detectors (SSNTD) were also used [131]. Many reports are available for estimation of inhalation dose across the world.

The inhalation radiation doses to the population living in HBRA of Kerala, India was investigated by Chougaonkar et al., [20]. About 200 houses from two villages in this region were monitored for 1y. The inhalation doses due to radon, thoron and their progenies were monitored using SSNTD (LR-115-II, CR-39) based twin-cup dosimeters.

Radiation exposure and effective dose received through external and internal, via inhalation, by residents of 10 villages belonging to HBRA of coastal regions of Kanyakumari District, Tamilnadu in India were studied by Devajayanthi et al.,[25]. The indoor gamma radiation levels were monitored using TLDs, the indoor radon and thoron gas concentrations were measured using twin chamber dosimeters employing SSNTD. Gross alpha activity was estimated by collecting air samples on glass fiber filter papers and counting in an alpha counter of known efficiency. The SSNTDs and TLDs were exposed for 90 d and replaced with new one in the same place for every quarter for one year. The annual effective dose equivalent due to the inhalation of radon, thoron and progeny to the population of coastal Tamilnadu varied from 2.59 to 8.76 mSv y^{-1} with an arithmetic mean of 4.72 mSv y^{-1} [25].

2.7.2.2 Ingestion

Activity concentration of naturally occurring radionuclide was also estimated in food samples collected from HBRA by various workers [5, 87, 116, 132–135]. The ^{232}Th concentration in duplicate diet collected from Chavara, Kerala was estimated by Dang et al. using NAA and have reported a daily intake of 27.8 µg (113.2 mBq) giving an annual intake of 40.6 Bq of ^{232}Th and an annual committed effective dose (CED) of 16 µSv [136]. The intakes of ^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K from food samples collected from villages in HBRA of Tamilnadu were estimated using gamma spectrometry. The concentration of ^{226}Ra ranged between 0.03 ± 0.02 (leafy vegetable) and 7.5 ± 0.5 (black gram dhal) Bq kg^{-1}_{fresh}. The concentration of ^{228}Ra ranged from 0.08 ± 0.005 (leafy vegetable) to 5.4 ± 0.5 (tapioca) mBq kg^{-1}_{fresh}. The concentrations of ^{228}Th varied from 0.14 ± 0.04 (cucumber) to 34.3 ± 2.7 (rice) mBq kg^{-1}_{fresh}. Daily intakes of these radionuclides were as follows: ^{226}Ra, 0.001–1.87; ^{228}Ra, 0.0023–1.26, ^{228}Th,

0.01–14.09 ^{40}K, 0.46–49.39 Bq d^{-1} [5, 132]. In another study conducted by Kantha et al., the ^{210}Po in duplicate diet and individual food item was estimated using radiochemical method followed by alpha spectrometry. The average concentration of ^{210}Po in the food groups was 2176 mBq kg^{-1}_{fresh} in leafy vegetables, 55 mBq kg^{-1}_{fresh} in vegetable, 251 mBq kg^{-1}_{fresh} in roots and tubers, 250 mBq kg^{-1}_{fresh} in fruits, 345 mBq kg^{-1}_{fresh} in fish, 117 mBq kg^{-1}_{fresh} in flesh food, 220 mBq kg^{-1}_{fresh} in milk and 290 mBq kg^{-1}_{fresh} in cereals. The average concentration of ^{210} Po in DDS was found to be 74 mBq kg^{-1}_{fresh} [6].

It is interesting to note that, there is little work carried out in these regions to evaluate ^{232}Th in the food material or duplicate diet from HBRA of south Tamilnadu. Hence there is a need to deliberate on the internal ingestion intake of ^{232}Th by the population residing in this area.

2.8 Behavior of radionuclides in human

Assessment of radiation dose from internal exposure is difficult than estimating the dose from external exposure. Internal exposure can be acute or chronic but causes both radiological and chemical toxicity. Hence it is necessary to understand the behavior of these radionuclides in human body. Once the radionuclide enters the body, it gets absorbed to the blood and blood serves as the medium for distribution to the target organs/tissue where it is either retained and recycled back to blood or eliminated through urine or feces. Behavior of radionuclide in the human body depends on the type of radionuclide, its decay characteristics and its chemical form [137]. The various biological stages involved in transport of radionuclide in the body, depends on physico-chemistry or the speciation of compounds and is described as kinetics. Biokinetic models are multi-compartmental mathematical models used for

describing the movement, distribution and retention of radionuclides in the human body. International Commission for Radiation Protection (ICRP) has given a series of radionuclide specific models for various routes of entry (ingestion and inhalation) for adults and children [7, 138–145]. Doses to the fetus following maternal intakes are also evaluated and presented [146, 147]. Human respiratory tract model (HRTM) describes the movement of inhaled radionuclides in respiratory tract and human alimentary tract model (HATM) gives the behavior of ingested radionuclide [138, 141, 148]. Movement of ingested radionuclides through the gastrointestinal tract is described by the transit times between the stomach, small intestine and large intestine. The ingested radionuclide that traverses through the alimentary tract is mostly absorbed into blood mainly from the small intestine [148]. The absorption of radionuclides from the alimentary tract to the blood depends on the chemical properties of the radionuclide and this absorption fraction can vary widely say as 0.1% (Th, Pu) to 99% (Iodine) [139]. Depending on the particle size of the inhaled particles containing radionuclides, deposition occurs in varying fraction in the nasal passage, the bronchial and bronchiolar airways of the lung, and the alveolar region [141]. Clearance of the deposited radionuclide from the lungs occurs by two competing process namely particle transport and absorption to blood. Absorption to blood is by dissolution of the particle. Radionuclide that is absorbed into the blood, behaves differently and is described by element-specific systemic models [139, 142, 143]. These element specific models may vary from very simple models to multi-compartmental recycling model and is provided by ICRP. The most complex models are those of bone seeking alkaline earth and actinides elements like strontium, radium, thorium and plutonium. Once the radionuclides are deposited on the bone surface they

get exchanged with or within bone mineral, and are distributed into the bone volume by bone formation and move to bone marrow by bone resorption.

Biokinetic models for individual elements and their radioisotopes provide information on the rate of transfer and the retention with in the body. Whereas the *dosimetric models* are used to calculate the deposition of energy in all important organs/tissues (targets) from each source region, taking account of the energies and yields of all emissions [149].

2.9 Radiation dose due to internal exposure:

Extent of radiation effect on any tissue/organ depends on the absorption of average energy deposited in the tissue. The primary unit of radiation absorbed dose is expressed in terms of average absorbed energy per unit mass of tissue.

$$\text{Absorbed Dose} = \frac{\Delta E}{\Delta M} \qquad \textbf{(2.1)}$$

The unit for radiation absorbed dose in the SI system is called the *gray (Gy)*. One gray is an absorbed radiation dose of one joule per kilogram [150]. Unlike external exposure dose calculation, internal dose is evaluated using indirect method. The evaluated dose depends on physical (type of radiation, energy of the radiation and the radiological half-life) and biological (kinetic behaviors like absorption rates, transfer rates and retention rates in various organs and tissues) factors.

The two important assumptions made for internal dose assessments for a charge particle are i) All the energy of the charge particle emitted by a radionuclide in an organ/tissue is absorbed within the tissue ii) an element deposited in an organ /tissue is uniformly distributed throughout the mass of that organ/tissue. For an organ/tissue containing a uniformly distributed radionuclide, the amount of absorbed energy must be equal to the amount of energy emitted. The energy absorbed per unit tissue mass

per transformation is called the *Specific Effective Energy (SEE)*. The concept of equivalent dose used by ICRP enables to compensate for the effect of different radiation on the tissue. Derivation of equivalent dose uses radiation weighting factors (W_R) to take into account of the relative biological effectiveness (RBE) of different radiation types in causing malignancy or genetic damage. Thus, absorbed doses (Gy in joules/kg) to the various organs/tissues, obtained using biokinetic and dosimetric models, are multiplied by a W_R of 20 for alpha irradiation and 1 for electron and gamma radiations to give equivalent doses (in Sievert (Sv) dose units).

$$H_{50,T}(T \leftarrow S) = U_s \times SEE(T \leftarrow S) \qquad \textbf{(2.2)}$$

Where $H_{50,T}(T \leftarrow S)$ is the equivalent dose accumulated during 50 y after intake, U_S is the total number of disintegrations during 50 y after intake, and SEE ($T \leftarrow S$) is the Specific Effective Energy absorbed per gram of target tissue from each radiation, R, emitted from activity in the source organ.

$$SEE(T \leftarrow S) = \sum_R \frac{Y_R \times E \times W_R \times 1.6 \times 10^{-13} \times AF(T \leftarrow S)_R}{m_T(kg)} \qquad \textbf{(2.3)}$$

Where Y_R is the fractional yield, per disintegration, of the radiation under consideration, E is the average energy of radiation R, W_R is the radiation weighting factor, AF $(T \leftarrow S)_R$ is the absorbed fraction from radiation R in target organ/tissue T per transformation in source organ/tissue S, and m_T is the mass of T, in kg.

Tissue doses are integrated over a 50 y period for adults and to age 70 y for children and the resulting values are referred to as committed equivalent doses. The ICRP uses the another concept of effective dose to evaluate the whole-body dose for internal emitters. To estimate the whole-body effective dose, tissue weighting factors (W_T) are assigned to various tissues and organs. W_T takes into account of the respective

contribution to the total incidence of radiation-induced fatal cancer and hereditary effects, with adjustments for the incidence of non-fatal cancer and years of life lost. *Committed Effective Dose* (CED) is the sum of all committed equivalent doses multiplied by the appropriate tissue weighting factors. For evaluating dose, the ICRP has given tables of dose coefficients for each radionuclide, giving values of committed equivalent dose and committed effective dose per unit intake of specified radionuclides by ingestion or inhalation (Sv Bq^{-1}) for various age group and fetus. Dose co-efficient are obtained by assuming some reference intake and calculating the committed effective dose from that intake based on the systems of models.

2.10 Thorium Processing in India

The southwest and southeast coastal regions of India have rich deposits of heavy minerals like ilmenite, zircon, rutile, garnet, monazite and sillimenite. The monazite content of the beach sands varies from <0.1% to 5%. Monazite of Indian origin contains approximately 9% Th as ThO_2 and 0.35% U as U_3O_8. Table 2.8 gives typical concentrations of NORM and total rare earth oxides (TREO) in monazite across the globe[151].

Table 2-8: Typical Composition of some monazite minerals from different regions

	Composition (%)			
	TREO	**U_3O_8**	**ThO_2**	**P_2O_5**
Monazite, Australia	61.33	0.34	6.55	26.28
Monazite, India	59.68	0.37	9.58	26.23
Monazite, Malaysia	59.65	0.24	5.90	25.70
Monazite, Thailand	60.20	0.44	5.76	26.52
Monazite, Korea	60.20	0.45	5.76	26.52
Monazite, DPRK	42.65	0.18	4.57	18.44

Mining and mineral separation is being carried out by Indian Rare Earths Ltd., an undertaking of the Department of Atomic Energy at Manavalakurichi[151]. Surface

mining, collection of beach washings and dredge mining are the mining methods adopted in India. The mineral separation plant makes use of the differences in the electrical and magnetic properties and differences in specific gravity of the constituent minerals to separate them. The dredged sand is concentrated by slurrying in water and passing down through spirals. The dried concentrate is passed through a series of high tension electric separators and magnetic separators of varying intensities.

Monazite, an orthophosphate of Th and rare earth (RE) elements, is chemically processed by reaction with caustic soda lye which results in Na_3PO_4, hydroxides of thorium, uranium and REs. This reacted mass is leached with water, where Na_3PO_4 gets dissolved leaving behind the hydroxides. The mixed hydroxides of thorium, uranium and REs are then treated with HCl at a controlled pH, where RE remains in solution as rare earth chlorides and the hydroxides of Th and U and the undissolved, unreacted sand remain in the sludge. the radium (^{228}Ra) and Pb present in the monazite are carried with the rare earth chloride and are removed from the product and lead is eliminated by precipitating with $BaSO_4$ and lead sulphide. The deactivated and lead-free composite REs chloride is evaporated and made into flakes and marketed. For the separation of individual REs, a solvent extraction process is employed. The stock of thorium hydroxide is dissolved in HCl and uranium is recovered by solvent extraction using alamine as solvent and thorium is extracted as thorium oxalate [152].

2.11 Application of Thorium

Thorium finds a lot of industrial application like for the manufacture of gas mantles, welding rods, thermistor, and catalysts. ^{232}Th is also used as nuclear fuel for ^{233}U fuel

based reactors. Aeronautical and aerospace thoriated alloys are used in aircraft engine parts, but only to a limited extent.

2.11.1 Incandescent gas mantles

For over a century, the main of use of thorium is in gas mantle industry. When the thoriated mantles are heated to a temperature of 1870-2370 ^{o}C, ThO_2 in the mantle causes incandesce[153]. The greatest incandescence is obtained with mantles that consist of 99% ThO_2 plus 1% cerium oxide after pre-burning. The heat energy accumulates in ThO_2 and then the absorbed energy is transferred to cerium oxide, which emits strong visible light [154]. Thorium in the form of nitrates with specific activity 2 mBq kg^{-1} of ^{232}Th , is used in the production of gas mantles [155, 156].

2.11.2 Welding Electrodes

Tungsten electrode with 1- 4% thorium oxide (ThO_2) are used in Tungsten Inert Gas (TIG) welding mostly in aluminum, stainless steel, thin sheets of metal industry that requires a very good and reliable weld. Good welding is achieved as the thoriated rod provides high temperature plasma in a gas atmosphere, usually argon. When thorium is added to the tungsten rods it helps to strike an arc and maintain a better arc stability, avoiding fluctuations in the flame [153].

2.11.3 Thorium as nuclear energy source

With increase in energy demand worldwide and growing concern on emission of greenhouse gases and their impact on climate, there is a need for clean and sustained energy production. Especially for a large country like India with large population, there is an inevitable requirement to meet the energy requirement. With depleting reserves of coal and associated environmental issues, nuclear energy is a clean alternate option for sustainable energy. Over the last 50 y, there has been increasing

interest in the utilization of ^{232}Th as nuclear fuel as India has large reserves of thorium. Currently, the highest research activity on ^{232}Th as a nuclear energy source is in India. All of the mined ^{232}Th is potentially useable in a reactor, compared with the 0.7% of natural U (^{235}U); therefore, more energy per unit mass is theoretically available from ^{232}Th. The isotope ^{232}Th is not fissile but can be used in combination with fissile ^{235}U or ^{239}Pu. Upon absorption of a neutron, ^{232}Th will transmute to a new fissile material – ^{233}U. The potential advantages of a Th-based fuel cycle over a U-based fuel cycle are the greater natural abundance of Th, needs no isotope separation, superior thermo-physical and nuclear properties of ThO_2 as compared to UO_2, a longer fuel cycle and higher burn up, better resistance to the proliferation of nuclear weapons (due to formation of ^{233}U that emits strong gamma radiation) and little Pu or other transuranic products [46].

2.12 Biokinetic model of Thorium

The population groups who get exposed to thorium in India are 1) people living in the monazite rich area, (2) occupational workers engaged in mining and processing of monazite sands and production of rare-earth salts and thorium nitrate (about 2000 workers) and (3) workers in production of gas mantle, ^{232}Th based fuel, welding rods etc. [157]. The bone surface seeking" biokinetic model structure for thorium provided by ICRP contains 5 main parts: blood, skeleton, liver, kidneys and other soft tissues, with sub compartment and is presented in Fig 2-4 [7]. The model is based on data obtained in beagle dogs and on semi-quantitative data in humans.

Blood is treated as a uniformly mixed pool. Compartment ST0 is a soft tissue pool that includes the extracellular fluids and exchanges material with blood over a period of hours or days. The thorium that enters the blood gets cleared with a half time of

0.25 d. ST0 is the compartment that defines the early build-up and decline of material in soft tissues. 30% of the activity leaving blood goes to a soft-tissue compartment ST0, and returns to blood with a half-time of 1.5 d. Soft tissue compartments ST1 and ST2 are used to represent intermediate retention (a few years) and long term retention (many years), respectively. 2% of activity leaving the circulation deposits in ST2 and 12.5% in ST1. The removal half-times from ST1and ST2 to blood are 2 and 100 y, respectively.

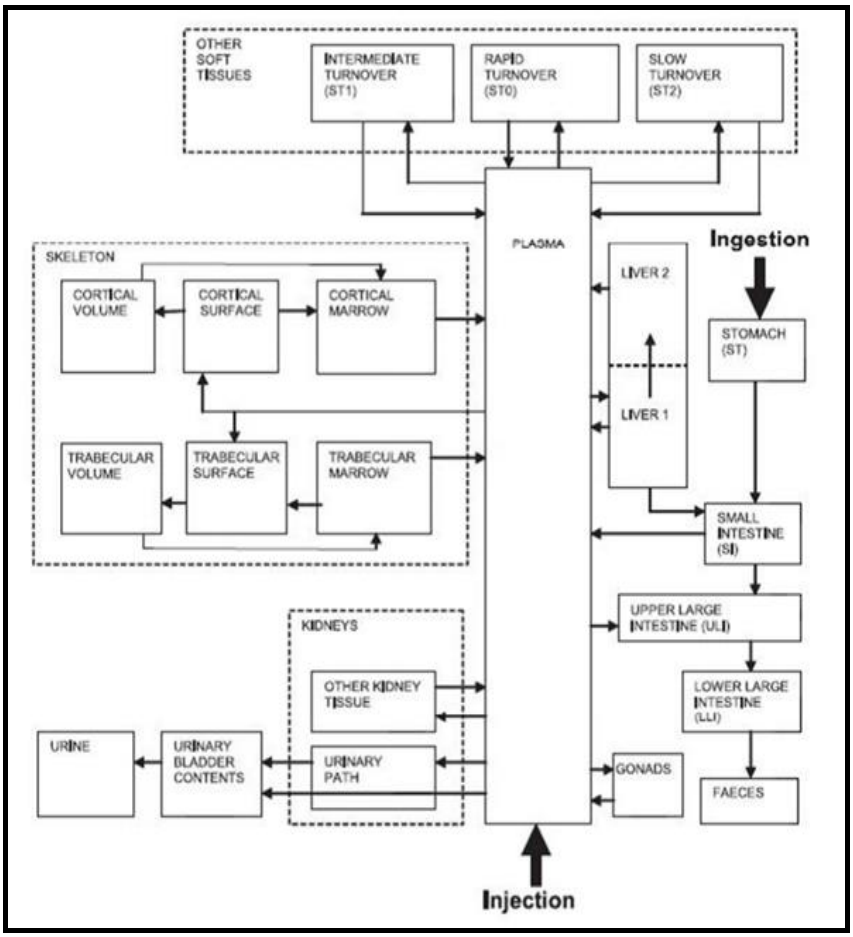


Figure 2-4: Biokinetic model for thorium [7]

The skeleton is divided into cortical and trabecular bones and these compartments are further subdivided into bone surfaces, bone volume, and bone marrow. Activity is transferred from bone surface to bone volume by bone formation, or to bone marrow

by bone resorption. Activity is removed from the bone marrow to blood in few months and consequently redistributed in the same pattern as the original input to blood. 70% for adult (80% for individuals under 15 y) of thorium leaving the circulation deposits on bone surfaces, equally on cortical bone and on trabecular bone.

The liver is divided into 2 compartments; Liver1 and Liver2. Liver1 represents short term retention, and Liver2 represents longer term retention ($t_{1/2}$ > 1 y). 5% of activity in the blood pool deposits in Liver1. Part of the activity that enters the liver1 is returned to blood (25%) and part is transferred to Liver2 (50%), and the gastrointestinal tract via biliary secretion (25%). The removal half-time from Liver2 to blood is 9 y.

The kidneys are compartmentalised into two, thorium is removed to urine via compartment one and another returns activity to blood. The "urinary bladder contents" is considered as a separate pool and the activity from the blood (5.5%) that reaches this pool is removed by urinary excretion. 3.5% deposits in renal tubules before being released to the urinary bladder with a half-time of 15 d.

2.13 Reference values and guidance level of Thorium in food and drinking water.

As discussed earlier, there is a large variation in the background levels of radionuclides around the world. Scientific data on ingestion of radionuclides of natural origin in food and drinking water was reviewed by UNSCEAR and have provided radionuclide specific reference values for important food groups. The following table (Table 2-9) gives the reference values of concentration of ^{232}Th in various food group and drinking water [1].

Table 2-9: Reference values for concentrations of ^{232}Th in foods and drinking water

	^{232}Th (mBq kg^{-1})
Milk products	0.3
Meat products	1
Grain products	3
Leafy vegetables	15
Root vegetables and fruits	0.5
Fish products	10
Drinking water	0.05

The recommended reference level of committed effective dose from drinking-water according to the WHO is 0.1 mSv y^{-1} [158]. The corresponding activity concentration value for ^{232}Th is 1 Bq l^{-1}. This guidance level is based on the reference dose level of 0.1 mSv y^{-1}, dose coefficient for ingestion by adults, and an annual consumption of drinking-water of 730 l. The reference dose level corresponds to 10% of the intervention exemption level recommended by the ICRP for dominant commodities for prolonged exposure situations and also to 10% of the dose limit for members of the population. The dose coefficients (Sv Bq^{-1}) for Th isotopes corresponding to the committed effective dose resulting from the intake of 1 Bq is given in the Table 2-10.

Table 2-10:Effective dose coefficient for intakes of thorium isotopes (Sv Bq^{-1})

		Inhalation, $e_{inh}(50)$			Ingestion	
Isotopes	**Half-life (y)**	**Type**	**1 µm AMAD**	**5 µm AMAD**	**f_A**	**E_{ing} (50)**
Th-228	1.9	M	3.1×10^{-5}	2.3×10^{-5}	5.0×10^{-4}	7.0×10^{-8}
		S	3.9×10^{-5}	3.2×10^{-5}	2.0×10^{-4}	7.0×10^{-8}
Th-230	7.7×10^{4}	M	4.0×10^{-5}	2.8×10^{-5}	5.0×10^{-4}	2.1×10^{-7}
		S	1.3×10^{-5}	7.2×10^{-5}	2.0×10^{-4}	8.7×10^{-8}
Th-232	1.4×10^{10}	M	4.2×10^{-5}	2.9×10^{-5}	5.0×10^{-4}	2.3×10^{-7}
		S	2.3×10^{-5}	1.2×10^{-5}	2.0×10^{-4}	9.2×10^{-8}

ATSDR (1990) reports a NOAEL (No Observed Adverse Effect Level) of 3043 mg Th kg $(bw)^{-1}d^{-1}$ from a 4 months study in rats which ingested thorium nitrate [159].

2.14 Quantification of Thorium in various matrices.

Owing to the large applications of thorium for human benefits, it is important to determine thorium in environmental and biological matrices. Determination of thorium can be achieved both by radiometric and non-radiometric techniques. The important ones are described in the following subsection

2.14.1 Radiometric Methods

2.14.1.1 Alpha spectrometry:

Silicon based semiconductor detectors are used in alpha spectrometry to measure the presence of radionuclides that emit α particles (i.e. helium nuclei). Typical alpha spectrometer is illustrated in Fig. 2-5. Passivated ion implanted silicon (PIPS) detectors have low backgrounds and can measure particles ranging from 3 to 10 MeV. When the emitted α particle deposits its energy in the detector media, a cascade of hole: charge pairs proportional to the energy is created. This charge carrier is then effectively collected as electrical signals and recorded.

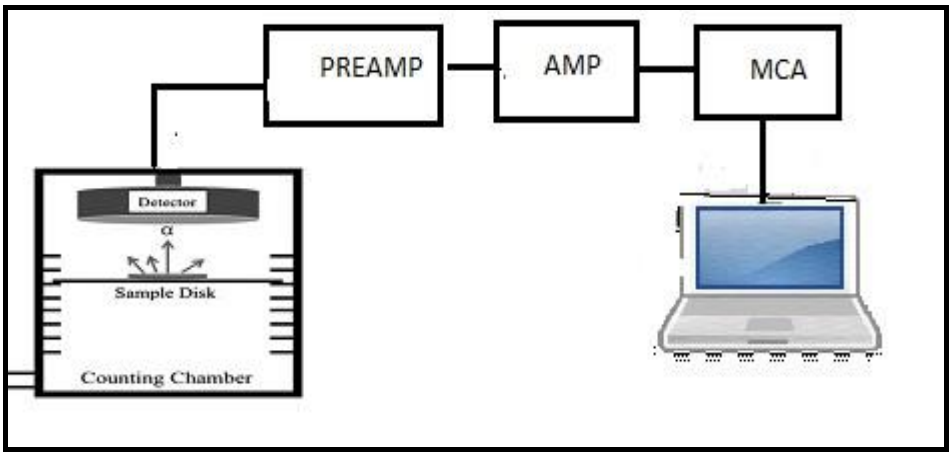


Figure 2-5: Schematic diagram of alpha spectrometry

Alpha spectrometry has many advantages like inexpensive equipment cost, low background and good throughput with the use of multi-chamber systems. Alpha spectrometry like mass spectrometry can be used to measure isotopic composition. Alpha spectrometry is of particular importance when compared to mass spectrometric methods for measurement of short-lived nuclides (e.g. species with $t_{1/2}$< 100 y). Another advantage using alpha spectrometry is that tracers can be added to account for the radiochemical recovery of the radiochemical procedure used to separate the element of interest from the matrices. In the case of thorium, ^{229}Th is usually selected as a tracer.

The main disadvantage of alpha spectrometry is that it is a destructive technique that requires laborious sample preparation like dissolution, chemical separation for reduction of spectral interferences and thin target preparation to reduce the self-attenuation. Limit of detection of 0.5 mBq g^{-1} for ^{232}Th in thorium ore and 0.26 mBq g^{-1} for ^{232}Th in soil was reported by Gingell [160]. Fissene et al and Pietrzak-Flis et al used alpha spectrometry to determine thorium in food samples [90,94]. Pietrzak-Flis reported an average chemical yield of 80% for Th with detection limit of 0.03 Bq g^{-1} ash with the counting time of 82,000 s.

A detection limit of 0.44 mBq L^{-1} (0.070 Bq kg^{-1}) for ^{232}Th, 0.80 mBq L^{-1} (0.13 Bq kg^{-1}) for ^{230}Th and 1.0 mBq L^{-1} (0.16 Bq kg^{-1}) for ^{228}Th in water (soil) samples, respectively using 100 L of water and 0.5 g soil and 864000 s counting time was reported by Jia et al. [16].

Concentrations of ^{230}Th and ^{228}Th in Korean food samples was determined by Min soek et al., using alpha spectrometry. Th in the samples were radiochemically separated and counted for 3,00,000 s.

2.14.1.2 Gamma ray Spectrometry

Gamma spectrometry is a non-destructive method for identification of gamma emitting radionuclides. Each gamma emitting radionuclide emits gamma rays with characteristics gamma energy between a few keV and 10 MeV which is used for quantifying the radionuclide content in the sample. Germanium semiconductor detectors are the most common detector used owing to good energy resolution when compared to other detectors. High purity germanium detectors have high resolution of 2 keV, but have less absolute efficiency compared to NaI(Tl) detector. But by using a large volume detector, this disadvantage can be overcome. When gamma rays interact with the detector material, primary excited electron are produced which in turn excites a cascade of secondary electrons in the process of dissipating its energy within the detector volume. The energy of the primary electron is spent in the production of electron hole pairs which are then collected. The numbers of electron collected will be proportional to the energy of the primary electron hence is proportional to the energy of the interacting photon. Gamma ray spectrometry is often used for evaluating ^{232}Th in the samples assuming that there is a secular equilibrium in the samples. ^{232}Th is determined using the gamma energies of ^{212}Pb and ^{228}Ac.

2.14.2 Non Radiometric Techniques

2.14.2.1 Spectrophotometric

Spectrophotometric methods are simple and inexpensive mostly used for field measurements of total element determination. This method used the principle of Lambert-Beer's law described below.

$$A = \varepsilon \times b \times c \qquad \textbf{(2.4)}$$

Where, A represents the absorbance, ε the molar absorptivity, b the optical path length and c analyte concentration. The measured absorbance is directly proportional to the path length and the concentration, hence by increasing the path length, magnitude in the signal can be improved.

The main disadvantage of using spectrophotometry for determination of uranium and thorium is the low sensitivity and selectivity of the spectrophotometric determinations. The reagents of chlorophosphonazo and arsenazo are the most significant ones for spectrophotometric methods for thorium, rare earths, scandium, and uranium determination. Spectrophotometric methods used as screening tools as they are very handy and hence enabling fast, sensitive and robust analyses.

2.14.2.2 Inductively coupled plasma–atomic emission spectrometry

Samples are analyzed as solutions with this technique. The solution is nebulized and the aerosol is introduced into argon plasma. In the plasma, the atoms are ionized and these ionized atoms which are in an energized state, spontaneously return to a lower energy state, and in doing so, emit a photon. This emitted light is broken into its constituent radiations by means of a diffraction grating and the intensities are measured at specific wavelengths for each element. The light intensity at a specific wavelength for each elemental line is measured either with an exit slit and photomultiplier tube, or with a semiconductor device.

In quantitative measurements, the emitted energy is assumed to be proportional to the concentration of the element present. The technique only allows the determination of total thorium. Detection limits around 10–15 μg L^{-1} have been reported for thorium in digested geological sample solutions. Solutions of digested samples may be analyzed

directly, but detection limits can be improved when thorium is separated from the matrix before analysis [161] .

Thorium has many lines in the spectrum which can be used for quantitative analysis, and the best one often depends upon the type of sample being analyzed. 283.231 nm, 326.267 nm and 353.959 nm are generally used[162].

2.15 Neutron Activation Analysis(NAA)

Neutron Activation Analysis (NAA) is a multi-elemental, sensitive, non-destructive method for determining the elemental composition of a sample and finds application in the fields of health sciences, radiation protection, environmental sciences, geology, material science and forensic sciences. Enrico Fermi was the first to report that radioactivity could be induced by neutron bombardment [163]. In 1936, George de Hevesy and Hilde Levi determined dysprosium in the yttrium samples by irradiating the sample with neutrons from Ra-Be source establishing the analytical utility of neutron irradiation [164].

2.15.1 Principle

When a sample containing target ${}^{A}_{Z}X$ is exposed for a period t_i to a flux of neutron, a fraction of the target atoms will capture these neutron and compound nucleus is formed in the excited state ${}^{A+1}_{Z}X*$ that will very quickly de-excite within `~10^{-14} s into lower configuration state of relatively stable radioactive nucleus through the emission of one or more γ rays with characteristics energies known as prompt γ rays. When this prompt γ rays are measured, the technique is called *prompt gamma neutron activation analysis* (PGNAA).

When the product nucleus ${}^{A+1}_{Z}X$ is radioactive and decays by emitting beta particle, an isotope of another element that de-excites to ground state by emitting characteristic

γ rays is formed. These are called *delayed γ rays* and their intensities are measured in NAA. Fig 2-6 shows the process of neutron capture and subsequent nuclear reaction used for NAA.

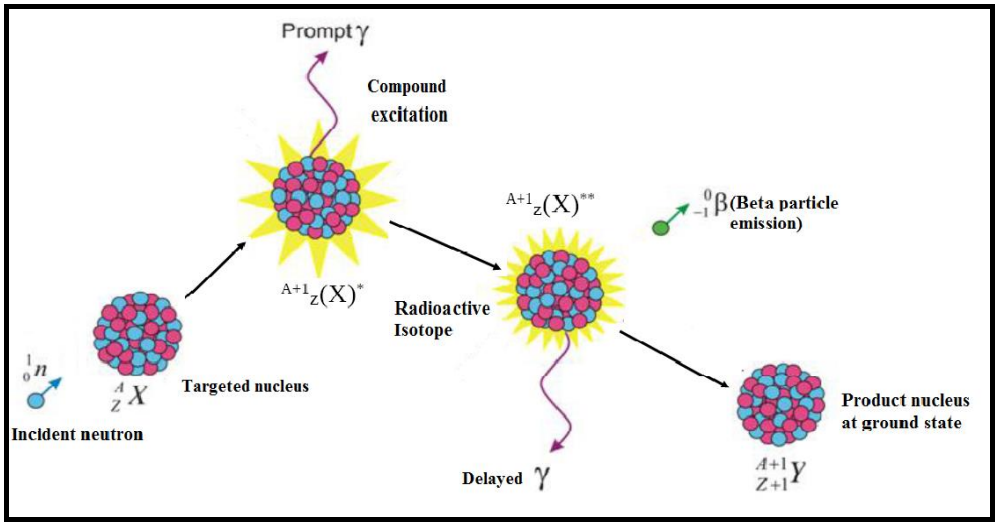


Figure 2-6: Diagram illustrating the process of neutron capture by a target nucleus followed by the emission of gamma rays (www.naa-online.net)

2.15.2 Radioactivity produced in NAA

Neutron induced reactions are energy dependent and (n,γ) is the most prominent reaction with low energy neutrons. For a nuclear reaction of the type ^{A}X (n,γ) ^{A+1}X, rate of formation of product atoms is given by,

$$\frac{dN_d}{dt} = N\sigma\phi - \lambda N_d \qquad \textbf{(2.5)}$$

Where N_d, is the number of daughter atoms formed, N is the number of target atoms of an element of interest in the sample, σ is the (n,γ) capture cross section in barns (10^{-24} cm^{2}), ϕ is the neutron flux (cm^{-2} s^{-1}) and λ is the decay constant of the activation product. Equation 2.6 gives the induced radioactivity A (λN_d) at the end of irradiation (t_i)

$$A = N\sigma\phi(1-e^{-\lambda t_i}) \qquad \textbf{(2.6)}$$

The activity after decay period of t_d is given by

$$A = N\sigma\phi(1-e^{-\lambda t_i})e^{-\lambda t_d} \qquad \textbf{(2.7)}$$

$$A = \left(\frac{N_A \theta m}{M}\right)\sigma\phi SD \qquad \textbf{(2.8)}$$

Where S= $(1\text{-}e^{-\lambda ti})$ is the saturation factor, D= $(e^{-\lambda td})$ is the decay factor, N_A is the Avogadro number, θ is the abundance of isotope of interest, m is the mass of the element and M is the mass number. The measurement of gamma rays is carried out mainly by high resolution r-ray spectrometry using HPGe detector. The net count rate corresponding to a photo peak is calculated using a PC based software.

The expression for the count rate is given by

$$cps = \left(\frac{N_A \theta m}{M}\right)\sigma\phi SDC\varepsilon\gamma \qquad \textbf{(2.9)}$$

Where C= $(1\text{-}e^{-\lambda CL})/\lambda.LT$ is the counting factor, which is the correction factor for the decay during counting , CL is the clock time , ε is the absolute full energy peak detection efficiency and γ is the absolute gamma ray abundance. When all the parameters determining the induced activity are known, the quantity of the element (m) can be calculated, in principle, from the measured radioactivity.

2.15.3 Neutron sources

The main requirement in NAA is the neutron source. There are a variety of neutron source and can be broadly classified into three categories depending on the mode of production and is tabulated below (Table 2.11). The isotopic sources use alpha and gamma radiation from radioactive nuclides. Neutrons with varying energy and flux are produced. Though these sources are compact, portable and easy to handle, the neutron

flux produced using isotopic sources are often low compared to nuclear reactor produced neutron flux.

Table 2-11: Neutron Sources for NAA

Source	**Half life**	**Average Neutron energy (MeV)**	**Neutron Flux**
Isotopic neutron sources			
Photonuclear (γ,n) reaction			
^{88}Y-Be	106.6d	0.16	1.0 x 10^5 n s^{-1} Ci^{-1}
^{124}Sb-Be	60.2 d	0.02	1.9 x 10^5 n s^{-1} Ci^{-1}
Alpha (α, n) reaction			
^{239}Pu-Be	2.4 x 10^4y	3.5	~107 n s^{-1} Ci^{-1}
^{226}Ra-Be	1600y	3.6	1.1 X 107 n s^{-1} Ci^{-1}
Spontaneous fission			
^{252}Cf	2.64 y	2.3	2.3 x 10^9 n s^{-1} mg^{-1}
Particle accelerators or neutron generators			
^{3}H(d,n)^{3}He	-------	14.7Mev	10^8-10^{11} n.s^{-1}
Nuclear Reactor			
Nuclear Reactor	----------	Varying energy	10^{11}-10^{15} n $cm^{-2}s^{-1}$

Nuclear reactor is a very important source of neutron and has been used in India for over many decades. A nuclear reactor produces neutron during fission of uranium. The neutrons produced are not monoenergetic. The energy of the neutrons is in the range of a few eV to about 10 MeV. According to the energy of the neutrons, they are classified as cold (0.003-0.15 eV), thermal (0.025-0.55 eV), epithermal (0.2-1 eV), intermediate (1-500 eV) and fast neutrons (500keV to 10MeV).

2.15.4 Methods for concentration calculation in NAA.

2.15.4.1 Absolute Method

The mass of the element (m) can be calculated from the measured activity, using the nuclear and reactor based data. The expression for "m" is given below

$$m = \left(\frac{cps}{SDC}\right) * \left(\frac{M}{N_A \theta \gamma}\right) * \frac{1}{\sigma\phi} * \frac{1}{\varepsilon} \qquad \textbf{(2.10)}$$

It is a direct analysis where the values of parameters from nuclear data tables, irradiation parameters and measuring parameters are directly used for evaluating the induced activity. The sensitivity and accuracy of absolute method depend on: nuclear parameters of the elements such as isotope abundance (θ), cross-section (σ), gamma intensity (γ), atomic mass (M), decay constant (λ) and half- life, the irradiation parameters such as neutron flux (ϕ), irradiation time (t_i), decaying time (t_d), and counting time (t_c) and measurement conditions like mass of the sample (M_{sam}), net peak activity (A) and detector efficiency (ε).

The disadvantage of the absolute method of analysis is the difficulties in evaluating the absolute values of flux and cross section as these values vary with neutron energy. Another limitation is the uncertainties associated from the nuclear parameters. These limitations can be overcome by use of relative method described below.

2.15.4.2 Relative Method

This method is a very simple method of analysis. Here each sample is co irradiated with a standard containing known amount of isotope of interest. The sample and standard are counted in identical conditions with respect to the detector and compared.

$$m_{samp} = m_{std} \times \frac{cps_{sam}}{cps_{std}} \times \frac{D_{std}}{D_{sam}} \qquad \textbf{(2.11)}$$

Using the mass of the element in standard, m_{std} and activities of the standards, cps_{std}, and sample, cps_{sam}, mass of element in the sample, m_{sam} is calculated.

Though the relative method is simple and precise, prior knowledge of the elements present in the sample is necessary to prepare corresponding standards in a similar matrix as that of the sample. The multi-element standards are mostly prepared from

their corresponding primary standards or sometimes certified reference materials (CRMs) of similar matrices are used in the irradiations.

2.15.5 Methodologies in NAA

NAA can be performed in a variety of ways depending on the element of interest and the interferences present in the sample matrix. NAA can also be classified into two major categories known as Chemical Neutron Activation Analysis (CNAA) and Instrumental Neutron Activation Analysis (INAA).

2.15.5.1 Instrumental neutron activation analysis

INAA technique is purely instrumental, sensitive and non-destructive method where the sample under investigation is not subjected to any physical and chemical change (or damage).

2.15.5.2 Chemical Neutron Activation Analysis

If the major or matrix element in a sample interferes in the determination of the element of interest, then the analysis by INAA is not reliable. Moreover, if the concentration of the element of interest is lower, INAA cannot be employed. In such cases, pre or post chemical separation is done in combination with NAA.

2.15.5.2.1 Pre-concentration NAA

If the element of interest is separated from their sample matrix prior to the irradiation, then the technique is called as *Pre-concentration NAA* (PCNAA). It is applied for the determination of single as well as complex sample matrices where INAA cannot be used. Pre-concentration results in increasing the amount of element of interest per unit mass, hence the sensitivity of the method is improved.

The pre-concentration procedure used should be simple, so that the contamination from handling and reagents are minimum thereby reducing the background and giving

better detection limits. Some of the commonly used pre concentration steps are co-precipitation, co-crystallisation, solvent extraction, ion exchange, chelating ion exchange, adsorption, chromatographic techniques, distillation, electro deposition and floatation.

Pre-concentration is a preferred method for analysing low concentration uranium and thorium in water, blood and urine. Thorium and uranium present in urine and water samples are co precipitated with calcium phosphate precipitate and further separated using ion exchange methods to remove the interference from Br, Cl and Na.

2.15.5.2.2 Radiochemical NAA

Radiochemical neutron activation analysis (RNAA) is a technique that is used when a desired element or elements cannot be detected or determined accurately by INAA, due to interferences resulting from the matrix elements. It involves the decomposition of the irradiated sample by the suitable method of separation such as chemical based ion exchange or precipitation for separation specific elements of interest.

Radiochemical method is important when the amount of an element is very small that the induced γ-rays activities associated with this element cannot be detected due to the effect of background activities or activities originated from other elements. For e.g., If two radionuclides with nearly equal half-lives emit gamma-rays of nearly same energy during (n, γ) reaction, there is an inevitable gamma interference and the elemental contents of the two radionuclides cannot be exactly identified or determined quantitatively by INAA technique. In such cases, it is necessary to separate the two interfering elements.

2.15.6 NAA based on the neutron energy

NAA can also be classified based on the energy of the neutron used as: Thermal neutron activation analysis (TNAA), Epithermal neutron activation analysis (ENAA) and Fast neutron activation analysis (FNAA) based on the energy distributions of the neutrons in a nuclear reactor.

2.15.6.1 Thermal Neutron Activation Analysis

Thermal neutrons are produced in a research reactor within the energy range between 0 and 0.55 eV. The average energy of the thermal neutrons in a nuclear reactor is approximately 0.025 eV. Instrumental NAA that is based only on thermal neutron fluxes is known as *Thermal Neutron Activation Analysis* (TNAA). Thermal neutron activation analysis takes the advantages of high intensity of neutron beams and large thermal cross-section for most isotopes. The higher sensitivity is achieved with TNAA as the neutron in thermal energy region, cross section follows 1/v law.

2.15.6.2 Epithermal Neutron Activation Analysis

Neutrons in the energy spectrum from 0.5 eV to 100 eV are known as Epithermal neutrons. In this region the neutron flux distribution is not proportional to the inverse of the velocity but it is proportional to inverse of the energy. The other unique property of epithermal neutrons is their cross-section as function of energy show strong resonance peaks phenomena. The flux and the resonance energy of this region is more important to identify and determine chemical elements in sample of interest whose cross-sections are very small. To get epithermal neutron flux separated from thermal neutron flux in a reactor, a cadmium foil of 1 mm thick is inserted into one of the irradiation channels inside the reactor. Cadmium absorbs thermal neutrons and will allow epithermal and fast neutrons to pass through it. In general, about 2 % of the

reactor's total neutron flux is the epithermal neutron flux. Thus, NAA that is based on only epithermal neutron flux is known as *Epithermal Neutron Activation Analysis* (ENAA).

2.15.6.3 Fast Neutrons Activation Analysis

Fast neutron activation analysis (FNAA) is the third type of activation analysis. The energy range of fast neutron component is above 0.5 Mev. Fast neutron consists of the primary emission neutrons which still have much of their original energy following fission. Fast neutrons don't induce (n,γ) reactions but instead they induce nuclear reactions that eject one or more nuclear particles (n, p),(n, n') and (n, 2n). This type of technique induces particles reaction is known as *fast neutron activation analysis* (FNAA). Fast neutrons with energies of several MeV's can be produced with a neutron generator in an isotopic neutron source.

2.15.7 Sensitivity and Detection Limit in NAA.

The sensitivities for NAA are primarily dependent on the nuclear parameters and reactor neutron fluxes. The sensitivity in NAA is defined as the count per unit mass (cps μg^{-1}) for a given set of irradiation conditions. The sensitivity can be improved by irradiating samples in a high neutron flux and measuring the radioactivity with a high efficiency detector.

The smallest amount that can be determined by NAA is governed by the minimum activity which can be reliably measured with sufficient precision. The minimum detectable activity of an analyte is known as its detection limit (L_D). The L_D in NAA varies from pictogram to milligram depending on the nuclear properties of the isotope of interest, background, sample matrix and pre or post chemical separations.

The Curries equation is used for the calculation of detection limit (L_D) in NAA [165].

$$L_D(mg.kg^{-1}) = \frac{2.71 + 3.29\sqrt{C_b}}{t_m SW} \qquad \textbf{(2.12)}$$

Where C_b is the background counts under the peak, t_m=time of measurement, W=mass of the sample and S=sensitivity in cps μg^{-1}.

2.16 Inductively Coupled Plasma Mass Spectrometry (ICP MS)

ICP-MS is an important and frequently used mass spectrometric technique for the determination of elements and isotope ratios in the trace and ultra-trace concentration levels. Use of ICP MS for determination of radionuclides in environmental, biological and waste samples has increased in the recent years. In ICP-MS, the chemical compounds contained in the sample solution are decomposed into their atomic constituents in an argon plasma at a temperature of 6000-8000 K. At this high temperature, highest degree of ionization with a low fraction of multiple charged ions is achieved. The positively charged ions are extracted from the ICP into a high vacuum of the mass spectrometer via an interface. The differences in the mass of the ions formed is used to separate the ions using a mass analyser either of quadrupole type, time of flight or combination of magnetic and electrostatic sector, and the ions separated are measured by an ion detector.

Thermal ionization mass spectrometry (TIMS) has better ion beam stability and better abundance sensitivity compared to ICP-MS. However, for thorium, ICP-MS is better than TIMS due to the low ionization efficiency at the TIMS filament.

Long-lived radioisotopes are best determined by mass spectrometric methods, while radiometric methods are preferred for short-lived ones. ICP MS offers lower detection limits for longer-lived radioisotopes, shorter analysis times, improved analytical precision and a simple procedures compared to radiometric methods. Another

advantage of ICP MS method is the ability of determining all the actinide elements within a minute, at ultra-trace levels (ng l^{-1}) in liquid samples. Hence, ICP-MS has been widely used for the determination of isotopes of uranium, thorium, plutonium, strontium, americium, radium, lead, technetium, palladium, neptunium, curium and iodine in environmental and waste samples.

Long-lived ^{238}U and ^{232}Th isotopes have low specific activity (12.3 and 4 Bq mg^{-1}, respectively) hence require long counting time (days–weeks) for good counting statistics. Moreover, the radionuclide needs to be separated from the sample matrix to obtain thin counting sources for good energy resolution. Therefore, ICP-MS provides a rapid and sensitive technique for the determination of these elements. However complex sample matrix can cause chocking of the sample introduction system and also causes interferences in the plasma resulting in a suppression of analyte ionization. Care should be taken to reduce the total dissolved solids (TDS) present in the solution when it is analyzed. As a general rule, TDS should not exceed 0.1%. Sample pretreatment like dilution is necessary for samples with high TDS. Sample dilution tends to decrease the matrix effects but will also decrease the U and Th concentrations. Viewing to the low sensitivity of alpha spectrometry, gamma spectrometry, ICP AES and Spectrophotometer methods are not very effective for determination of Th in biological and human materials. INAA and ICP MS are two methods that are preferred for quantification of Th in biological and vegetation samples. Hence ^{232}Th in samples were analysed using INAA and ICPMS.

CHAPTER 3

EXPERIMENTAL

3.1 Introduction

Determination of radionuclides in diet or food samples play a very important role in many areas of radiation protection like surveillance, dose assessment and biokinetic studies. The dietary intake studies include sample collection (sampling), processing and analysis. Same care should be taken while sampling as taken for processing and analysis. Populations residing in HBRAs are prone to higher radiation exposure both externally and internally. Hence it is necessary to evaluate the radiation dose received by the inhabitant of such regions. Ingestion is an important pathway for internal radiation exposure. The steps involved in the estimation of radiation dose from ingestion intake of is depicted in Fig 3-1.

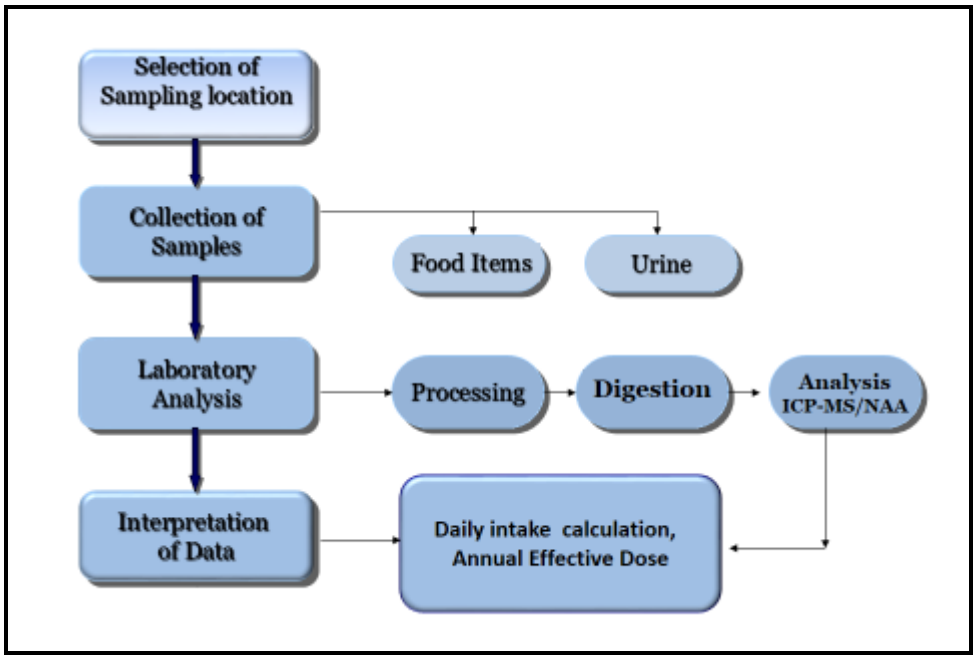


Figure 3-1: Methodology for dietary intake studies

3.2 Description of the study area

The study area is located in the Kanyakumari district of Tamil Nadu and is shown in Fig 3-2. There are regions in this district that have the oldest known monazite deposits. The monazites in these areas are present as beach placer deposits. Complex coastal

and geological processes that have been occurring for millions of years have resulted in formation, transportation, accumulation and concentration of placer deposits in the beaches.

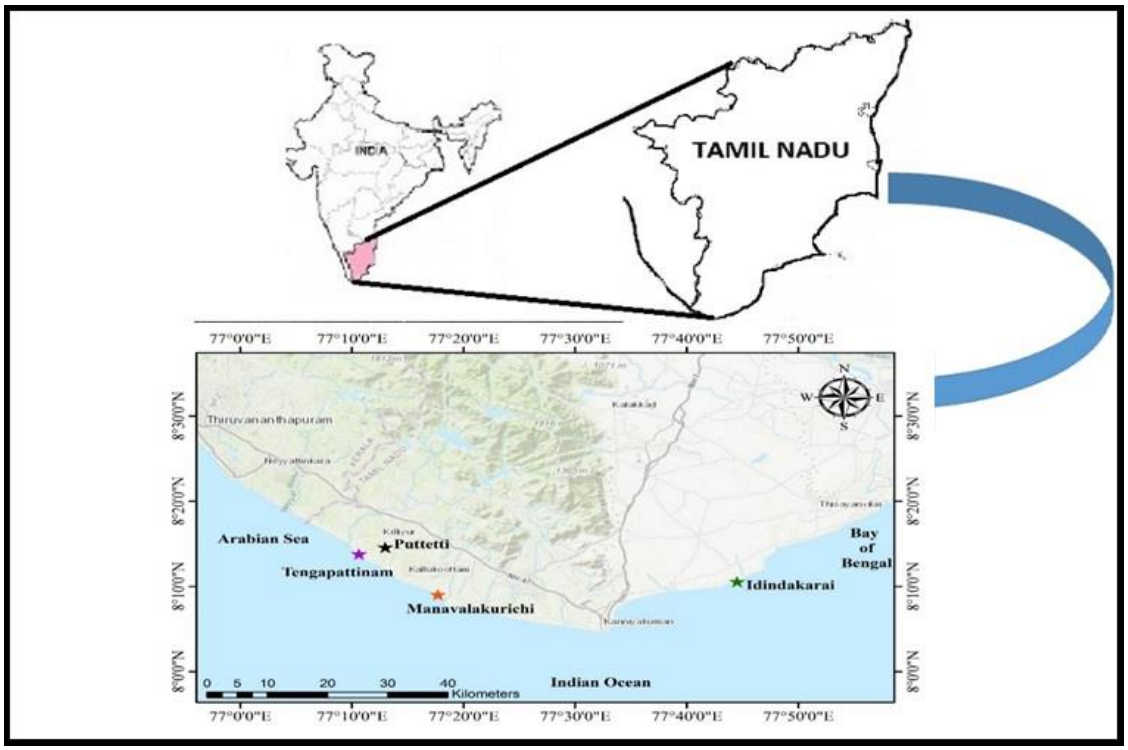


Figure 3-2: Map of study area

Weathering of hinterland rocks resulted in liberation of minerals from the rocks. These minerals were then enriched and transported by the well-connected drainage systems in the vicinity to the coastal zone. Dynamic actions within the coastal zone further enabled the concentration and enrichment of minerals in the adjacent beaches. Waves sorted out heavy minerals and transported them onshore based on size and specific gravity. The study on radioactivity of beach sands of Manavalakurichi region along the southwest coast of India in Tamilnadu, has revealed the presence of high concentration of the monazite sands spanning across the Kadiapattinam estuary on the eastern side of Manavalakurichi. The Valliyar river that originates from the western Ghats reached the coast of Kadiapattinam. This served to transport minerals from the

weathering rocks of the Western Ghats. The deposit extends to a length of about 16 km from the north of Muttom promontory to Kolachel, with an average width of 45m. The hinterland consists of khondalite suite of Archean age composed of quartzite of arenaceous facies, calc silicates with pockets of crystalline limestone representing calcareous facies and quartz garnet sillimanite graphite schists and gneisses or argillaceous facies. Charnockite intrudes into khondalites in some places. Muttom and adjacent areas are characterized by extensive occurrence of fine sandy loam known as Teris [166]. The total average content of heavy minerals is around 39 %. Of these, ilmenite forms the major constituent (24%) with rutile (1.8%), leucoxene (0.9 %), zircon (2 %), monazite (5%), sillimanite (3.5%) and garnet (5.5%). The monazite has a total of 58% rare earth element (REE) oxides and 8% ThO_2. The total reserves of heavy minerals in the Manavalakurichi-Kolachel stretch are estimated to be about 1.6MT. The study area is located in the south west coast of Tamil Nadu, India consisting of many villages namely Manavalakurichi, Putteti, Keezhkulam, Thengapattinam, Midalam, Inaiyam, Kurumpanai, Kadiapattinam, Kolachel, Mandaikadu, Muttom, Kanyakumari, Chinnamuttum, Rajakkamangalam, Manakudu, Kovalam, Puthulam, Neendakara, Manapadu, Koodankulam and Idindakarai.

3.3 Dietary sampling Methods

Dietary radionuclide intakes are estimated by several methods [167]. The sampling methods employed should be such that food sampling is truly representative of the dietary consumption of the population group under study and should ensure the exclusion of external contamination. There are different approaches while sampling for dietary intake studies. Each approach has its own advantage and disadvantage. World Health Organization (WHO) has provided guideline for national food

contamination monitoring using Duplicate Portion Study (DPS) method, Market Basket Study (MBS) method, 24 h recall method and food records methods.

Although DPS offer the greatest degree of reality compared to other methods, market basket studies are advantageous regarding identification of what kinds of food are critical for radionuclide intakes.

In the present study, two methods namely MBS and DPS methods were adapted.

3.3.1 Market Basket Study method

This diet sampling procedure is based on analysis of representative food items purchased locally and on regional food consumption statistics. The intake estimates are then calculated by multiplying the concentration estimate in each food by the respective consumption rate estimates. As most of the reports provided by the national bodies on the consumption rate estimates gives region, age and gender specific data, this method is an easy method. It is also possible to reduce the number of foods or select only those food item that is consumed by the population of interest hence by reducing the cost and efforts. Another advantage of this method is that the analysis of a number of foods or food groups gives more information than the analysis of a single composite diet sample. In India, the state specific food consumption data is provided by National Nutrition Monitoring Bureau (NNMB). NNMB is the national body responsible for region wise collection of food consumption data. The data given in the report considers ethnic, age, gender and income difference. The NNMB has classified the diet into 13 major categories. The report also gives data for different age group and gender. The latest NNMB report for Tamil Nadu and Kerala was used for this study [168].

The food items are collected from the markets which ensures that the sample collected represents the food available for public consumption. Care should be taken while choosing a food item in a category. For e.g. in case of Kerala, Tamilnadu, Andhra and Karnataka the major cereal used is rice whereas in Punjab it is wheat. Millet is seldom consumed by population residing in southern part of the country. Millet in the form of corn and bajra are consumed in Punjab and Gujarat during winters.

3.3.2 Duplicate Portion Study method

Another sampling procedure often used is to duplicate the actual foods consumed by an individual during a day, a week or some specified time period. Hence this method is also called as Duplicate Diet Study (DDS) method. For bio-kinetic studies intake rate per day is preferred. The household or the participant should be thoroughly educated about the purpose of the study. The success of this type of study lies in the selection of household and active involvement of the participant. The participant is properly explained about the procedure to provide a duplicate portion of the diet consumed by him. The participants plate plus meal is weighed before consumption and weighed again at the end of the meal. This also enables a correction to be made to the amount of food consumed for any inedible and unconsumed portions that remain. The procedure is repeated each time when food is consumed in a day. In case the cooked food is brought from outside it should also be taken into account. For a good cooperation of participant, it is necessary to provide monetary compensation for the extra food collected.

3.4 Sampling methodology

Multistage random sampling was used for selection of households. Multistage sampling refers to sampling plans where the sampling is carried out in stages using

smaller and smaller sampling units at each stage. For e.g., in a two-stage sampling design, a sample of primary units is selected and then a sample of secondary units is selected within each primary unit. The simplest version of two-stage sampling is to use simple random sampling (SRS) at each stage. The primary units do not need to be the same size and one need not select the same number of secondary units within each primary unit.

Stratified random sampling and cluster sampling can be viewed as special cases of two-stage sampling. A stratified random sample is a survey of the primary units (the strata) followed by an SRS of the secondary units within each primary unit. A cluster sample is a SRS of the primary units (the clusters) followed by a census of the secondary units within each selected primary unit.

In the present work, three stage stratified random sampling was used. In the first stage of the sampling design, the villages were chosen based on the ground radiometric survey. In the second stage, streets were chosen randomly in the selected villages and in the third stage, house hold from each street was selected based on the willingness of the house head to participate in the study.

3.4.1 Selection of sampling location

This was the first stage of the sampling design where the villages were selected based on the radiation level. Southwest coastal region of Tamilnadu is a well-documented HBRA in India [15, 169]. In situ radioactivity surveys were conducted using a portable radiation survey meter to determine the high background radiation spots in the study region. Portable Atomtex radiation survey meter 1123 (Atomtex Inc., USA) was used for ground radiation field survey. Atomtex Radiation Monitor 1123 (Fig 3-3) is a portable high-sensitivity plastic scintillation detector based radiation monitors

designed to search and detect sources of gamma radiation and measure ambient gamma radiation field. The radiation survey meter was first calibrated.

Figure 3-3: Portable hand-held survey meter (Atomtex 1123)

The survey was carried out along the coastal stretch of 45 km (Thengapattinam to Idindakarai) of Tamil Nadu with the latitude and longitude coverage of 8.1-8.2º N and 77.2-77.8ºE. The ground radiation field survey locations are given in Fig 3-4. Based on the ground radiometric survey data, villages were chosen.

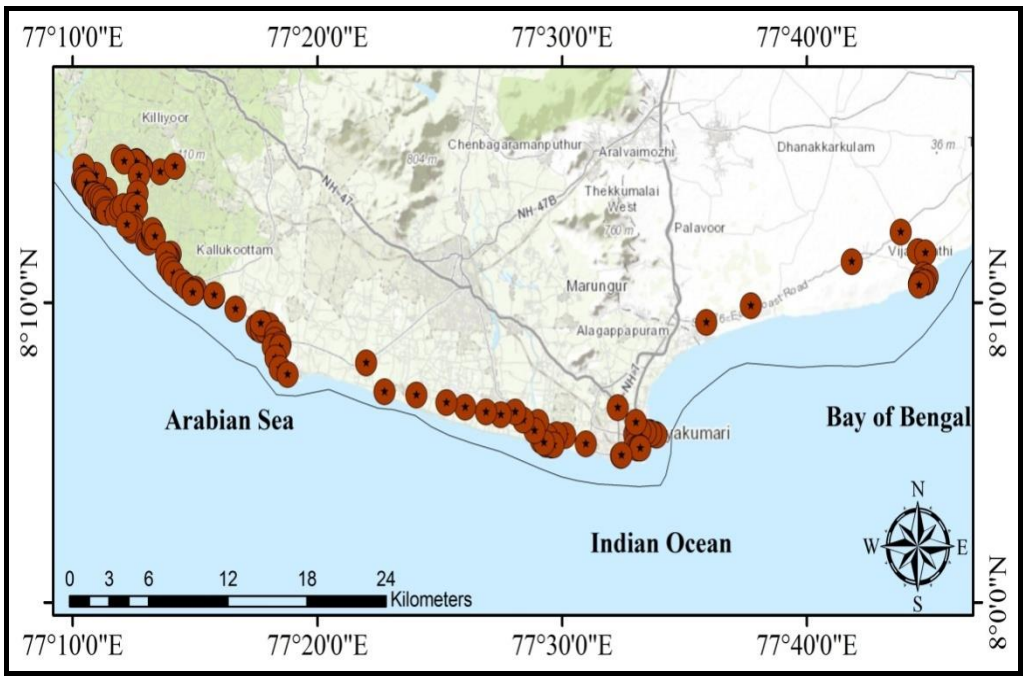


Figure 3-4: Radiation survey spots (locations) in the study region

3.4.1.1 Selection of Households for DPS

Once the villages were selected, the information on the population and the streets in the villages were collected from the village office. The villages were divided into blocks and information on the blocks were obtained from the village office. Households were selected based on the willingness to participate.

3.4.1.2 Selection of sites for MBS

In the study area, there are two important wholesale farmer markets from where food items are mostly purchased. The small retail shops also stocked items purchased from these markets. Hence samples for this study were purchased from the two markets. The vegetables and fruits that are cultivated in the region is also sold in one of these markets itself.

3.5 Sample collection

Sample collection, handling and storage is a very important part in any dietary intake study. Any error in sampling and the sample preparation of any study is considerably higher than that in the methodology itself, as illustrated in Fig 3-5.

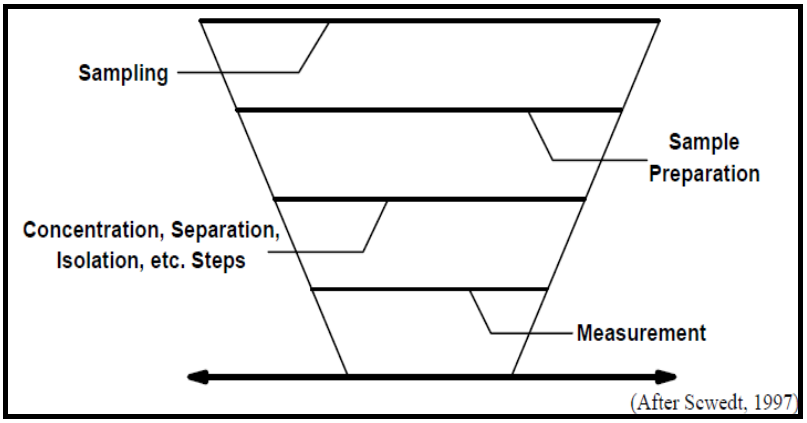


Figure 3-5: Degree of error in various stage of an analytical methodology*[170]*

The materials required for diet sampling are sample preparation equipment (e.g., weighing balance, volume measuring device, gloves), sample preservation equipment

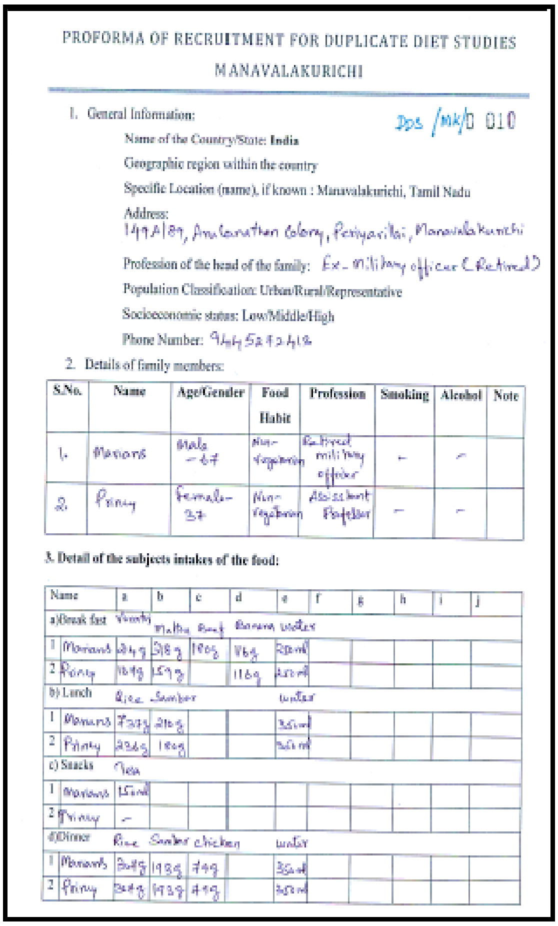
and agents (e.g., ice box, ice, formaldehyde or acid additives), maps, global positioning systems (GPS), sample tags, labels, appropriately labeled sample containers, bags etc. For sampling food items high density polythene bags and containers were used. All these items were pre cleaned with acid beforehand.

3.5.1 Duplicate Portion Diet

Diet samples were collected as per guidelines of WHO. The participants were informed beforehand so that an additional portion of food consumed by them is prepared. They were also instructed to prepare normal food consumed by them routinely. The identical portion of cooked food that is actually consumed in each meal was weighed and collected in a pre-cleaned food bag. The weight of the diet in each food items in each meal (breakfast, lunch, dinner and beverages) were measured using a weighing balance and recorded so that the error is minimized. The same was done for each member of the family. Only one duplicate portion was collected in a pre-cleaned bag from each family. This bag was immediately stored in a cool box (5^{o}C). Participants received a monetary reimbursement for the products collected.

Additionally, a questionnaire was used to record the food intake of each individual present in the family. Fig 3-6 shows the sample questionnaire. The forms were filled by communicating with the volunteers in local language (Tamil). The questionnaire included the information like age, employment, dietary habit (vegetarian and non-vegetarian), smoking, alcoholic, the details of food intake etc.

The survey was conducted on a voluntary basis from the families recruited from the study villages. The sample collection was conducted during the period of 2010-2013.



PROFORMA OF RECRUITMENT FOR DUPLICATE DIET STUDIES

MANAVALAKURICHI

DDS /MK/D 010

1. General Information:

Name of the Country/State: **India**

Geographic region within the country

Specific Location (name), if known : Manavalakurichi, Tamil Nadu

Address:
149A/89, Amalanathan Colony, Periyarillai, Manavalakurichi

Profession of the head of the family: Ex-military officer (Retired)

Population Classification: Urban/Rural/Representative

Socioeconomic status: Low/Middle/High

Phone Number: 9444 527412

2. Details of family members:

S.No.	Name	Age/Gender	Food Habit	Profession	Smoking	Alcohol	Note
1.	Marians	Male - 67	Non-Vegetarian	Retired military officer	-	-	
2.	Priny	Female - 37	Non-Vegetarian	Assistant Professor	-	-	

3. Detail of the subjects intakes of the food:

Name	a	b	c	d	e	f	g	h	i	j
a)Break fast	[illegible]	Malta	Bread	Banana	water					
1 Marians	244 g	318 g	180g	86g	250ml					
2 Priny	184g	159g		116g	250ml					
b) Lunch	Rice	Sambar			water					
1 Marians	737g	210g			350ml					
2 Priny	236g	180g			350ml					
c) Snacks	Tea									
1 Marians	150ml									
2 Priny	-									
d)Dinner	Rice	Sambar	chicken		water					
1 Marians	304g	198g	74g		350ml					
2 Priny	304g	193g	49g		350ml					

Figure 3-6 :Questionnaire and proforma for DPS

Urine collection: Participants were given verbal instructions for 24 h urine collections. The urine collection started after discarding the first voiding on the morning of the collection day and finished after the first voiding on the morning of the next day.

3.5.2 Market Basket Sampling:

The food items of both plant as well as animal origin were collected from wholesale local markets located at Karungal and Manavalakurichi (Fig 3-7). Milk samples were purchased from local vendors. MBS was classified into 12 categories such as Cereals, Pulses, green leafy vegetables, other vegetables, roots and tubers, fruits, fish, flesh food, milk, coconut and spices based on the NNMB report. The details of the foot items purchased from each market are given in Table 3-1.

Table 3-1: Food items collected from major wholesale local markets

Market	Food items
Karungal	Amaranthus, Drumstick leaves, Curry leaves, Brinjal, Plantain stem, Plantain, Bittergourd, Green chilies, Bottle gourd, Drumstick, Ladies finger, cucumber, snake gourd, pumpkin, capsicum, ivygourd, yam, Tapioca, Taro root, Tamarind, Cucumber, Coconut, Banana, Mango, Jackfruit, Papaya, Mackerel, Indian anchovy, Barracuda, mutton, Beef, Chicken and Rice
Manavalakurichi	Amaranthus, Drumstick leaves, Curry leaves, Brinjal, Plantain, Bittergourd, Green chilies, Bottle gourd, Drumstick, cucumber, snake gourd, capsicum, yam, Tapioca, Taro root, Tamarind, Cucumber, Coconut, Banana, Mango, Jackfruit, Papaya, Chicken and Rice
Fish Harbor, Kadiapattinam	Anchovy, Barracuda, Mackerel, Trevally, Squid, Tuna, Belt fish, shark and herring

Figure 3-7: Farmers market at Karungal and Manavalakurichi, Tamilnadu

Careful analysis was done before collection so that the collected dietary components are the true representative of the most commonly consumed food item by the study

group. Vegetables like carrot, cauliflower and cabbage that are not popularly consumed by the inhabitants were not collected.

3.6 Sample processing:

The main objective of sample preparation is to provide representative of the diet without any sample loss and sample contamination. A general procedure for sample processing involves cleaning, drying, obtaining a constant weight, grinding, mixing, and sub-sampling. A careful study on the concentration of few elements namely, Cr, Cs, Fe, Th and Zn in washed and unwashed samples of cereals and legumes was conducted by Dang et al. It was observed that there were significant differences in the concentrations of the elements in washed and unwashed samples[171].

3.6.1 Vegetables and fruits

Taking into consideration on the food habits of the study population, the most commonly consumed vegetables like brinjal, pumpkin, ladies finger, yam, tapioca, drumstick, amaranths, plantain, etc. were purchased from whole sale market. Vegetables were purchased from at least two different vendors in each market to ensure the necessary representation of the samples. The samples were aggregated within varieties so that the final samples to be composed represented the region. The purchased vegetables were brought to the laboratory for processing. In the laboratory, the vegetables, fruits and tuber samples were carefully washed under running water, scrubbed with brush to remove any adhered soil or dust. The initial washing was done in a laboratory space away from the space where the final preparation of the samples was performed. This is very important in order to avoid soil contamination that will totally destroy the possibility of obtaining meaningful results. The vegetables were then washed with distilled water before peeling them. Wherever necessary, the non-

edible peel was removed and cut on a cutting board into small pieces, about 1 cm^3. The cubes were mixed and transferred to a large tray and was dried in a hot air oven at temperatures of 105 to 110^o C for a few hours to obtain constant weight. The weight of the sample was then recorded for the fresh weight. The cubes were then packed into acid-washed tray and frozen at -20^o C. In case of green leafy vegetables, non-edible parts were removed with a knife and cut into small pieces. All the frozen vegetables were then freeze-dried and homogenized using a food processor equipped with titanium blades.

3.6.2 Flesh food and fish

In case of meat and beef, tenderloin and shoulder were collected. Liver of beef was also collected. In case of chicken, the skinned chicken was collected. Two 0.5 kg flesh samples were collected per shop. The samples were packed immediately into polyethylene bags, coded with tags and then frozen. As the laboratory was away from the study location, the samples were stored in an interim cold storage unit before transportation to the lab. The samples were then transported to the laboratory in a frozen state. Stainless-steel knives were used for cutting the meat samples. The samples were thawed and cut into 1 cm^3 pieces and freeze dried. The skin, bones and fat were discarded and only the edible parts were utilized. For all sorts of meat samples, only a food processor equipped with Ti blade was employed for the final sample homogenization.

Fish samples were allowed to thaw out naturally. Samples were rinsed under a cold running tap to remove fish scales and any extraneous particulate material. Flesh and muscle parts were removed from bones except for Indian anchovy where only the tail and head parts were removed and then filleted. The fillets were again rinsed to remove

extraneous material, minced, dried to constant weight and freeze dried and homogenized.

3.6.3 Milk

Whole milk sample were collected from the local vendors. The samples were frozen immediately after collection and transported to the laboratory in frozen state. The milk was thawed to room temperature, then heated up to 40^{o} C and shaken to homogenize the fat and frozen again. These samples were then freeze dried.

3.7 Instrumentation and measurements

3.7.1 Freeze dryer

Operon FDT 8612 Bulk tray and Martin Christ Alpha 1-2 LD plus bench top freeze dryer were used for drying the samples (Fig 3-8). Freeze-drying or lyophilization is an effective way of drying materials without harming them. It makes use of the physical phenomenon of sublimation which involves the direct transition between the solid state and the gaseous state without passing through the liquid phase. To achieve this, the frozen product is dried under vacuum without being allowed to thaw out. The frozen samples were transferred to a Petridish and frozen to -20^{o} C and placed inside the vacuum chamber of the freeze dryer.

Figure 3-8: Freeze drying of samples

3.7.2 Nuclear reactor

Nuclear reactors are broadly classified as power reactor and research reactor. Research reactors are used for research activities and for production of various radioisotopes for application in agriculture, food irradiation processing, health care, industry and chemical research utilizing neutron flux. In the present study, irradiation of samples was carried out in *CIRUS* and *Dhruva* research reactors at Bhabha Atomic Research Centre (BARC), Trombay, Mumbai.

3.7.2.1 CIRUS reactor

The reactor was extensively used for condensed matter research, material irradiation, fuel testing, NAA and production of radioisotopes for application in the fields of medicine, agriculture and industry using neutron beams extracted from its core. It is a vertical tank type reactor of 40 MW capacity fueled with metallic natural uranium, moderated with heavy water and cooled by de-mineralized light water. Sample and RMs were irradiated (for 8h) in self-serve position of *CIRUS* reactor of BARC, Mumbai at a neutron flux of 3×10^{13} cm^{-2} s^{-1}.

3.6.2.2 Dhruva reactor:

Dhruva reactor is 100 MW uranium metal fueled reactor, moderated, primary cooled with heavy water and secondary cooled by de-mineralized light water with neutron flux is ~1.8×10^{14} cm^{-2} s^{-1}. Cadmium absorbers are used as shut off rods. Long as well as short time irradiation facilities are available at Dhruva reactor using tray rod position and pneumatic carrier facility (PCF), respectively. Tray rod position was used for sample irradiations. The thermal neutron fluxes at tray rod position and PCF are of the order of 10^{14} cm^{-2} s^{-1} at full power operation [70].

3.7.3 High resolution gamma ray spectrometry

Delayed gamma ray emitted in INAA was assayed with high resolution gamma ray spectrometry using HPGe based detection system. Interaction of gamma rays with matter, gamma ray detection system and its electronics is briefly discussed [172, 173].

3.7.3.1 Interaction of Gamma-rays with matter

Photoelectric absorption, Compton scattering and pair production are three important interaction of gamma rays, though many other ways are present. These interaction processes are shown in the Fig 3-9.

3.7.3.1.1 Photoelectric absorption (PEA)

When a gamma-ray interacts with an atom, the incident photon is absorbed by the atom resulting in ejection of an electron from the atom. The energy of the ejected electron (E_{e^-}) is equal to the difference between incident energy of gamma ray (E_γ) and the binding energy of electron (E_b), and is expressed as below:

$$E_{e^-} = E_\gamma - E_b \qquad \textbf{(3.1)}$$

The ejected electron interacts with the detector material resulting in ionization. The vacancy created due to ionization is filled either by capture of a free electron in the medium or by electronic rearrangement of electrons. In the process of rearrangement, X-ray or Auger electron is released. These x-rays can further ionize the medium and the energy is converted to electrons by the photo-electric effect resulting in conversion of all the gamma ray energy into electron kinetic energy. This is reflected as full energy deposition and seen as photo peak in the spectrum. The photoelectric cross-section is given by the following equation:

$$\tau = \text{constant x} \frac{Z^n}{E_\gamma^{3.5}} \qquad \textbf{(3.2)}$$

The exponent ‘n’ varies between 4 and 5 depending on the gamma-ray energy [172]. The probability of the process increases with Z (atomic number) of the medium and decreases with the gamma ray energy. The photoelectric process is the main mode of interaction for relatively low energy gamma rays and high atomic number material. Due to this property, lead (Z=82) is used as common shielding material for gamma rays.

3.7.3.1.2 Compton scattering

In Compton scattering, part of the photon energy E=hυ is transferred to a weakly bound electron in a collision and the incident photon gets scattered away with reduced energy at an angle θ with respect to its original direction. The scattered photon with reduced energy hυ' undergoes further interaction with the detector material, either by the Compton process or the photo-electric effect. The collision between electron and photon is treated as elastic collision and the energy of scattered photon is given by the following equation:

$$h\nu' = \frac{h\nu}{1 + \frac{h\nu}{m_o c^2}(1 - \cos\theta)} \qquad \textbf{(3.3)}$$

where, hυ is the energy of incident photon, m_0c^2 is rest mass of the electron in the unit of energy, and θ is the angle of incidence between photon and scattered photon of gamma-ray. The energy of scattered electron varies from zero (θ=0) to a maximum value at θ=180°. As seen from the above equation, there is continuum in the gamma-ray spectrum from zero to a maximum value equal to E_γ - 0.255 MeV. The Compton process cross-section is given by following relation:

$$\sigma_c \propto \frac{Z}{E_\gamma} \qquad \textbf{(3.4)}$$

Compton scattering is much significant for photons with energy ranging from 1-5 MeV, for high Z materials and over a wide range of energies in the low Z materials.

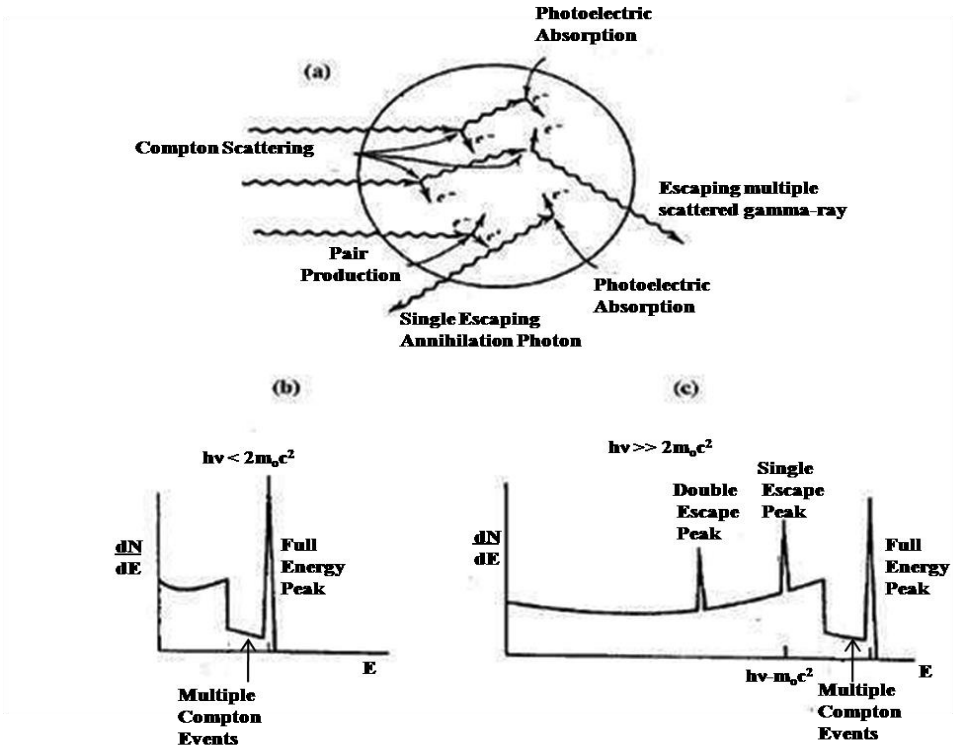


Figure 3-9: (a) Different interaction processes in HPGe detector, (b) Full energy peak with multiple Compton events, (c) Full energy peak and multiple Compton events with 1st and 2nd escape peaks[173]

3.7.3.1.3 Pair production

When energy of gamma ray photon is greater than $2m_0c^2$, an electron –positron pair may be produced. The excess energy of gamma-ray photon (E_γ-$2m_0c^2$) is shared equally as the kinetic energy of electron and positron. The electron and positron lose their energy by ionization and excitation with detector material. Positron is stopped in the material and annihilates with a nearby electron to form two gamma photons with energy 0.511 MeV which moves in opposite direction. These photons may interact with the medium to deposit its energy or escape the material. If both the gamma photon deposits it energy then it contributes to the full energy deposition, whereas

when one photon escapes the material, the energy deposition is at E_γ-m_0c^2 and if both the photon leaves the detector material without interaction, then the energy deposition is at E_γ-$2m_0c^2$. The cross-section for pair production phenomena is given by the following equation:

$$\sigma_p \propto Z^2 \ln(E_\gamma - 1.022) \qquad \textbf{(3.5)}$$

3.7.3.2 Gamma ray detection system

Nucleus in excited state de-excites to a lower energy state by emitting γ rays. Gamma ray spectrometer uses this phenomenon to quantify the concentration of radionuclides that emits γ rays. Two types of detectors are generally used for detection of γ ray from the source: NaI(Tl) scintillation detector and high purity germanium (HPGe) semi-conductor detector. As NaI(Tl) detector has high efficiency, and low price, it is used in routine low-level measurements with a few well-separated gamma-ray peaks where resolution is not of prime importance.

The HPGe detector has superior resolution and is available in larger size with higher relative efficiency. HPGe detectors have been used in the present study and will be discussed briefly. The high resolution γ ray spectrometer system consists of HPGe detector, high voltage (HV) unit, amplification system, analogue to digital convertor (ADC) and multi-channel analyzer MCA[173].

3.7.3.2.1 HPGe detector

HPGe is a semiconductor detector which replaced the Li based semiconductor devices in the mid 1970's. With advancements of technology, ultrapure germanium with impurity levels as low as 10^9 cm^{-3} were developed. If low-level impurities are acceptors, the property of the crystal is mildly p-type while if the impurities are donor then they are n-type. Based on the shape, HPGe detectors can be classified as planar

or co axial. Coaxial P-type germanium detectors are used for gamma ray with energy range from 100 keV to about 10 MeV. For X-ray spectroscopy, n-type planar germanium detectors are used for low energy photon detection because of the thin beryllium entrance windows. The p-type HPGe detectors used for gamma-ray spectrometry have relative efficiency in the range of 10 % to over 150 %. Relative efficiency is defined with respect to the efficiency of 3"x 3" NaI(Tl) detector at a detector to source distance of 25 cm for 1332 keV gamma ray of ^{60}Co [69]. The resolution of an HPGe detector defined by full width at half maximum i.e., FWHM is in the range of 1.8 to 2.1 keV at 1332 keV. The Ge crystal of HPGe detector is attached to a liquid nitrogen dewar via Cu rod for cooling to minimize the leakage current. A P type co axial detector with 50% relative efficiency was used in this study. This type of detector is made with p type material with Li diffusion (n^+) contact of 0.3 mm Li and 0.3μm, p^+ contact created by boron ion implant.

3.7.3.2.2 High Voltage Supply

The semiconductor detectors operate in a depleted condition also called as the sensitive region. The depletion region is created by applying electric field. The bias supply is required for collection of the charge carrier formed in the detector sensitive volume. A typical bias voltage of ±1500 V to ±5000 V with current capacities of 100 A is applied.

3.7.3.2.3 Preamplifier

Preamplifier is the most important part of the detector and has two main function 1) conversion of the charge into a voltage pulse 2) serves to maximize the signal to noise ratio. The pre amplifier also helps in matching the high impedance of the detector and the low impedance of coaxial cables. The charge collected by the pre amp is converted

to a tail pulse whose height is proportional to the gamma-ray energy. As the resolution depends on the noise generated here, components like resistor are cooled and kept under vacuum along with the detector crystal. The remaining part is mounted just outside this vacuum assembly. The output tail pulse will have a height of few mV and decay time typically 50-100 μs.

3.7.3.2.4 Amplifier

The pulses from preamplifier are amplified and shaped by the spectroscopic amplifier. The height of the pulse (normally in mV) is proportional to the incident gamma-ray energy. The output pulse from pre-amplifier is fed to the amplifier where it is shaped and amplified. The gain is adjusted to cover the energy range of interest; the highest energy peak should be within the ADC input range (normally 0-10 V). The Gaussian peak shape has two advantages; the signal to noise ratio is improved and the pulses return to the base line faster. Pole zero circuit maintains a stable baseline and the pileup rejection circuit improves the performance of the amplifier during high count rate measurements.

3.7.3.2.5 Multichannel analyzer

The pulse height analysis (PHA) of gamma-ray pulses coming from the main amplifier is carried out in MCA. The most important function of MCA is to convert the pulse height of the input pulses into a digital value and save the count in the appropriate counter that corresponds to digitized channel height. This is achieved by analogue to digital converter (ADC). Generally, an ADC of 4k (12 bit-4096 channels) or 8k (12 bit-8192 channels) is used in gamma-ray detection system.

3.7.3.2.6 Energy calibration

It is important to co-relate the channel number to the energy deposited by the gamma ray photons in the detector. This is achieved by energy calibration and involves allocation of channel number to energies covering the entire range of interest. Standard sources such as ^{241}Am, ^{57}Co, ^{60}Co and ^{152}Eu are used for this purpose.

3.7.3.2.7 Resolution of detector

Resolution of a detector is the ability to resolve two nearby peaks. For application in NAA, a detector with high resolution is required and hence HPGe is a preferred detector. The energy resolution of the HPGe detector is governed by the variation in the number of charge carriers, variation in the charge carrier collection, and the contribution of electronic noise. Resolution of the detector is measured using the following equation:

$$\text{Resolution}(\%) = \frac{FWHM\,(\text{in keV})}{\text{Peak Position}, E_o\,(\text{in keV})} \times 100 \qquad \textbf{(3.6)}$$

The calculation of energy resolution for a detector is shown in Fig. 3-10.

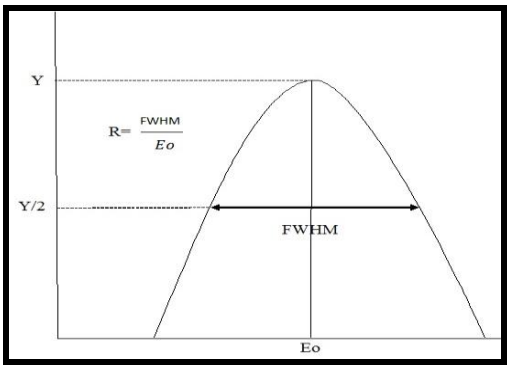


Figure 3-10: Determination of resolution of detector from FWHM

3.7.3.2.8 Efficiency calibration

Efficiency is an important parameter for correct quantification of the measured activity. This parameter is a proportionality constant that relates the activity of the

measured to the observed counts. The absolute full-energy peak efficiency of full energy peak/absolute photon detection efficiency (ε_{abs}) can be expressed as:

$$\varepsilon_{abs} = \frac{\text{Total number of photon detected in full energy peak}}{\text{Total number of photon emitted by source}} \qquad \textbf{(3.7)}$$

The detection efficiency depends on the sample-to-detector distance, the detector characteristics, the sample geometry and energy of the gamma-ray. Efficiency is determined as a function of energy by measuring the efficiency at a number of energies and fitting the experimental efficiency with an appropriate function. The absolute efficiency ε is calculated using the equation below.

$$\varepsilon = \frac{cps}{dps \times \gamma} \qquad \textbf{(3.8)}$$

Where dps is disintegration per second of the known source and γ is the gamma ray abundance of the energy E.

The activities of irradiated sample were measured using a PC-based gamma-ray spectrometry set-up that consisted of ORTEC p type coaxial HPGe detector coupled to a standalone electronic module(DSPEC-LF) as shown in Fig 3-11.

Figure 3-11: P type HPGe detector assembly with electronics(ORTEC)

For data acquisition and analysis, GammaVision-32 ver. 6 Software (ORTEC) was used. Full peak efficiency calibration of the detector was performed by point calibration sources of ^{133}Ba, ^{137}Cs, ^{60}Co and ^{152}Eu.

3.7.4 High Resolution (HR) ICP MS

An ICP-MS consists of the following components and the schematic diagram of an ICP MS system is shown below (Fig 3-12).

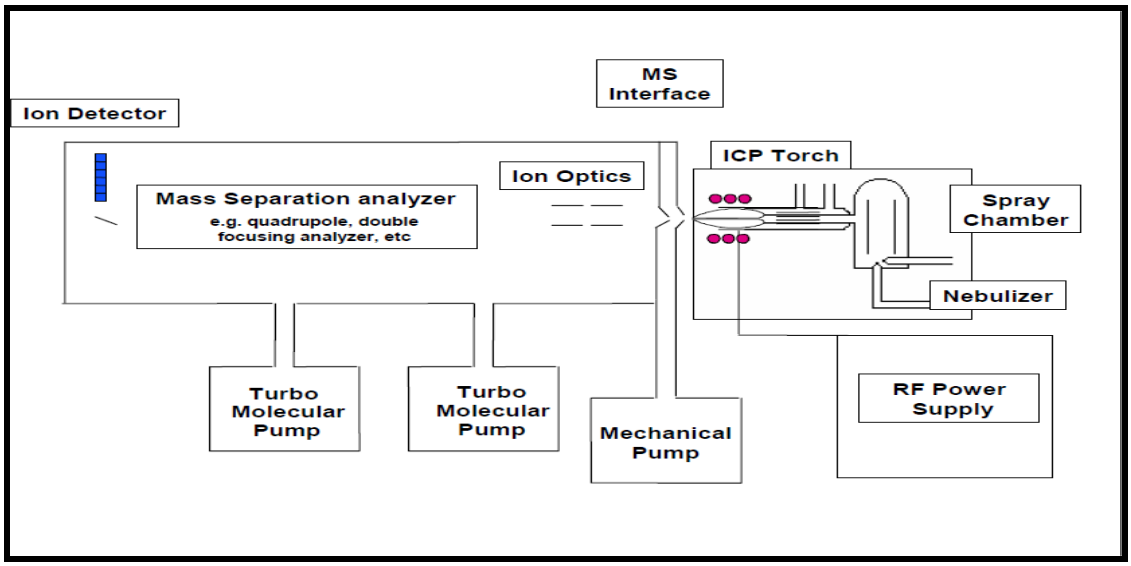


Figure 3-12: Schematic diagram of an ICP- MS[174]

3.7.4.1 Sample introduction system

The important components of a sample introduction system are nebulizer and spray chamber which introduces samples into the system. Liquid sample is broken into small droplets and introduced into the argon plasma. The liquid sample is introduced by a peristaltic pump or through self-aspiration to a nebulizer where aerosol of fine droplets is produced which is then passed through a spray chamber. The spray chamber separates the aerosols or the droplets according to the size. Only the small droplets created by the nebulizer are allowed to enter the plasma and larger droplets are discarded.

3.7.4.2 ICP torch and RF coil

The samples are ionized in the plasma. Intense magnetic field produced by RF coil on a tangential flow of gas generates the argon plasma. The RF coil is wrapped around a series of concentric quartz tubes (the ICP torch). The argon gas passing through this tube and energy supplied to the coil by the RF generator couples with the argon to produce the plasma. The sample liquid droplets containing the elements of interest are first dried to a solid and then heated to a gas as they pass through the plasma. Dried droplets are then decomposed to produce atoms. As these atoms travel through the plasma, they absorb more energy and get ionized and forms a singly charged ions. The singly charged ions exit the plasma and enter the interface region.

3.7.4.3 Interface

The plasma region is in lower vacuum region while the mass analyzer is in a high vacuum region. High vacuum is important for effective mass separation. Besides, the pressure difference between the two region, there is also a high temperature difference between the two regions. Hence it is necessary to have an interface that connects the atmospheric pressure ICP ion source to the high vacuum mass analyzer region. The interface consists of two or three inverted funnel-like devices called cones.

3.7.4.4 Vacuum system

Vacuum system provides high vacuum for ion optics, mass analyzer and detector. When the ions travel from the interface to the detector, they undergo collision with any gas molecules on their path. Therefore, it is important to remove all gas molecules in the space between the interface and the detector. The turbo-molecular pump is capable of rapidly pumping a chamber to a pressure of 1×10^{-5} Torr or less. The mechanical pump evacuates the interface region.

3.7.4.5 Ion optics

The ions that comes out of the interface undergoes substantial divergence as it exits the second cone, hence it is required to focus the ions. Ion optics positioned between the skimmer cone and mass analyzer, guides only the ions into the mass analyzer while the unwanted signals like neutral species and photons are removed from the ion beam.

3.7.4.6 Mass analyzer

Mass analyzer sorts the ions by their mass to charge ratio (m/z). There are four kinds of commercially available mass analyzers: quadrupole mass filters, double focusing magnetic sector, time of flight, and collision–reaction cell technology. As in this study only doubly focused magnetic sector field was used. The details are explained below.

Double focusing magnetic sector analyzer: This type of analyzer consists of two parts namely an electromagnet and an electrostatic analyzer (ESA). In the forward design, the ESA is positioned before the magnet, and in the reverse design it is positioned after the magnet. A schematic of a reverse Nier-Johnson spectrometer is shown in Fig 3.13.

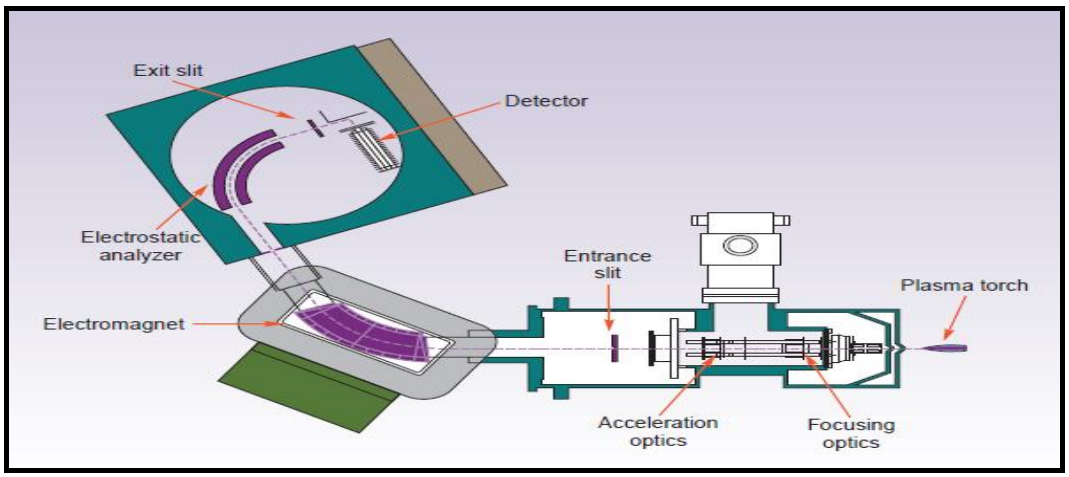


Figure 3-13: Schematic of a reverse Nier-Johnson double-focusing Magnetic sector mass spectrometer[174]

The magnetic field, has a mass dispersive and direction focusing and focuses all the ions with diverging angles of motion from the entrance slit. The ESA, which is only dispersive with respect to ion energy, then focuses the ions onto the exit slit, where the detector is positioned. If the energy dispersion of the magnet and ESA are equal in magnitude but opposite in direction, they will focus both ion angles (first focusing) and ion energies (second or double focusing), when combined together. Changing the electrical field in the opposite direction during the cycle time of the magnet, has the effect of freezing the mass for detection. Then as soon as a certain magnetic field strength is passed, the electric field is set to its original value and the next mass is frozen. The voltage is varied on a per-mass basis, allowing the operator to scan only the mass peaks of interest rather than the full mass range [175].

3.7.4.7 Detector system in ICP-MS

The ions exiting the mass spectrometer strike the active surface of the detector also known as dynode to generate a measurable electronic signal. The dynode, releases an electron each time an ion strikes it and an amplification process is initiated. The electrons released from the first dynode strike a second dynode where more electrons are released. This cascading of electrons continues until a measurable pulse is created. By counting the pulses generated by the detector, the system counts the ions that hit the first dynode. The detectors used in commercial instruments are capable of a wide dynamic range using a dual mode, which includes both digital and analog modes.

3.7.4.8 Data handling and system controller

Data handling and system controller controls all aspects of instrument control and data handling to obtain final concentration results.

3.8 Experimental work on neutron activation analysis (NAA)

In NAA method, a sample is irradiated in a flux of neutrons (from neutron sources like nuclear reactor and neutron generator) and subsequent induced radioactivity (β, γ) is measured to evaluate the concentration of an analyte of interest present in the sample.

In NAA,^{232}Th is determined via the (n, γ) reaction and subsequent beta decay of the short lived ^{233}Th ($t_{1/2}$=22.3 m) product to ^{233}Pa ($t_{1/2}$=27.1 d). ^{232} Th has large (n,γ) thermal neutron cross-section (σ_{th}-737 b) and ^{233}Pa is determined by measuring the 300 (6.2%), 312 (36%) or 340 (4 .2%) keV gamma rays. The nuclear data is presented in Table 3-2.

Table 3-2: Nuclear Data of ^{232}Th

Parameter		
Isotope	^{232}Th	
Isotopic abundance (θ,%)	100	
Thermal cross section (σ_0)	7.26 b	
Activation products	^{233}Th	^{233}Pa
Half life	22.3 min	27.1d
Energy, E (gamma-ray abudance a_γ%)	86(2.7)	300.1(6.62) 311.9(38.6) 340.5(3.88)

3.8.1 NAA using CIRUS reactor

The freeze dried samples were homogenized thoroughly and aliquots of the homogenized sample (80-110 mg) mg were sealed in high purity Al foil for irradiation. Samples standard and the reference material/CRM packed in thin Al foil were irradiated in self-serve facility of *CIRUS* reactor for 8 h. The irradiated samples were brought to the laboratory after sufficient cooling and repacked in fresh paper. The

sample masses of repacked samples were noted and were mounted on clean counting plates using piece of paper below the sample to avoid contamination of the plate.

3.8.2 NAA using Dhruva reactor

Long as well as short time irradiation facilities are available at Dhruva reactor at tray rod position and PCF respectively. The samples were irradiated for 7 d in the tray rod position. The irradiated samples were brought to the laboratory after sufficient cooling (30 d). As the freeze dried vegetation samples contained moisture content, the samples and CRM along with the Al foil were melted and fused into one solid mass. The samples were then irradiated in tray rod position for three days and still the problem persisted for some samples. Hence the samples were ashed to remove any residual moisture. The ashed samples were then packed in thicker Al foil and irradiated for 3 d and this attempt was successful. The method was then optimized for irradiation with three different certified reference methods.

The gamma ray activities of the samples were measured by a high-resolution gamma spectrometer consisting of a 50% P-type HPGe detector. The spectrum analysis was done using Gamma-vision software for evaluating the peak area under the energy of interest. The concentrations of Th in the samples were determined by relative method of INAA using the Eq.2.11.

Quality Control

For good quality assurance and measurements, standard reference material (SRM) obtained from National Institute of Standards and Technology (NIST), USA was analyzed. The expected sensitivity (counts μg^{-1}) and its standard deviation (σ) were established by replicate sample analyses of SRMs. Precision and accuracy of the

method was checked. The precision of the method was calculated by evaluating the percentage relative standard deviation (%RSD = P)

$$P = \frac{\sigma}{\mu} \times 100 \quad \textbf{(3.9)}$$

where σ is the standard deviation of replicates and μ is the arithmetic mean.

The accuracy in terms of percentage deviation (Z) was measured by comparing the measured value (A_{meas}) from the certified values (A_{cert}) of the NIST Standard as

$$Z = \left(\frac{A_{meas} - A_{cert}}{A_{cert}} \right) 100 \quad \textbf{(3.10)}$$

3.9 Experimental work using HR ICP MS

^{232}Th contents in water samples were determined in 5 L of water sample using HR ICP MS. The water was filtered and acidified with addition of conc. HNO_3 and brought to the laboratory. Urine samples (24 h) were collected from volunteers from the study area belonging to different age groups and gender. In the laboratory, known quantity of ^{229}Th was spiked for tracer recovery analysis for the radiochemical separation procedure.

Sample co-precipitation: 20 mL con. HNO_3, 200 mg calcium carrier and 15ml phosphoric acid were added to each sample (water and urine) and digested on hot plate. The pH was adjusted to ~9.5 with addition of concentrated ammonium hydroxide to precipitate calcium phosphate. Samples were centrifuged at 3500 rpm and the supernatant was discarded, the precipitate was rinsed twice with 20 ml of water and centrifuged again at 3500 rpm. The precipitate was then dissolved in 10ml conc. HNO3 and evaporated to dryness. The residue was then dissolved in 8M HNO_3. This column load solution was subjected to column separation.

Column separation: The sample solution was loaded on to anion exchange resin (Dowex 1x8, 100-200 mesh) pre conditioned with 8M HNO_3. The rate of loading was in the range of 0.7-0.8 ml per minute. Column was washed with 20 ml each of 8M HNO_3. Thorium was then eluted with 25ml 9M HCl [176]. The eluted thorium fraction was evaporated to dryness and were diluted with deionized MilliQ water up to 10 ml and acidified to 2% HNO_3.

The clear solutions were analyzed at CSIR-NGRI, Hyderabad, using high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) (Nu Instruments Attom, UK) in jump-wiggle mode that permits the analytes of interest (viz. ^{238}U, ^{232}Th) to be measured accurately (Fig 3-14).

Figure 3-14: HR-ICP-MS (ATTOM, Nu Instruments, UK)

The samples introduction consisted of a standard Meinhard nebulizer with a cyclonic spray chamber housed in Peltier cooling system. All quantitative measurements were performed using the instrument software (Attolabv.1), while the data processing was done using Nu Quant. Instrumental parameters are given in Table 3-3.

Table 3-3: Instrumental parameters

Coolant gas flow (L/min)	13.0
Auxillary gas flow (L/min)	1.05
Nebulizer gas flow (psi)	33.3
Forward RF Power (W)	1300
Peristaltic rate (RPM)	15.0
Peltier cooling temperature (^{o}C)	5.0
Spray chamber	Glass-Cyclonic
Sample uptake (ml/min)	0.2
Detector	Ion counter and faraday
Sensitivity	1.1 x 106 counts for ^{115}In
	2.1 x 106 counts for ^{238}U
Scan type	Magnet jumping with electric scan over a small mass range
Ion lens setting	Optimized for sensitivity and resolution peaks

3.10 Calculation of daily intake and total annual effective dose

For the purpose of verifying compliance with dose limits, the total annual effective dose was determined. The total annual effective dose to members of the public was calculated using ICRP dose calculation method [149]. The daily intake ($I_{ing,232Th}$) of ^{232}Th was estimated using the following equation below.

$$I_{ing,^{232}Th} = A_f \times U_f \times h \quad \textbf{(3.11)}$$

Where A_f is the activity concentration of ^{232}Th (Bq kg^{-1}_{fresh}) in food group f, U_f is the intake of food group in kg d^{-1} and h is the dry to fresh weight ratio

The analytical expression for the total annual effective dose is determined by summing all the individual equivalent doses for the exposure pathways considered in this study. These include: external gamma irradiation from ground radiation field survey ($E_{\gamma,ext}$) and committed dose from ingestion of food and water E_{ing} (food, water). The annual effective dose ($E_{\gamma,\ ext}$) is estimated from the measured average outdoor external gamma dose rate from the equation below:

$$E_{\gamma,ext} = D_{\gamma,ext} \times T_{\exp} \times F \times DCF_{ext} \textbf{ (3.12)}$$

Where $D_{\gamma,ext}$ is the average outdoor external gamma dose rate μGyh^{-1}, T_{exp} is the exposure duration per year, 8760 h (365 d), F is the outdoor occupancy factor of 0.2 and DCF_{ext} is the effective dose to absorbed dose conversion factor of 0.7 Sv Gy^{-1} for environmental exposure to gamma rays.

The annual effective dose E_{ing} (food, water) is estimated from the evaluated daily intake of radionuclide(^{232}Th) through food and water intake using following equation

$$E_{ing} = I_{ing,^{232}Th} \times DCF_{ing,^{232}Th} \times 365 \qquad \textbf{(3.13)}$$

Where $I_{ing,232Th}$ is the daily intake of ^{232}Th (Bq d^{-1}) and $DCF_{ing,232Th}$ is the age dependent ingestion dose coefficient in Sv Bq^{-1}.

CHAPTER 4

RESULTS AND DISCUSSION

DIETARY INTAKE OF THORIUM USING MARKET BASKET STUDY (MBS) METHOD

4.1 Introduction:

The population is exposed to ionizing radiation from a number of sources, both natural and man-made. Exposure to natural sources is described by two principal routes namely *external exposure* from irradiation by radiation emitted from cosmic rays, or radioactive decays of radionuclides of cosmogenic or terrestrial origin and *internal exposure* following ingestion or inhalation of terrestrial radionuclides. Radionuclide gets transferred through the environment by various possible pathways, like atmospheric deposition, terrestrial pathway and aquatic pathway. Radionuclides appear in plant either through direct atmospheric interception onto external plant surfaces or indirectly from re-suspended material or through uptake of radionuclides via the root system [70]. The level of terrestrial radiation varies from one geographical location to another depending upon the variation of radionuclide in the soil which largely depends on the local geological occurrence. Dietary intake can occur by ingestion of vegetation into which radionuclides are incorporated via root uptake or by atmospheric deposition on the vegetation. The animals grazing on this vegetation may ingest this vegetation and also inadvertently ingest soil. The study area is well investigated region for its high natural background radiation levels. The region has high deposition of thorium rich monazite minerals in the beach soil. Due to higher levels of radionuclides, the inhabitants of HBRAs may ingest more radionuclides through their food and water; consequently, these individuals may have higher ingestion levels of primordial radionuclides especially radionuclides from ^{232}Th series than residents from NBRAs. As the radiological and biological half-life of thorium is high, it is important to assess the dose via ingestion of food and water.

Duplicate Diet Study (DDS) and Market Basket Study (MBS) are two commonly employed methods for the study of daily dietary intake (DDI). MBS procedure is based on analysis of representative food items purchased locally and on food consumption statistics. MBS method helps to provide information on the contribution by each food category and food to the radiation dose and also helps to identify potential radioactivity carriers in case of emergency.

The main purpose of the present study was to determine the concentration in various food categories namely cereals, pulses, vegetables, fruits, milk, fish and flesh food like chicken and beef. The annual intake and the annual committed effective dose were evaluated using the determined ^{232}Th concentration.

4.2 Methodology:

The study area is situated in the state of Tamil Nadu, southern India. The area is enclosed by latitude 8.12-8.33 ^{o} N and longitude 77.21-77.32 ^{o} E. The stretch of about 45 km of beach length from Idindakarai to Thengapattinam belonging to Kanyakumari district was chosen for the study. The coastal areas have coconut cultivation and the hinterlands have paddy and seasonal vegetable cultivation. NNMB, India gives the average consumption rates for different states for different food categories [168]. Karungal farmers market and Manavalakurichi farmers market are wholesale market from where the retail shopkeepers buy to sell in the respective small villages or blocks. Hence samples (vegetables, fruits, meat and fish) were purchased from these wholesale markets. The milk samples were purchased from local vendors in the individual selected villages. Fish samples were also purchased from the fish harbor located at Iniyam and Kadiapattinam village. Fig 4.1 shows the sampling location (Karungal wholesale market), the locations of agricultural fields from where the

vegetables (brinjal, tapioca, plantain and coconut) were brought to the local market and the fish harbor.

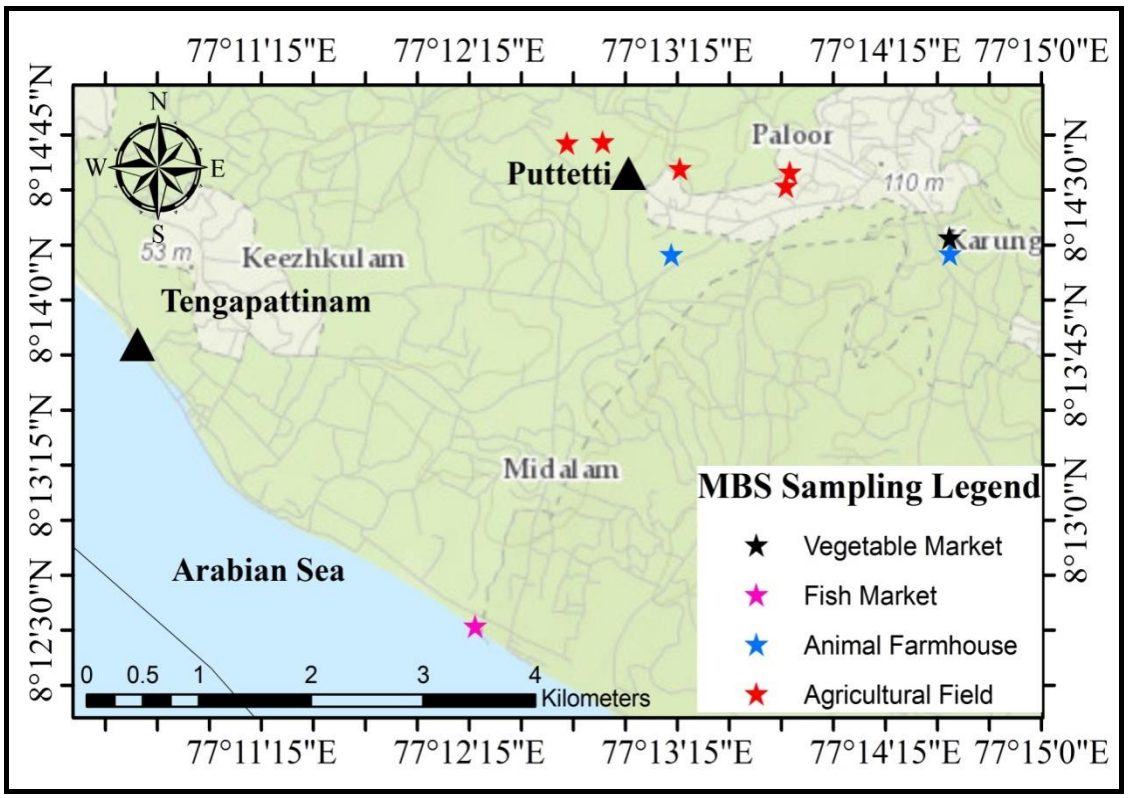


Figure 4-1: Location of Karungal Market

Fig 4-2 shows the sampling location (Manavalakurichi wholesale market), the locations of agricultural fields from where the vegetables (brinjal, cucumber, plantain and coconut) were brought to the local market and the fish harbor.

The collected food samples were rice, pulses (udad dhal, tur dal and bengal gram), green leafy vegetable (amaranths, moringa, curry leaves), other vegetables (brinjal, drumstick, ladies finger, plantain, pumpkin, beans, cucumber etc.), roots and tubers (tapioca, yam, taro roots), fruits (mango, banana, papaya, jackfruit, guava), milk (goat, cow and buffalo), meat (beef, chicken and mutton), fish and curated fish.

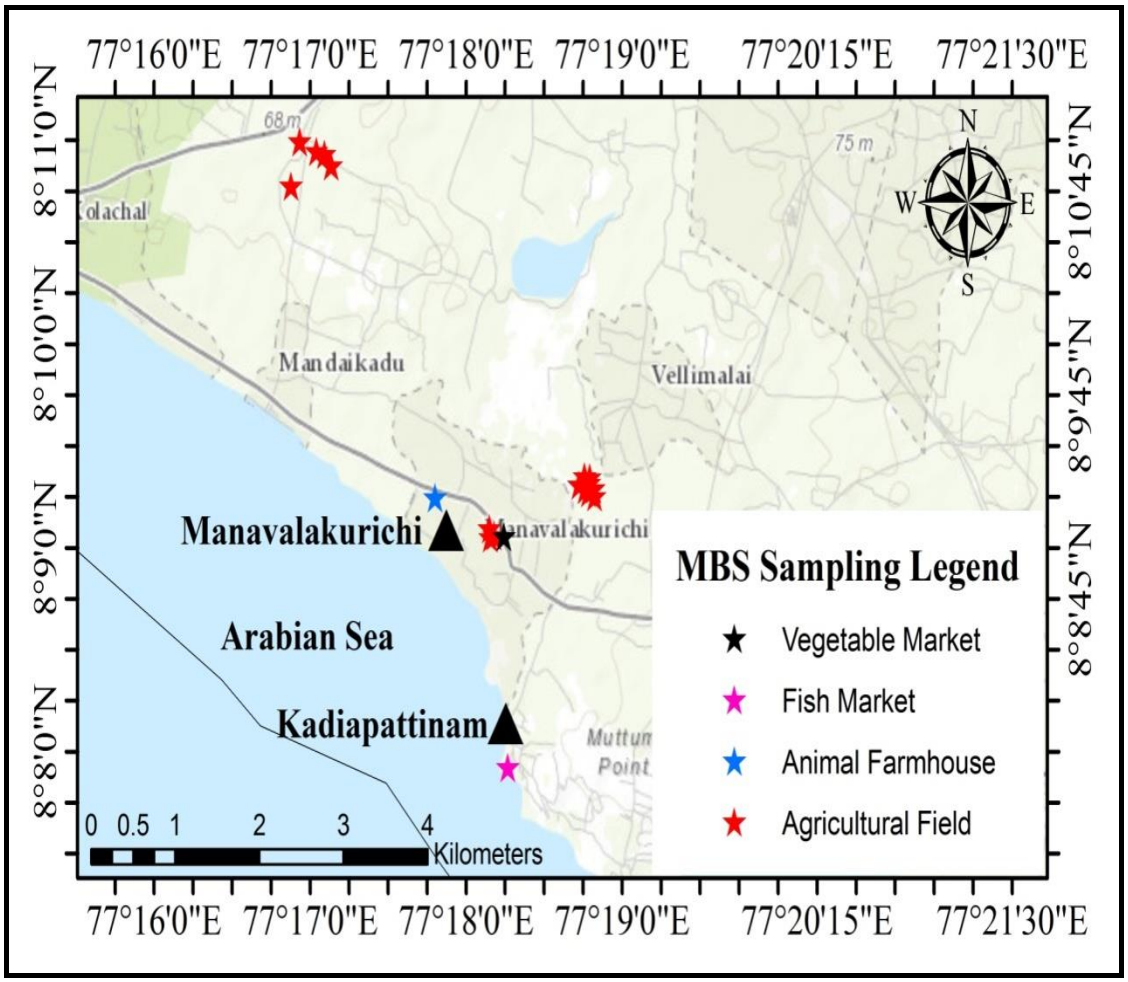


Figure 4-2: Location of Manavalakurichi Market

The details of the collected samples are provided in Table 4-1. A minimum of three samples in each food item were collected and analyzed. In case of most consumed locally grown vegetables like tapioca, plantain, brinjal, amaranths and drumstick leaves, 5 to 6 samples were analyzed.

All the samples were collected in a pre-cleaned polythene bags and kept in icebox at -4 ^{o}C and stored in an interim cold storage unit for transportation to the laboratory located away from the sampling sites.

Table 4-1: Classification of food category with common and scientific name

Food Category	Scientific Name	Common Name
Cereals	*Oryzasativa*	Rice
Pulses	*Phaseolus mungo Roxb.*	Black gram
	Cajanuscajan	Tur dhal/Pigeon pea
Green leafy vegetable	*Amaranthusspinosus*	Amaranthus
	Moringa oleifera	Drumstick
	Murrayakoenigii L.	Curry leaves
Other vegetables	*Solanummelongena*	Brinjal (Green)
	Musa sapientum	Plaintain
	Momordicacharantia	Bitter Gourd
	Lagenaria vulgaris	Bottle gourd
	Abelmoschusesculentus	Ladies Finger
	Cucumissativus	Cucumber
	Trichosanthesanguina	Snake Gourd
	Cucurbita maxima	Pumpkin
	Lycopersiconesculentum	Tomato
	Cyamopsistetragonoloba	Cluster beans
	Moringa oleifera	Drumstick
Roots and Tuber	*Manihotesculenta*	Tapioca
	Amorphophalluspaeoniifolius	Elephant yam
	Colocasiaesculenta	Taro root
Fruits	*Magniferaindica*	Mango
	Carcia papaya	Papaya
	Musa paradisaca	Banana
	Artocarpusheterophyllus	Jackfruit
	Psidiumguajava	Guava
Fish	*Stolephorusindicus*	Indian Anchovy
	Sphyraena barracuda	Barracuda
	Rastrelligerkanagurta	Indian Mackerel
	Carangoidesmalabaricus	Malabar Trevally
	Uroteuthisduvauceli	Squid
	Euthynnusaffinis	Little Tuna
	Lepturacanthussavala	Silver ribbon fish
	Sardinellalongiceps	Indian Oil Sardine
	Chirocentrusnudus	Wolf Herrings
	Rhizoprionodonacutus	Milk Shark
Curated Fish	*Stolephorusindicus*	Achovy
	Carangoidesmalabaricus	Malabar Travelly
	Sardinacaerulea	Sardine
Flesh Food	*Capra hyrchusb*	Mutton
	Bostaurus	Beef
	Gallus domesticus	Chicken
Milk	*Bostaurus*	Cow
	Capra hyrchusb	Goat
	Bubalusbubalis	Buffalo

Figure 4-3: Market Basket sampling locations in the study area

The samples were cleaned, freeze dried and homogenized. About 3g of freeze dried samples were weighed and transferred to porcelain crucibles, heated up to 450 ^{o}C at the rate of 50 °C/h in a muffle furnace and ash dried for 24 h wherever required. About 100 mg aliquots each of sample and NIST standard reference material (SRM 1570a, Spinach leaves) were packed in a high purity Al foil of 25 µm thickness. The samples were irradiated in the tray rod facility of Dhruva reactor for 3 d at a neutron flux of 5×10^{13} cm^{-2} s^{-1} and were allowed to cool for 30 d and repacked into a clean paper. Samples were assayed by measuring 311.6 keV by high-resolution γ-ray spectrometry with a 50% relative efficiency HPGe detector coupled to standalone DSPEC LF module. The resolution of the detector was 1.9 keV at 1332 keV of ^{60}Co. Peak areas under the full energy peaks were evaluated by peak fit method using the Gammavision software. A typical gamma ray spectrum of an irradiated vegetable

sample is shown in Fig 4-4. The concentrations of Th in the samples were analyzed using relative NAA method using Equation 2.11. The concentration given in the tables presented for each food group studied is the arithmetic mean of each food item (n=3-6). The activity concentration was evaluated using the following equation,

$$A_i = C_i \times h \times 4.07 \quad \textbf{(4.1)}$$

where A_i = Activity concentration (mBq kg^{-1}_{fresh}), C_i= ^{232}Th concentration in samples measured using INAA (µg kg^{-1}_{dry}), h= dry to fresh weight ratio, 4.07 is activity conversion factor (mBq μg^{-1})

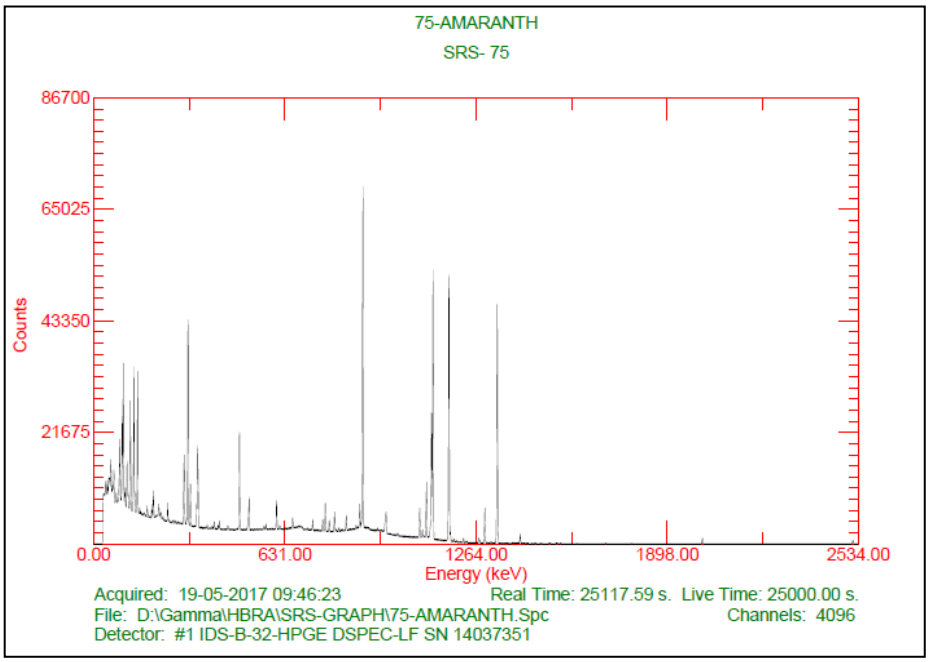


Figure 4-4: A typical Gamma ray spectrum for vegetable sample

4.2 Results and discussion

4.2.1 Quality Control Analysis

Three standard reference materials (SRMs) obtained from the National Institute of Standards and Technology (NIST) namely orchard leaves (SRM 1571), apple leaves (SRM 1515) and tomato leaves (SRM 1573a) were used to evaluate the precision and accuracy of the analytical method. In this work, NIST biological SRMs 1571, 1515

and 1573a were analyzed by relative method of INAA. The gamma ray spectrum of an irradiated sample of NIST SRM 1573a is shown in Fig 4-5.

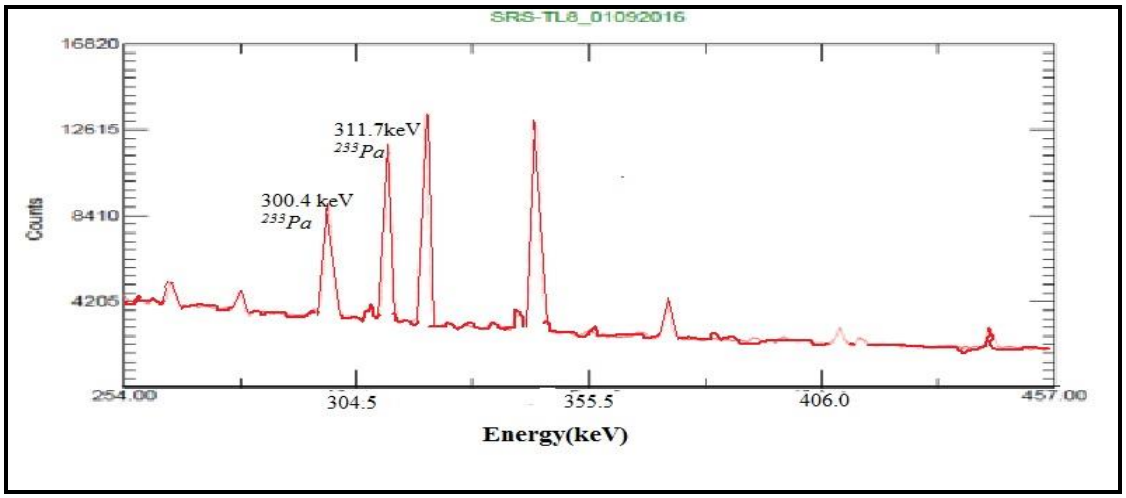


Figure 4-5: Gamma ray spectrum of irradiated reference material(SRM 1573a)

Tables 4-2 and 4-3 show the determined concentration values of Th (^{232}Th) obtained from four independent sample analyses as well as certified or information concentration values for INAA by irradiation at *CIRUS* and *Dhruva* Reactor respectively. The uncertainties on determined Th concentrations (in Table 4-2 and 4-3) are standard deviation at ±1 s confidence limit arrived from quadruplicate sample analyses and they are in the range of ±1–3%. The results are in good agreement (within ± 6 %) with the certified or information values, indicating accuracy of the optimized INAA method for low concentration Th determination in biological materials.

In addition, the precision and trueness of the counting system was also calculated as percentage relative standard deviation P (Eq. 3.10). It was seen that most of the values were observed within ± 7 % indicating high order of accuracy and precision of our data.

Table 4-2: Thorium concentration (ng g^{-1}, dry weight basis) in biological reference materials by INAA(CIRUS)

Sample ID	This work (mean ± SD)	Certified (info) value	% Deviation
NIST SRM 1515, Apple leaves	28.3 ± 0.9	(30)	-5.7
NIST SRM 1573a, Tomato leaves	115.8 ± 1.8	(120)	-3.5
NIST SRM 1571, Orchard leaves	63.1 ± 1.4 (u=0.15)	64 ± 6	-1.4

Table 4-3: Thorium concentration (ng g^{-1}, dry weight basis) in biological reference materials by INAA (Dhruva)

Sample ID	This work (mean ± SD)	Certified (info) value	% Deviation
NIST SRM 1515, Apple leaves	28.8 ± 0.8	(30)	-4.0
NIST SRM 1573a, Tomato leaves	123.8 ± 1.6	(120)	+3.2
NIST SRM 1571, Orchard leaves	66.1 ± 1.1 (u=0.34)	64 ± 6	+3.3

The trueness of the proposed method was also evaluated using the criterion of the u-test score. This parameter (u) was calculated from the reference activity, A_{ref}, the measured activity, A_{meas}, and the respective combined uncertainties, U_i, as

$$u = \frac{|A_{ref} - A_{meas}|}{\sqrt{U_{ref}{}^2 + U_{meas}{}^2}} \quad \textbf{(4.2)}$$

For t_α=1.95 for (n=4), if $t \leq 1.95$, the result does not significantly differ from the reference value at the 95% significance level. As certified uncertainty was available only NIST 1571 (Orchard leaves), the u test was done for orchard leaves. According to the accuracy test, our results were in agreement with the reference values for the thorium and showing good precision evaluated as the relative standard uncertainty.

The detection limit L_D was calculated using curries formula,

$$L_D = 2.71 + 3.29\sigma_b \quad \textbf{(4.3)}$$

where σ_b is the square root of the background counts under the characteristics photo peak of interest. The L_D (counts) was converted to L_D (µg) and L_D (µg kg^{-1}) by dividing the sensitivity of thorium (cps μg^{-1}) and sample mass, respectively. The L_D values are in the range of 0.08-0.2 µg kg^{-1}. The variation in detection limits can be attributed to differences in background due to sample matrix and varying decay period (cooling) of the samples. The ^{232}Th concentration in each food item represented in the tables are arithmetic mean (n=3-6).

4.2.2 Activity concentration in cereals

Rice is an important staple food for population in this region. Other cereals like bajra, wheat and corn are hardly consumed by the inhabitants. The concentrations of Th measured (Table 4-4) in cereals (rice) purchased from the wholesale markets in the region were found between 0.8 to 3.4 µg kg^{-1}_{fresh} with an average concentration of 2.3 ± 1.2 µg kg^{-1}_{fresh} (n=5). The average activity concentration is 9.5 mBq kg^{-1}_{fresh}.

Shiraishi et al., have reported an activity concentration of 0.46 mBq kg^{-1}_{fresh} in rice sample in Japan[92]. While an activity concentration of 0.1 mBq kg^{-1}_{fresh} and 0.77 mBq kg^{-1}_{fresh} were reported by Fisenne et al and Minsoek et al., in rice samples collected from USA and Korea respectively using alpha spectrometry [90, 95] .

In the study conducted by Dang et al., it was reported, an average activity concentration of 13.4 mBq kg^{-1}_{fresh} in rice samples collected from four major cities of India [177] which is only slightly lower than the value observed in this study. ^{232}Th content in samples collected from HBRA in Brazil varied from 0.7 - 7.9 mBq.kg^{-1}_{fresh}, while Jha et al, have reported a value of 5.3 ± 0.24 mBq kg^{-1}_{fresh} in rice samples collected from North eastern regions of India [120]. Kritsananuwat et al. have

estimated ^{232}Th content in rice grains grown in Thailand using ICP MS and reported a concentration range of 1-11 mBq kg^{-1}_{fresh} [181].

The average activity levels of ^{232}Th in rice was found to be comparable to those reported from Brazil, north east India and Thailand but was higher compared to values reported from Japan, USA and Korea. Many investigations on thorium content in rice samples were carried out using gamma ray spectrometry. Activity concentrations in samples of 1800, 6150 and 5020 mBq kg^{-1}_{fresh} were reported by Lenka et al., Olomo et al and Mlwilo et al., [43, 112, 178] respectively. The concentrations in the samples are found to be much higher than those reported using other methods like α-spectrometry, ICP-MS or NAA.

4.2.3 Activity concentration in pulses

Table 4-4 gives the ^{232}Th contents in pulses. Black grams and pigeon peas are two important pulses consumed by the people in the study region on a daily basis. Pulses are not cultivated in this region but are brought in by the traders from other parts of the Tamilnadu State.

The concentration in black gram ranged from 5.1 to 7.1 μg kg^{-1}_{fresh} with an average activity concentration of 24.7 ± 5.8 mBq kg^{-1}_{fresh} (n=3). The thorium content in pigeon pea varied from 1.2 to 1.9 μg kg^{-1}_{fresh} with an average activity concentration of 6.3 ± 2.1 mBq kg^{-1}_{fresh} (n=3). The average concentration of Th in pulses was 15.5 mBq kg^{-1}_{fresh}. An average concentration of 2.92 ± 0.19 mBq kg^{-1}_{fresh} was reported by Shiraishi et al, in bean products from Japan [92]. Dang et al., have reported an activity concentration of 8.4 mBq kg^{-1}_{fresh} which is slightly lower than that found in the present work [177]. The activity concentration in the pulses in this study is less than the reported value of El-Sweify (51-87 mBq.kg^{-1}_{fresh}) who used INAA to estimate

^{232}Th content [179]. Not enough data are available to compare the results obtained in this study.

Table 4-4: ^{232}Th content (± 1s) in cereals and pulses

Food group	Food item	No of samples	Concentration (mBq.kg^{-1} $_{fresh}$)
Cereals	Rice	5	9.5 ± 4.9
Pulses	Black gram	3	24.7 ± 4.1
	Pigeon pea	3	7.3 ± 2.3

4.2.4 Activity concentrations in green leafy vegetables

The ^{232}Th concentrations in green leafy vegetables are presented in Table 4-5. The concentration ranged from 14.9 to 18.6, 5.9 to 15.9 and 12.8 to 25.3 µg kg$^{-1}_{fresh}$ with an average activity concentration of 69.1 ± 6.2, 48.0 ± 14.3 and 78.4 ± 21.3 mBq kg$^{-1}_{fresh}$ in amaranths leaves, drumstick leaves and curry leaves respectively. The highest concentration was found in curry leaves. A typical gamma ray spectrum of neutron irradiated Amaranth leaves is given in Fig 4-6. The mean activity concentration in green leafy vegetable was 64.2 ± 18.1 mBq kg$^{-1}_{fresh}$.

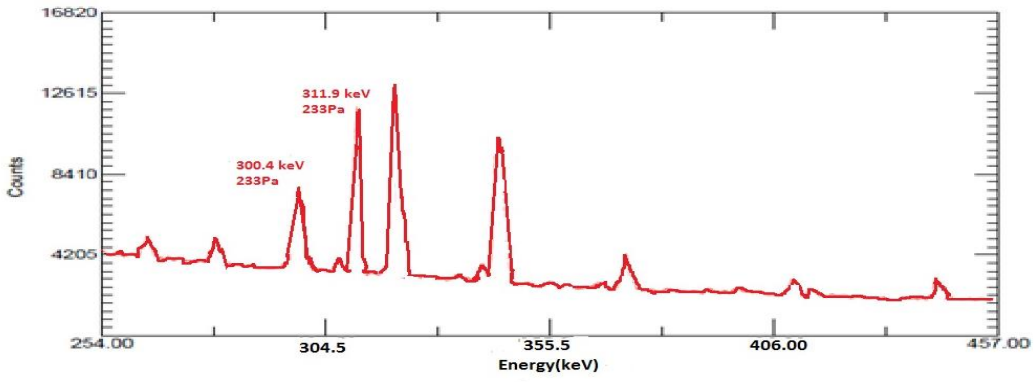


Figure 4-6: A typical gamma ray spectrum of a leafy vegetable(Amaranth leaves)

Dang et al., have reported the Th concentration in green leafy vegetable for samples collected from Mumbai to vary from 14.7-39.1 µg kg$^{-1}_{fresh}$ with mean concentration of 25.6 µg kg$^{-1}_{fresh}$ [8]. In another study on samples collected from four major states

(West Bengal, Kerala, Punjab and Maharashtra), the average concentration of 8.5 mBq kg^{-1}_{fresh} was reported [177].

The mean activity concentration was higher than the values reported from Japan (6.13 mBq kg^{-1}_{fresh}), Poland (1.5-5.9 mBq kg^{-1}_{fresh}) and Korea (0.15-5.08 mBq kg^{-1}_{fresh}). In a recent study much higher values were reported by a group of French investigators. The investigators have reported values ranging from 5.25 to 156.9 mBq kg^{-1}_{fresh} for lettuce [107]. Concentrations of ^{232}Th in lettuces from various kitchen gardens near a uranium mine in Portugal was studied by Carvalho et al., and they have reported a range of 2.2 to 28.5 mBq kg^{-1}_{fresh} [180].

Table 4-5: Activity concentration of ^{232}Th (± 1s) in Green leafy vegetables and roots and tubers

Food group	**Food item**	**No of samples**	**^{232}Th (µg kg^{-1}_{dry})**	**Dry to wet ratio**	**^{232}Th (mBq kg^{-1}_{fresh})**
Green leafy vegetable	Amaranths	5	99.8 ± 8.9	0.17	69.1 ± 6.2
	Drumstick	5	63.2 ± 19.5	0.19	48 ± 14.3
	Curry leaves	4	53.5 ± 14.6	0.36	78.4 ± 21.4
Roots and Tubers	Tapioca	6	71.8 ± 19.3	0.30	87.7 ± 23.6
	Elephant yam	3	74.6 ± 11.4	0.21	63.8 ± 9.7
	Taro root	3	63.6 ± 8.5	0.41	106.1 ± 14.2

Th concentration in curry leaves were in the range reported by Choudhary et al., (9.33 to 115 ng g^{-1}) [181]. Activity concentrations of ^{232}Th in leafy vegetables were measured by Jha et al., in samples collected from a proposed mining site and the concentration ranged from 26.5 to 48.8 mBq kg^{-1}_{fresh} which is comparable to results obtained in the present study [120].

Different mechanisms have been reported for foliar uptake in plants. The results of study by Gaelelle et al., have proposed the mechanism for uptake of heavy elements by leaves. The particles first deposits on the leaf surface, this particles undergo chemical transformation to a secondary element containing phase and gets

accumulated on the circular ledges of stomata and anticlinal cell walls of cuticles[182]. The deposition of radionuclides is further supported by occurrence of epicutilar wax layer on the surface of leaves [183].

Many investigators have used gamma spectrometry to analyze ^{232}Th concentration in leafy vegetables. ^{232}Th was determined by the peaks of ^{212}Pb (239 keV), ^{208}Tl (583 keV) and ^{228}Ac (911 keV) which are daughter products in ^{232}Th series. They have reported higher values, for e.g., Arogunjo et al., have reported a value of 1279 mBq kg^{-1}_{fresh} in spinach samples. This is mainly due to the difference in the mobility and transfer rate of Ra and Th by plants.

Jeambrun et al., have reported that the activity concentration of ^{228}Ra was higher than that of ^{232}Th in vegetation samples with value of ^{228}Ra/^{232}Th ratio ranging from 4 to 8 in lettuce. Similarly, the activity concentration of ^{228}Th was also higher than that of ^{232}Th with a ^{228}Th/^{232}Th ratio ranging from 1.5 to 2.2 in lettuce [168]. This enrichment of ^{228}Th compared to ^{232}Th was also demonstrated by Pietrzak-Flis et al. and was explained by in-growth of this radionuclide following the decay of ^{228}Ra which is added to the direct intake of ^{228}Th [87]. ^{228}Ra had always higher activity concentrations compared to ^{232}Th due to the lower mobility of thorium.

4.2.5 Activity concentration in other vegetables

Minimum of two samples in each vegetable was analyzed except for most consumed locally grown vegetables like tapioca, plantain, brinjal, amaranth and drumstick leaves where 5 to 6 samples were analyzed. The estimated ^{232}Th concentration in vegetation sample is presented in Table 4-6. Statistical analysis of data was performed by MiniTab 18 (Minitab Inc.). The Anderson–Darling test was applied to test the normality of ^{232}Th in vegetable samples. ^{232}Th concentrations were log-normally

distributed and are hence presented with geometric mean and range. Vegetable that are typically consumed were purchased from local markets. The concentration in the samples varied from 0.17 to 7.9 μg kg^{-1}_{fresh} with a geometric mean activity concentration of 4.4 mBq kg^{-1}_{fresh}. ^{232}Th concentrations were in the range (0.1– 33 mBq kg^{-1}_{fresh}) reported in the UNSCEAR report. The lowest concentration was found in tomato and highest in brinjal samples.

Brinjal, plantain and drumstick are locally grown. There is a large scale cultivation of brinjal in villages in the study area. The brinjal grown in the villages in and around Manavalakurichi is sold in the wholesale farmer's market of Karungal and Manavalakurichi. The activity concentration in brinjal varied from 11.7 to 34.6 mBq kg^{-1}_{fresh}. Brinjal samples that were purchased for the study were all cultivated in and around Manavalakurichi area, hence ^{232}Th content is higher compared to other vegetables due to the higher concentration of ^{232}Th in the soil. It is interesting to note that there is a large variation in the ^{232}Th in brinjal samples. As reported by Sauve et al., all radionuclides have a high complexing ability to bind tightly to solid surfaces [184]. ^{232}Th in soil is absorbed by the organic matter present in soil and renders the ^{232}Th non available for the plants which infers that the differences in the organic content in the soil may have resulted in different uptake of ^{232}Th into plant and therefore a variation in the ^{232}Th content in brinjal.

Bolca et al. have studied the difference in the soil properties and plant species resulted in a variability in TF for a given radionuclide [185]. Pulhani et al., have also inferred from their study that the transfer factor of an radionuclide greatly depends on the soil properties [71]. A detailed study of the soil characteristics needs to be carried out to substantiate the observation.

Similarly, it can also be noticed that other vegetables like plantain and drumstick also had higher concentration. Plantain grown in this region is also sold in the whole sale market. Wide variation in concentration of radionuclides was found in different species of vegetables and the same species also. A slight modification in any of the factors like physico-chemical characteristics, clay and pH of the soil in which they grow, may lead to variability in the concentration of the radionuclide, in same food crops or among different food crop samples.

Santos et al, studied ^{232}Th concentration in vegetables consumed by inhabitants of Rio de Janeiro, Brazil and have reported a range of 0.01 to 4.1 mBq kg^{-1}_{fresh}.

Table 4-6: Activity concentration of ^{232}Th (± 1s) in vegetables

Food Item	**No of samples**	**^{232}Th (µg kg^{-1}_{dry})**	**Dry to wet ratio**	**^{232}Th (mBq.kg^{-1}_{fresh})**
Brinjal (Green)	6	61.7 ± 18.5	0.09	22.6 ± 6.8
Brinjal (Blue)	4	48.9 ± 11.8	0.09	17.9 ± 4.3
Plantain	4	9.8 ± 1.4	0.33	13.6 ± 1.9
Plantain stem	3	27.3 ± 5.0	0.15	16.7 ± 3.1
Bitter Gourd	3	2.5 ± 1.1	0.1	1.1 ± 0.4
Bottle gourd	3	13.1 ± 1.2	0.04	2.1 ± 0.2
Ladies Finger	3	2.4 ± 0.5	0.10	1.0 ± 0.2
Cucumber	3	9.1 ± 1.9	0.03	1.1 ± 0.2
Snake Gourd	3	4.4 ± 0.6	0.04	0.7 ± 0.1
Pumpkin	3	9.8 ± 0.9	0.06	2.4 ± 0.2
Tomato	3	1.7 ± 0.7	0.04	0.3 ± 0.1
Cluster beans	3	7.2 ± 2.2	0.13	3.8 ± 1.2
Drumstick	4	16.5 ± 3.6	0.24	16.1 ± 3.5

Jha et al., used INAA to estimate ^{232}Th in vegetable consumed by tribal population residing around the proposed uranium mine in North East of India and reported a geometric mean of 27.2 mBq kg^{-1}_{fresh} which is higher than the values reported in the present study [120].

The average activity concentrations ^{232}Th ranged between 0.35 to 0.67 Bq kg^{-1} in local vegetable consumed by Malaysian population using gamma spectrometry.

The activity concentration of cucumber was comparable with values reported by Flis et al (0.75 mBq kg^{-1}_{fresh}) but slightly higher than the value(0.21 mBq kg^{-1}_{fresh}) reported by Minsoek et al [41, 95]. An activity of 0.3 mBq kg^{-1}_{fresh} in tomato was reported by Flis et al., and is comparable with value (0.3 ± 0.1 mBq kg^{-1}_{fresh}) observed in this study. Tomatoes available in the local markets are not cultivated in the study area but are brought to the market from outside.

4.2.6 Activity concentration in Roots and Tubers

The ^{232}Th content is high in tubers compared to other food samples of plant origin and the value ranged between 15.4 – 26.9 μg kg^{-1}_{fresh} with an average activity concentration of 90.9 ± 29.1 mBq kg^{-1}_{fresh} and is presented in Table 4-5. The highest concentration was found in taro root (106.1 mBq kg^{-1}_{fresh}) and lowest concentration was found in elephant yam. The tubers taro root and tapioca are usually thin and long compared to yam hence can penetrate into soil with increased ability to absorb more natural radionuclides in the soil.

The ^{232}Th in tapioca varied from 15.9 to 26.9 μg kg^{-1}_{fresh}. This variation in the ^{232}Th content may be because of the varying time at which the tapioca was harvested. In an investigation conducted by Asaduzzaman et al., on concentration of radionuclides in tapioca with age, have concluded that the concentration increases with time [186].

Plants absorb radionuclides that have similar chemical behavior as the essential nutrient. Therefore, radionuclides are transported to specific tissues based on the function of the element in plant metabolism and which is often reflected in its higher concentration in a particular part than others. According to Chen et al., there are considerable differences in the uptake and trans-location of long-lived radionuclides among different plant species [187].

There are many reports that support our observation that concentration of Th in roots are much higher than in leaves and in seeds [192-193]. Shtangeeva, studied the uptake of radionuclides by estimating the concentration in various parts of the plant and concluded that plants grown in the radionuclide enriched soils demonstrated significant increase in concentrations of Th and U in roots, while concentrations of the radionuclides in upper plant parts were rather low [188].

In the soil system, radionuclides are distributed between various solid components and soil solution. The bioavailable fraction for absorption by the plants are the soluble, exchangeable and loosely adsorbed radionuclides found in the solid components and soil solution. In a study conducted by Shanti et al., for estimation of radium isotopes in food items using gamma ray spectrometry, they have also indicated that highest concentration was observed in vegetables of root origin [132].

Shiraishi et al., have reported a concentration of 1.76 mBq.kg^{-1}_{fresh} in root and tubers which is the highest among the vegetables consumed by Japanese population [92]. In another study conducted by Kučera et al., Th content in vegetables was estimated using INAA. The concentration of Th (274 μg kg^{-1}_{dry}) was highest in roots samples [188]. Kritsananuwat et al, have also reported a higher concentration in root vegetable (Galangal) in vegetables samples from Thailand[189]. The concentration in galanjal was 2500 mBq kg^{-1}_{fresh} which is much higher than the concentration in other roots and tubers found in this study. This may be due to the different absorption (uptake) behaviors among various species.

4.2.7 Activity concentration in fruits

^{232}Th concentration was estimated in fruit samples consumed by the inhabitants of the study area and is presented in Table 4-7. The ^{232}Th content varied from 0.9 to 2.0 μgkg$^{-1}_{fresh}$with a weighted average activity concentration of 6.1 ± 2.3 mBq kg$^{-1}_{fresh.}$ Fisenne et al., estimated ^{232}Th in fresh fruits using α spectrometry and reported an activity concentration of 0.12 ± 0.18 mBq kg$^{-1}_{fresh.}$ Intake of the radionuclides with food was evaluated from the analysis of foodstuffs collected in central Poland by Flis et al. ^{232}Th in fruit samples (apple, cherry, plum, black currant, red currant and strawberry) varied from 0.54 to 3.04 mBq kg$^{-1}_{fresh}$[41].

Table 4-7: Activity concentration of ^{232}Th (± 1s) in Fruits

Food item	No of samples	^{232}Th (μg kg$^{-1}_{dry)}$	Dry to wet ratio	^{232}Th (mBq kg$^{-1}_{fresh}$)
Mango	3	10.4 ± 3.3	0.14	5.9 ± 1.9
Papaya	3	18.2 ± 3.4	0.08	5.9 ± 1.1
Banana	3	7.1 ± 0.8	0.32	9.2 ± 1.1
Jackfruit	3	8.7 ± 0.9	0.12	4.2 ± 0.4
Guava	3	3.2 ± 0.9	0.34	4.4 ± 1.2

Samples of fruits and vegetables produced and consumed in Elazıg˘ Region, Turkey were analyzed for ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs activity concentrations using gamma ray spectrometry. The average activity concentration in fruits were 980 ± 230 mBq kg$^{-1}_{fresh}$ which is higher compared to the results in this study [97].

The concentration of ^{232}Th was estimated in foodstuff consumed by tribal population residing in north east part of India using INAA. An activity concentration of 3.3 to 4.9 mBq kg$^{-1}_{fresh}$ was found in papaya which was in the range observed in this study[120]. The concentrations of ^{232}Th was determined in fruits (orange, banana, apple, papaya and pineapple) consumed most by the adult inhabitants of Rio de Janeiro City, Brazil. The activity concentration varied from 0.08 – 3.5 mBq kg$^{-1}_{fresh}$[103].

In another study conducted by Harb et al, ^{232}Th was estimated in fruit samples using gamma ray spectrometry. They have reported an activity concentration ranging from 10 to 240 mBq $kg^{-1}_{fresh.}$[98] . Similar trends were observed in studies that were conducted using passive method like gamma ray spectrometry [190–192].

Activity concentrations of ^{238}U, ^{232}Th, ^{226}Ra, ^{40}K and ^{137}Cs were measured in milk, egg, fruit and fish samples collected around a proposed site for BARC facility at Vishakhapatanam, India by Patra and co workers, and reported that the activity concentration in the range of 100-2000 mBq kg^{-1}_{fresh} in fruits which is higher than other results [193].

Thorium contents in fruits were the lowest among plant origin food stuff. Plants take up and accumulate elements in their tissue through root and part of the element is translocated to other plant parts. Nuclides can be deposited on the external plant component directly from the atmosphere by wet or dry deposition, via resuspension from soil, and via contamination from either aspersion or irrigation waters. In general, roots serve as a natural barrier preventing the transport of many trace metals, including radionuclides to upper plant parts. Hence concentration in fruits is less compared to roots and shoots. Moreover, the rate of radionuclide translocations from roots to shoots is probably species-dependent. It may be different for different species and even different part of a plant [194].

4.2.8 Activity concentration in fish

The major occupation of the people in the study area is fishery. Fish is an integral part of diet consumed by the population residing in this area. The fish consumed by the population is mainly from sea. Activity concentrations in the different types of fish purchased from the local market were determined and ranged from 3.9 to 20.8 μg kg^{-}

$^{1}_{fresh}$ and is tabulated in Table 4-8. The activity concentration ranged from15.6 ± 1.5 to 76.3 ± 8.3 mBq kg^{-1}_{fresh} with an arithmetic mean of 30.4 mBq kg^{-1}_{fresh}.

The difference in ^{232}Th concentration in different types of fish could be due to the differences in metabolism, feeding pattern and other factors in the marine ecosystem such as chemical form of the radionuclides, salinity, temperature and pH [25].

Table 4-8: Activity concentration of ^{232}Th (± 1s) in Fish

Food item	No of samples	^{232}Th (µg kg^{-1}_{dry})	Dry to wet ratio	^{232}Th (mBq kg^{-1}_{fresh})
Indian Anchovy	3	85.3 ± 9.3	0.22	76.3 ± 8.3
Barracuda	3	50.7 ± 3.7	0.19	39.1 ± 2.9
Indian Mackerel	3	27.4 ± 6.7	0.14	15.6 ± 1.5
Trevally	3	18.7 ± 2.1	0.32	24.2 ± 2.7
Squid	3	19.9 ± 2.8	0.34	19.9 ± 2.3
Little Tuna	3	22.8 ± 1.4	0.25	23.1 ± 1.4
Silver ribbon fish	3	21.5 ± 1.6	0.19	16.6 ± 1.2
Indian Oil Sardine	3	26.7 ± 2.9	0.26	28.2 ± 3.1
Herrings	3	35.7 ± 2.7	0.18	26.1 ± 2.0
Shark	3	44.5 ± 6.9	0.27	48.8 ± 7.6

The highest concentration was observed in Indian anchovy. Anchovy is a small, common salt-water fish which is consumed with the bone. Hence during sample preparation, the bones were not separated but included for analysis. As it is well known that though most of the thorium ingested although passes through the digestive tract but that which is taken up into the blood deposits in bone. Once deposited, Th binds strongly with bone and is removed only very slowly. Hence concentration of Th in anchovy may be high as the sample was analyzed with bone.

Among other fish varieties, the lowest was found in mackerel and highest in shark. Mackerel is again a small pelagic fish coastal fish with a life span of 2.5-3 y whereas shark is generally a large pelagic fish with a longer life span (8 -14 y).

The average ^{232}Th concentrations in fish were 12.7 and 12.5 mBq kg^{-1}_{fresh} in Poland and Japan respectively [41, 92]. In the result of study carried out by Fisenne et al.,

average concentration in fish samples from USA was 1.17 mBq kg^{-1}_{fresh} [91]. A study reported average activity of ^{232}Th in fish samples (anchovy) from Korea as 38.1 mBq kg^{-1}_{fresh} [95]. The activity concentration in fish samples determined in our study is considerably higher compared to that reported from Japan, USA, Poland. The concentration in samples other than anchovy was comparable with the results obtained in Korean seafood.

Conversely, the higher activity concentration was reported by many investigators. The range of activity of ^{232}Th in sea fish samples from the Black Sea Region of Turkey have been reported as 120 ± 40 to 1030 ± 150 mBq kg^{-1}_{fresh} [174]. The average concentrations of ^{232}Th activity in fish samples from Nigeria have been reported as 115 Bq kg^{-1}_{fresh} [175]. In another study by Ademola et al., on ^{232}Th content in marine fish samples collected from Ondo State, Nigeria, an activity concentration of 26.2-112 Bq kg^{-1}_{fresh} was reported [195].

The ranges of activity concentration of ^{232}Th in marine fish samples from the Bay of Bengal to the off the coast of Bangladesh, have been reported as 240-2280 mBq kg^{-1}_{fresh} [196]. This may be due to the ^{232}Th content in the samples were measured using gamma ray spectrometry.

In a study conducted by Kantha et al., for estimation of ^{210}Po in food items procured from the local markets in the study area, highest concentration was found in fish products [6].

4.2.9 Activity concentration in curated fish

^{232}Th in the dry fish was also analyzed (Table 4-9) and the average concentration in dry fish was 435.9 ± 35.4 mBq kg^{-1}_{fresh}. The activity concentration ranged from 349.7

– 550.3 mBq $kg^{-1}_{fresh.}$ The highest concentration was found in sardines. Two samples in each food item was measured in this food group.

Table 4-9: Activity concentration of ^{232}Th (± 1s) in Curated Fish

Food item	^{232}Th (µg kg^{-1}_{dry})	Dry to wet ratio	^{232}Th (mBq kg^{-1}_{fresh})
Indian Anchovy	132 ± 10	0.65	350 ± 26
Malabar Trevally	119 ± 8	0.83	403 ± 28
Indian Oil Sardine	215 ± 20	0.63	550 ± 51

The main occupation of the population residing in the study area is fishing and fish forms the main ingredient in the diet. In Tamilnadu, a ban is enforced every year from mid April to mid June for fishing which is aimed at safeguarding fishes during their breeding season and conserve fish stock. During this banned period and rainy season curated fish is consumed extensively by the local population. Curated fish also known as dried fish are processed fish where the fresh fish of various species are first rinsed in sea water, salted and sun-dried in open, mainly on coir mats and stored for several months to years based on species. As the fish is dried in open on the shorelines along the coast, there is high probability of extraneous mixing of sand rich in monazite. This could be the reason for higher concentration of ^{232}Th in the samples. The data obtained in the study is first of its kind for determination of thorium in curated fish.

4.2.10 Activity concentration in flesh food

Activity concentration of ^{232}Th in flesh food (chicken, beef and mutton) was determined (Table 4-10) and ranged between 4.1 ± 0.2 and 26.1 ± 0.6 mBq kg^{-1}_{fresh} with an mean of 10.9 mBq kg^{-1}_{fresh}. Among the flesh food, highest concentration was found in beef liver. This may be due to selective retention of ^{232}Th in liver and the life of a cow is considerably longer than chicken and goat. Dang et al., have reported the Th concentration in mutton (goat meat) to range between 1.2 - 3.3 mBq kg^{-1}_{fresh} for

samples collected from Mumbai which is lower than the value obtained in this study. A similar study conducted to measure the ^{232}Th in food component in north eastern India, have reported a concentration of 121.8 mBq kg$^{-1}_{fresh.}$in beef which is higher than that observed in this study [120].

Table 4-10: Activity concentration of ^{232}Th (± 1s) in Flesh Food

Food item	No of samples	^{232}Th (μg kg$^{-1}_{dry)}$	Dry to wet ratio	^{232}Th (mBq kg$^{-1}_{fresh}$)
Mutton	3	12.5 ± 0.9	0.21	10.7 ± 0.8
beef	3	11.8 ± 1.6	0.22	10.5 ± 1.4
Beef liver	3	25.3 ± 2.7	0.25	25.7 ± 2.6
chicken	3	5.1 ± 0.7	0.27	5.6 ± 0.8

On the other hand, the concentration of ^{232}Th in beef observed in this study was higher than the reported value of other places like Poland and Ukraine. An activity concentration of 4.07 and 0.27 mBq kg$^{-1}_{fresh}$ in poultry food was reported in Poland and USA respectively and is closer with this results of 5 mBq kg$^{-1}_{fresh.}$for chicken [41, 90]. The ^{232}Th concentration in beef samples was close to values (1.0 to 5.4 mBq kg$^{-1}_{fresh}$) reported by Lin et al, of Korea.

Table 4-11 compares the activity concentration in poultry items in the present study with literature values.

Table 4-11: Activity concentrations of ^{232}Th in chicken meat from the literature (mBq kg^{-1} fresh weight)

Country	^{232}Th	Method	Reference
Korea	1.27 ± 0.15	α-Spectrometry	Choi *et al.*, 2008
S-W Poland	1.65 ± 0.6	α-Spectrometry	Pietrzak-Flis *et al.*, 1997
Central Poland	1.31 ± 0.33	α-Spectrometry	Pietrzak-Flis *et al.*, 2001
USA	0.27 ± 0.63	α-Spectrometry	Fisenne et al.,

A work was done to investigate the natural radioactivity levels (^{226}Ra, ^{40}K and ^{232}Th) in different organs of cattle slaughtered for consumption by Ademola et al., and they

have reported that liver has more concentration compared to the beef itself. Similar trend was also found in this study [199].

Similarly, the mean specific activity of ^{232}Th ranging between 0.67 –2.84 Bq kg^{-1} in goat was reported by Tchokossa et al using gamma ray spectrometry [202].

4.2.11 Activity concentration in milk

Thorium concentration in milk samples collected from cow, goat and buffalo was determined and presented in Table 4-12. Milk from cow was the most consumed dairy products by this population. The determined concentration in the samples ranged between 8.9 ± 0.3 and 15.3 ± 0.5 mBq kg$^{-1}_{fresh}$ with an average of 12.4 ± 1.9 mBq kg$^{-1}_{fresh.}$

Table 4-12: Activity concentration of ^{232}Th in milk

Food item	**No of samples**	**^{232}Th (µg kg$^{-1}_{dry}$)**	**Dry to wet ratio**	**^{232}Th (mBq kg$^{-1}_{fresh}$)**
Cow	4	36.7 ± 6.4	0.08	11.9 ± 1.9
Goat	3	21.2 ± 1.1	0.09	7.1 ± 1.1
Buffalo	3	31.9 ± 3.5	0.1	12.7 ± 1.8

An activity concentration of 3.1mBq kg$^{-1}_{fresh}$ was reported by Dang et al., for samples collected from normal background area in India [27]. The concentration of ^{232}Th in milk samples observed in this study was higher than the values reported by other workers. A value of 1.19, 0.158, 0.27, 0.39, 0.08 and 2.9 mBq kg$^{-1}_{fresh}$ was reported in milk samples of Poland, Japan, USA, Ukraine, Korea and Morocco respectively [41, 45, 199, 200]. Though the results obtained was higher compared to some of the similar studies in other countries, the value was lower than the reported value of 24 mBq kg^{-1} in milk product from a thorium rich area in Brazil by Lauria et al. [42]

4.2.12 Activity concentration in spices and coconut

^{232}Th content in tamarind and green chilly which are used in the dishes prepared by the inhabitants as spices or for seasoning. The average activity concentration in green chilly and tamarind was 4.02 ± 1.2 and 51.2 ± 13.01 mBq kg^{-1}_{fresh} respectively. The concentration in tamarind was higher because of the preservation practices by the villagers. Tamarind is sundried in open and stored for later use. This open drying might have resulted in extraneous contamination with monazite containing sand.

Coconut is used extensively by the population in almost all preparations. Coconut cultivation is also carried in large parts of the region. The concentration varied from 3.2-5.0 μg kg^{-1}_{fresh} with an activity concentration of 16.9 mBq $kg^{-1}_{fresh.}$ There are no data on ^{232}Th content in coconut.

Fig 4-7 compares the activity concentration in the important food groups studied. The activity concentration in plant origin food was in the order: roots and tubers >leafy vegetables > vegetables > pulses > fruits. Similar trend was also observed and reported by Kritsananuwat et al., in a study to investigate the activity concentration in various parts of a plant [189]. Pulhani et al. have reported in wheats about uranium decreasing trend root > shoot > husk > grains. It has also been reported in a number of publications that concentration of U and Th in root are much higher than in leaf and stem.

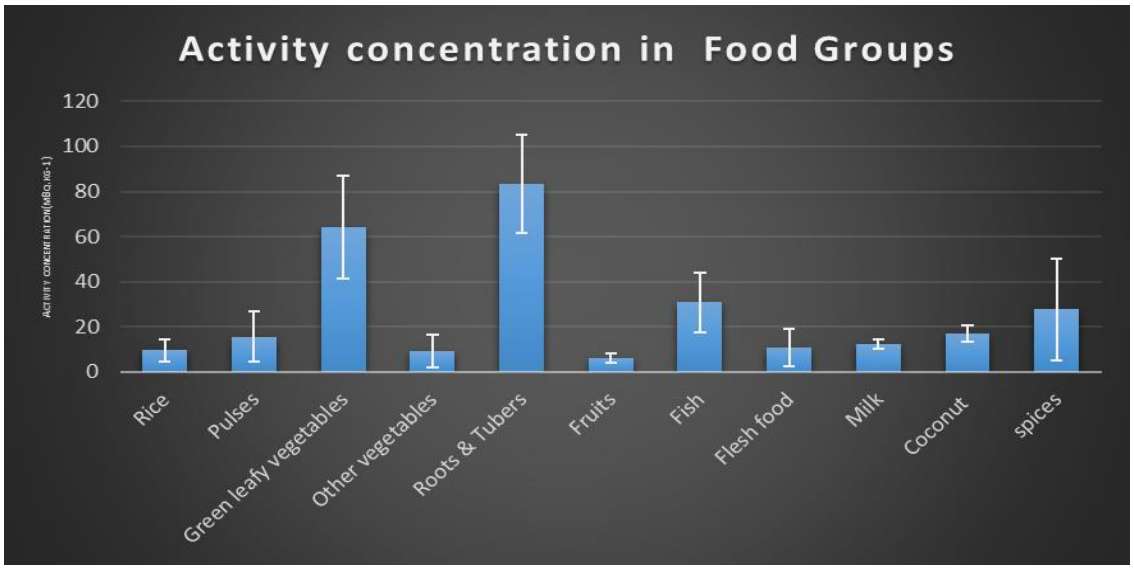


Figure 4-7: Average activity concentration in 11 important food groups

Shtangeeva et al., have intensely studied the uptake of Th by various plant parts (roots, leaves and stem) with respect to different growth environment. They in their study have observed that addition of a small amount of thorium to the media resulted in a significant increase of thorium concentration both in roots and leaves. There was a significant accumulation of Th in roots of plants grown in distilled water media and they concluded that deficiency in all minerals in the medium enhances the uptake of Th[184].

Root secret fluids that play a very significant role in solubilization and mobilization of elements in soil. Roots and microorganism on the roots secrete a variety of organic acids especially oxalic acid which results in creation of microenvironment in the rhizosphere that is different from the bulk soil [201]. Dissolution of Th in oxalic acid is higher than in nitric or hydrochloric acid [61]. Hence more the surface, more is the absorption by the roots. The above factors support the observation of more accumulation of Th in roots.

4.3 Daily intake

Ingestion intake of natural radionuclides depends on the consumption rates of food and on the radionuclide concentrations. The average daily consumption of different food items was taken from the data published by NNMB, Hyderabad, India. NNMB has reported the average consumption rates for different age group and gender for different states in India.

The study area is located on the border of Tamilnadu and Kerala, hence the food habits is a mixture of these two states. Therefore, the average consumption rates of the two states were assumed for evaluation of daily intake. Though NNMB has reported the average consumption rates for different age group in children category, in our study only four age groups were considered, namely 1–3, 4–9, 10–17 y and adult. As the consumption rate didn't vary much for the age groups between 4-9 and 10–17 y, the average consumption rate was considered. The age dependent consumption rates for different food group are shown in Table 4-13.

Table 4-13: Daily intakes (in g per person) of food used in Market basket Studies

Food Group	Children (1-3y)	Children (4-9y)	Adolescent (10-17y)	Adult (>18y)
Cereals	94.0	172.5	258.7	344.0
Pulses	10.0	19.0	23.0	23.5
Leafy Vegetables	3.5	4.5	7.8	10.3
Other Vegetable	10.5	21.8	36.5	51.0
Roots and Tubers	16.5	33.3	45.7	59.3
Fruits	22.0	24.3	32.8	34.0
Fish	8.0	20.3	26.8	32.8
Flesh food	9.5	14.5	14.5	10.8
Milk	13.9	98.3	85.5	75.5
Coconut	5	11	15.3	18.5
Spices	8	13.5	21.8	24.5

For the total daily intake evaluation, the weighted average for ^{232}Th in food group was calculated, and then multiplied by the respective consumption rate. In case of vegetables where the activity concentration followed a lognormal distribution, geometric mean was used for evaluating the daily intake.

The daily intake of ^{232}Th through foodstuff for different age group is presented in Table 4-14. Intake was higher in men than in women as the per capita consumption of food was higher among boys and men. The daily intake by adult is higher than the global mean of 5.5 mBq d^{-1}[1].

Table 4-14: Daily intake of ^{232}Th (mBq d^{-1}) through food group

Food Group	Children (1-3y)	Children (4-9y)	Adolescent (10-17y)	Adult (>18y)
Rice	0.9 ± 0.5	1.6 ± 0.9	2.5 ± 1.3	3.3 ± 1.7
Pulses	0.2 ± 0.1	0.3 ± 0.2	0.4 ± 0.3	0.4 ± 0.3
leafy vegetables	0.2 ± 0.1	0.3 ± 0.1	0.5 ± 0.1	0.5 ± 0.1
Other vegetables	0.05 ± 0.04	0.09 ± 0.1	0.5 ± 0.4	0.3 ± 0.2
Roots and Tubers	1.5 ± 0.5	3.0 ± 0.9	4.2 ± 1.3	5.4 ± 1.7
Fruits	0.13 ± 0.05	0.15 ± 0.06	0.2 ± 0.1	0.2 ± 0.1
Fish	0.2 ± 0.1	0.6 ± 0.3	0.7 ± 0.3	1.0 ± 0.3
Flesh food	0.1±0.1	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1
Milk	1.7 ± 0.2	1.2 ± 0.2	1.0 ± 0.2	0.9 ± 0.1
Coconut	0.1 ± 0.02	0.2 ± 0.04	0.3 ± 0.1	0.3 ± 0.1
spices	0.22 ± 0.23	0.38 ± 0.39	0.61 ± 0.62	0.68 ± 0.7
Curated fish	3.5 ± 0.8	8.8 ± 2.1	10.7 ± 2.4	14.2 ± 3.4

The intakes of thorium in the Asian countries was studied and reported as a part of IAEA coordinated research Program. There was a variation of more than an order of magnitude. The highest daily intake was reported in Bangladesh as 14.4 mBq d^{-1} and the lowest of 0.61 mBq d^{-1} was reported from the Philippines. The median value of intake for the Asian population was 4.1 mBq $d^{-1}$and is 3 times lower than the ICRP reference man value of 12.2 mBq d^{-1}. The reported activity concentration of daily

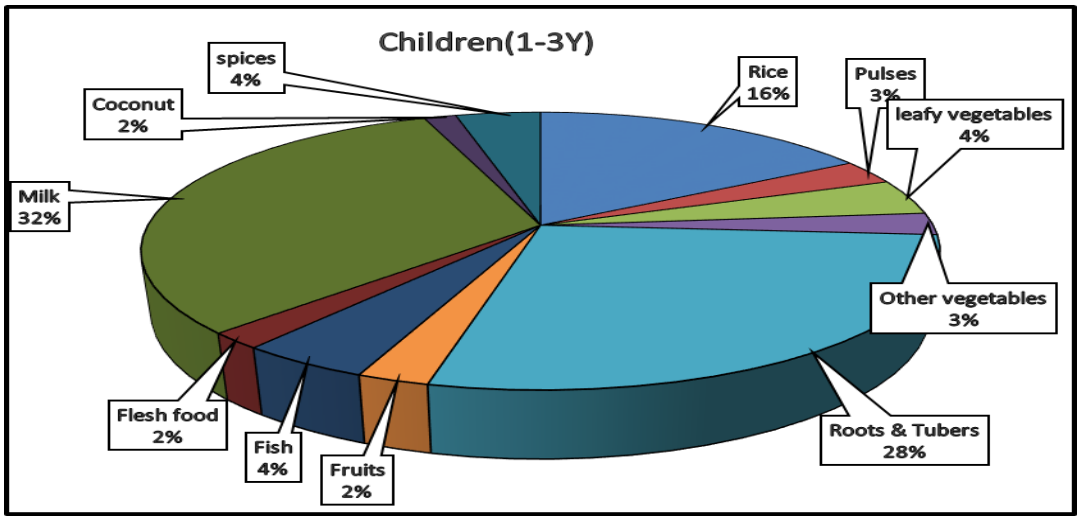
intake was evaluated in samples from natural background radiation area and it was found lower than the evaluated daily intake in this study.

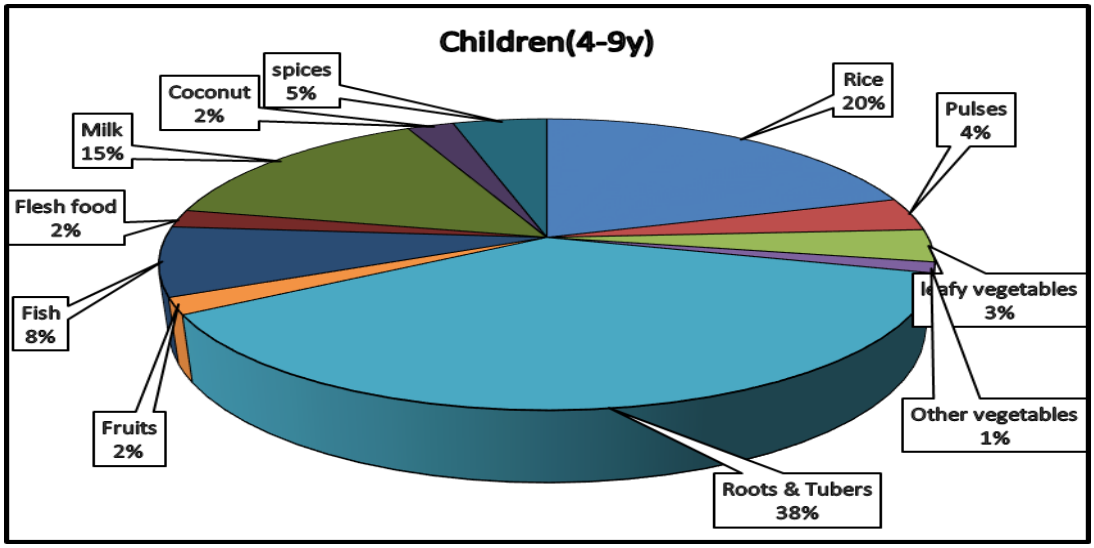
The daily intake of thorium reported for New York residents (belonging to Caucasian population) was also 4.1 mBq d^{-1} which is similar to the median Asian intake value. Another group of workers in Japan estimated the daily intake of 2.8 mBq d^{-1} thorium for Japanese population, and it was based on market basket study of 18 food categories.

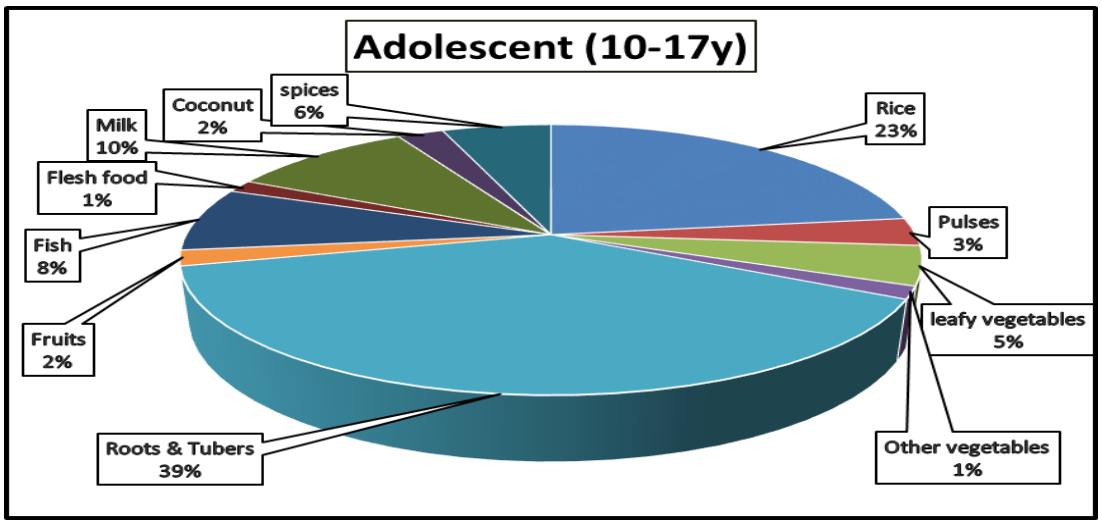
Total intake of ^{232}Th by the population residing at the Domiasiat, India was 3.4 μg d^{-1} (14 mBq d^{-1}) which is lower compared to the intake of 27.4 mBq d^{-1}evaluated in this study [121]. The average per capita intake of thorium in food is reported as 1.3 μg d^{-1}(5.3 mBq d^{-1}) [90] and 1.5 μg d^{-1}(6.1mBq d-1) in japan[199]. The total daily intake from ^{232}Th measured in a study from Korean foods based on MBS method was evaluated as 1.2 mBq d^{-1}. The average daily intake of ^{232}Th by the Buena inhabitants (an established HBRA in Brazil) was estimated using MBS to be 26 mBq d^{-1} which is comparable to the values observed in this study [42]. Similarly a higher intake of 20.4 mBq d^{-1} was observed in another HBRA of China[202].

4.4 Contribution of food groups to daily intake

Contribution of the food groups (except for curated fish) to the ^{232}Th intake for different age group is presented in Fig 4-8. Three foods namely milk, rice and roots and tubers were the biggest contributor in children between age 1 to 9y.


Children(1-3Y)
spices 4%
Coconut 2%
Milk 32%
Rice 16%
Pulses 3%
leafy vegetables 4%
Other vegetables 3%
Roots & Tubers 28%
Flesh food 2%
Fish 4%
Fruits 2%


Children(4-9y)
spices 5%
Coconut 2%
Milk 15%
Flesh food 2%
Fish 8%
Fruits 2%
Rice 20%
Pulses 4%
leafy vegetables 3%
Other vegetables 1%
Roots & Tubers 38%


Adolescent (10-17y)
spices 6%
Coconut 2%
Milk 10%
Flesh food 1%
Fish 8%
Fruits 2%
Rice 23%
Pulses 3%
leafy vegetables 5%
Other vegetables 1%
Roots & Tubers 39%

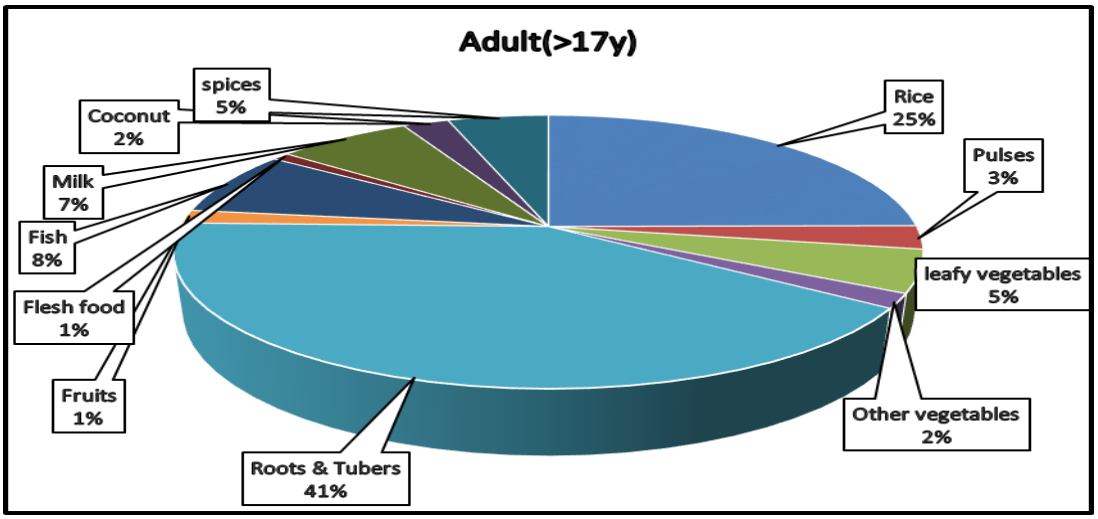


Figure 4-8:Contribution of different food groups to the intake by different age group

The group of roots and tubers (38%) was the biggest contributor to adult population and milk (32%) was the highest contributor among children between age group of 1 to 3 years. The next biggest contributor was cereals (25%) and roots and tuber (28%) for adult and children respectively. The lowest contributor was from vegetables, spices and coconut in all the age groups. Although two groups, fish and green leafy vegetables had higher ^{232}Th contents, their contributions to the daily intake were lower than milk due to the small consumption rate (Table 4-13).

With increase in age, contribution from milk decreased due to higher intake of other food groups. From the above comparison, it is clearly seen that it is important to consider the ^{232}Th intake from two viewpoints, i.e.,^{232}Th concentrations in each foodstuff and the daily intake of each foodstuff as taken by the population.

Shiraishi et al., studied the contribution of 18 important food group on ^{232}Th by Japanese population. They have demonstrated that group of fish and shell fishes contribute the maximum of 44%, followed by vegetables (11%), beans (8%). They have not estimated the contribution from root and tubers. Moreover, daily

consumption estimate for fish and green leafy vegetables were higher compared to other food groups. Fisenne et al, collected foodstuff from New York city and analyzed for ^{232}Th. Contribution to daily intakes in the city residents was highest from vegetables (65%) followed by grains (17%). Animals and fish products contributed about 13%.

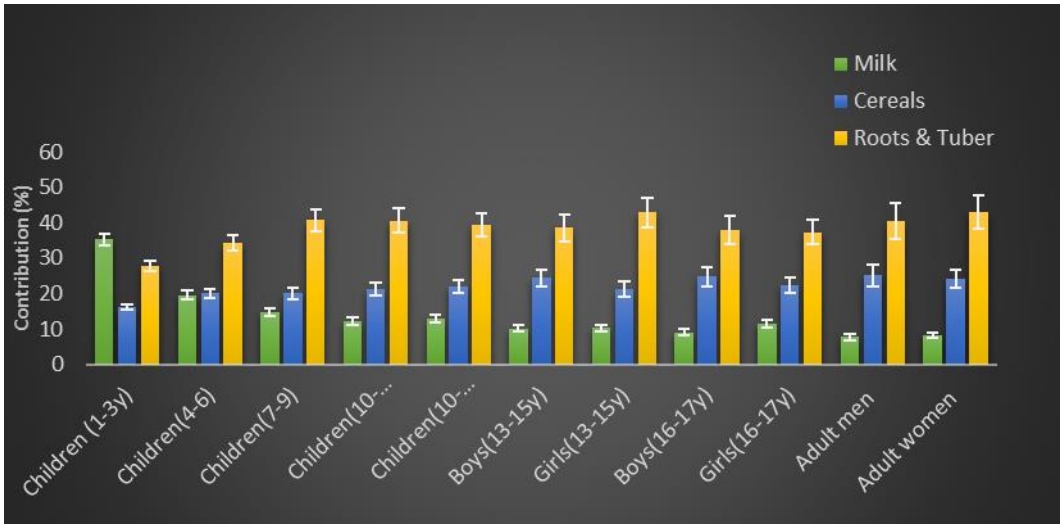


Figure 4-9: Contribution of ^{232}Th dietary intakes of three food groups For different age groups

Among milk, cereals(rice) and roots and tubers, roots and tubers were the major contributor (Fig 4-9) to daily intake of ^{232}Th except in children (1-3y). ^{232}Th contribution from roots and tubers were constant for all the age groups whereas the contribution from milk decreased with age.

The critical pathway in Japanese and USA residence was through marine products (50%) and agricultural products respectively. In present study agricultural products and marine products contributed the maximum to the daily intake.

From the above comparisons, it is clearly demonstrated that the daily intake varies from country to country based on the geological and food habit patterns. Therefore, it

is important to study the contribution to intake by each food group and individual item in each food group.

4.5 Annual effective dose due to ^{232}Th

In order to calculate the dose received by inhabitants under the area of study, the rates of consumption of different food category as given by NNMB were used. Annual Effective ingestion dose E_{ing} (Sv y^{-1}) from radio- nuclide in food and annual intake (kg y^{-1}) was calculated using equation 3.13.

Table 4-15: Age dependent dose co efficient [144]

Age	Dose Coefficient (Sv/Bq)
1year(1-2)	4.5E-07
5 year(3-7)	3.5E-07
10 year(8-12)	2.9E-07
15 year(13-17)	2.5E-07
Adult(≥18)	2.3E-07

Table 4-15 gives the dose coefficients (in Sv Bq^{-1}) for ^{232}Th corresponding to the committed effective dose, $DCF_{ing,232Th}$, resulting from the intake of 1 Bq for different age groups. As in this study, the age group was classified into four namely 1-3 y, 4-9y, 10-17y and >17y, $DCF_{ing,232Th}$ of 4.5 × 10^{-7}, 3.2 × 10^{-7}, 2.7 ×10^{-7} and 2.3 × 10^{-7} was used respectively.

Table 4-16 shows data obtained for the annual committed effective doses due to dietary intakes of ^{232}Th for different age groups of individuals in the study area. The total annual ingestion dose evaluated from contribution due to intake of 12 food groups studied varied from 1.5 μSv y^{-1} for children (1-3y) to 3.4 μSv y^{-1} for adult. The dose to the adult men was slightly higher than women due to higher consumption estimate for men. As the daily consumption estimate for curated fish is not available,

the consumption estimate of fish was used to evaluate intake and annual dose. Effective dose due to consumption of curated fish was the highest among all age group.

Table 4-16: Annual committed effective dose (μSv y^{-1}) of three age groups from intake of ^{232}Th

Food Group	Children (1-3y)	Children (4-9y)	Adolescent (10-17y)	Adult (>18y)
Rice	0.15	0.19	0.29	0.38
Pulses	0.03	0.03	0.04	0.04
leafy vegetables	0.04	0.03	0.06	0.08
Other vegetables	0.23	0.01	0.02	0.03
Roots and Tubers	0.25	0.35	0.48	0.63
Fruits	0.02	0.02	0.02	0.02
Fish	0.04	0.07	0.09	0.22
Flesh food	0.02	0.02	0.02	0.01
Milk	0.28	0.14	0.12	0.11
Coconut	0.02	0.02	0.03	0.04
spices	0.04	0.04	0.07	0.08
Curated fish	0.57	1.03	1.36	1.73
Total	1.46	1.97	2.61	3.36

An annual effective dose of 1.4 μSv y^{-1} was estimated for the vegetables and derived products consumption by Santos et al., for inhabitants of Rio de Janeiro City, Brazil which is in the order observed in the study. A higher value was estimated for population residing in HBRA Buena, Brazil. An annual effective dose of 0.67 μSv y^{-1} from ^{232}Th dietary intake was reported by Wu Quan et al., for Chinese population leaving in NBRA.

The annual internal dose from ingestion of ^{232}Th for an adult population residing in Walbrzych region of Poland was estimated as 0.49 μSv y^{-1}. Min soek et al., evaluated the annual ingestion dose using MBS for Korean population as 0.1 μSv y^{-1}which is much less compared to this study values. An average annual effective dose of 76 μSv y^{-1} for adult population was estimated for ^{210}Po intake from the consumption of food

items in this study and is an order higher compared to the average dose (3.4 μSv $y^{-1)}$ evaluated for ^{232}Th intake [6]. Using recommended dose conversion coefficient for ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K of 0.23, 0.8, 0.072 and 0.0062 mSv Bq^{-1} respectively, Shanthi et al., have evaluated total annual internal dose from intake of south Indian food as 0.201, 0.659, 0.475 and 0.460 mSv y^{-1} [5]. Compared to the dose received from the other radionuclides using MBS, the dose received from ^{232}Th is less.

MBS is a suitable method for identifying the contribution from each food groups and hence it is a beneficial method for classifying the critical pathway in case of accidental increase in a radionuclide in soil or atmosphere. Furthermore, food items in food groups that significantly contributed to total intake and the individual food item having high content of the nuclides should be analyzed in detail to find individual critical foods in the food chain.

CHAPTER 5

DIETARY INTAKE OF THORIUM USING DUPLICATE PORTION STUDY (DPS) METHOD

5.1 Introduction

Information on daily intake of ^{232}Th is important for estimating the metabolic factors of uptake and deposition of the radionuclide in the human body. The incorporated thorium is retained in skeleton, liver and other tissues resulting in internal radiation dose. As the consumption of food is usually the most important route by which natural radionuclides can enter the human body, an assessment of radionuclide levels in different food and diets is therefore important to estimate the intake of these radionuclides by human. In India, natural radioactivity has been measured in some specific food products but there are a few data for total diet especially in the study area. Dietary exposure assessment is a tool to estimate the internal exposure via ingestion. Duplicate Portion Study (DPS) and Market Basket Study (MBS) are two commonly employed methods for the study of daily dietary intake. The DPS is a direct method where the intake is evaluated by analyzing the 24 h diet sample collected from individuals in a population sub group. Instrumental Neutron Activation Analysis (INAA) is a very sensitive and reliable method for estimating the absolute concentration of Th (^{232}Th) in environmental and biological matrices.

5.2 Methodology

Preliminary work was carried out by ground radiometric survey to determine the high background radiation spots in the study region. Based on the radiometric survey duplicate diet samples were collected from volunteers from four villages namely Putteti, Manavalakurichi, Thengapattinam and Idindakarai. The samples were collected in a pre-cleaned polythene bags and stored in icebox at -4^0C for transportation to the analytical laboratory. The frozen diet was thawed and homogenized and then wet weight was recorded. The homogenized samples were

freeze dried using lyophilizer. The samples were analyzed for ^{232}Th using relative method of INAA.

Dietary record was also recorded from three age groups though only one individual's food sample was collected from the selected house hold. Based on the daily dietary intake details recorded from the family members, annual intake (consumption rate) was evaluated. Annual intake of ^{232}Th was evaluated for three different age group groups like children (4-11 y), adolescent (12-17 y) and adults (18-60 y) using the estimated ^{232}Th concentration in duplicate diet.

5.3 Results and discussion

5.3.1 Ground Radiometric Survey

Ground radiometric survey was carried out along the coastal region from Idindakarai to Thengapattinam. The spots were located and marked using Handheld Global Positioning System (GPS) (Trimble, USA). A total of 135 in situ radiation observations were obtained from the study area and the values lie between 74 and 13270 nGy h^{-1}. The average radiation field observed in villages is presented in Table 5-1. Survey data indicates the presence of radioactivity zones between Thengapattinam and Kanyakumari (Fig 5-1). High to very high radiation levels were recorded in certain pockets along the beach sectors. In an investigation by Singh et al., 2007, they have also indicated the presence of monazite deposits throughout the coastal line of Kerala and Tamil Nadu [15]. In their study, it has been shown that the beach sectors of Kanyakumari district have high radiation because of the high radioactive black sand deposits across the coastal belt.

There was a large variation in the observed radiation levels in these regions demonstrating that the placer deposits are not homogeneously distributed, and areas with low radiation levels intercalate with areas of high radiation levels.

Table 5-1: Natural radioactivity observed in the beach sectors as well as adjacent hinterlands

	Absorbed Dose Rate (nGy h^{-1})	**Range (nGy h^{-1})**	**Outdoor Effective Dose (mSv y^{-1})**	**Topographical regions**
Puttetti	505 ± 355	173-1204	0.62	Hinterland
Thengapattinam	334.3 ± 81	220-420	0.41	Beach Sector
Iniyam	371 ± 148	184-710	0.46	Beach Sector
Midalam	1450 ± 675	370-2300	1.78	Hinterland and Beach Sector
Kurumpanai	276 ± 93	149-430	0.34	Hinterland and Beach Sector
Kolachal	210 ± 75	113-340	0.26	Beach Sector
Manavalakurichi	1634 ± 341	891-1930	1.81	Hinterland
Manavalakurichi	9014 ±3004	4901-13270	11.1	Beach Sector
Kanyakumari	239±132	96-510	0.29	Hinterland and Beach Sector
Idindakarai	157± 39	74-216	0.19	Beach Sector
Kudankulam	189 ±78	79-330	0.23	Beach Sector

The highest dose rates were found in the beach sectors of Manvalakurichi village. Radiation field was higher in hinterlands of Manavalakurichi and it was lowest at Idindakarai village. Hence for sampling location, Manvalakurichi, Puttetti, Thengapattinam and Idindakarai were selected.

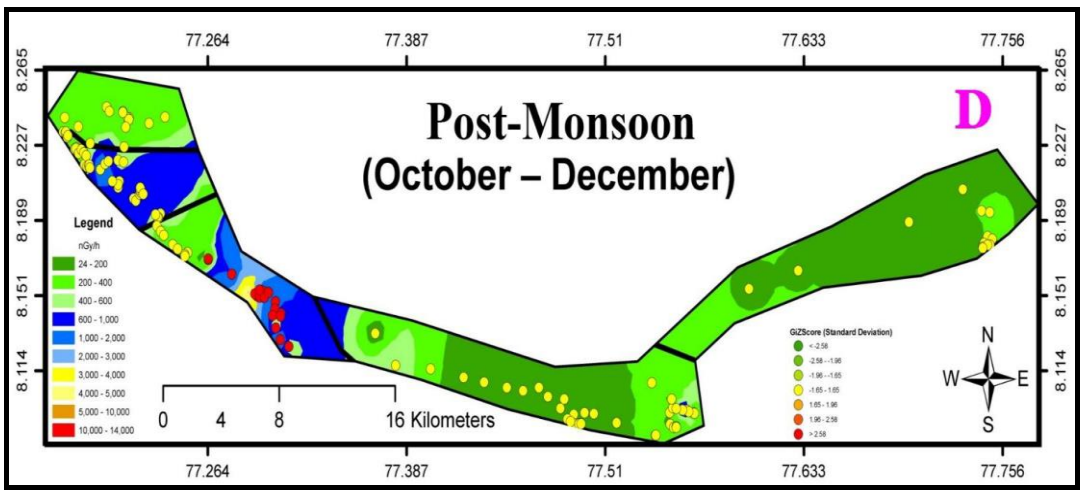


Figure 5-1: Spatial mapping of absorbed dose rate

The dose rates in the study region was higher when compared to the average value (58 $nGyh^{-1}$) reported for normal background areas of the world. The recorded dose rates were higher than the national average of outdoor natural gamma radiation levels (32nGy h^{-1}) in India [203]. A study conducted by Singh et al., have reported a higher levels of radiation fields in rock units of Puttetti synetitie compared to our observation [7].

5.3.2 Outdoor Committed Effective Dose

The annual effective dose for human was calculated from the outdoor terrestrial gamma radiation by radiometric survey using equation 3.12, is represented in Table 5-1 for the survey region.

The outdoor annual effective doses evaluated using the ground radiometric data ranged from 0.20 to 11.1 mSv y^{-1}. The annual effective dose in Manavalakurichi beach sector showed an average of 11.1 mSv y^{-1} which was the highest followed by Manvalakurichi hinterland. However all the villages in our survey showed above 0.07 mSv y^{-1} reported in UNSCEAR, (2000) for outdoor external terrestrial radiation [1]. The HBRA of Ramsar in Iran has an annual effective dose of 30 mSv y^{-1} which is 3-10 times higher than our values [204]. In Guarapuri, Brazil of south American continent, the annual effective dose is 5.5 mSv y^{-1}[205] and in Lambwe East, Kenya the yearly dose is 5.7 mSv y^{-1}[206] for African continent. In Nigeria of the same continent, the annual effective dose was reported to be in 8.7 mSv y^{-1}[207].

Based on the absorbed dose rate four villages namely Thengapattinam, Manvalakurichi, Putteti and Idindakarai, were selected for DPS methods. The absorbed dose rate was the least in Idindakarai and was chosen as control group for the DPS as the food habits and preparation methods were similar to the study group.

5.4 Recruitment of volunteers for DPS and evaluation of age dependent annual consumption rate

Preliminary survey was carried out in selected villages based on the ground radiometric survey. About 223 volunteers from 42 families belonging to various age groups were interviewed for DPS sample collection. The summary of the survey for selection of household is presented in Table 5-2. The age groups were classified into three categories : (a) children(4-11y), (b) adolescent(12-17y) and (c) adult.

Table 5-2: List of volunteers recruited for DPS and 24 hr diet record

Village	Subjects	Families/ Samples	Gender/Age Groups (y)					
			Male			Female		
			a	b	c	a	b	c
Puttetti	48	10	5	5	12	3	5	18
Thengapattinam	69	11	5	9	20	9	3	23
Manavalakurichi	49	11	5	6	17	3	4	14
Idindakarai	57	10	10	3	17	8	5	14

To collect data from the local population, a detailed questionnaire was prepared which includes questions on the socioeconomic related aspects of the families, the main components of their diet, the quantity and origin of foods consumed. 24-hour dietary record method, was used to evaluate the dietary intake estimate for different age groups. For this, while collecting 24-hour diet sample from an individual in a house hold, an additional questionnaire was filled and the food amount consumed in actuals from other members of the household was simultaneously recorded. The annual diet intake of each age group from the four selected village is presented in Table 5-3.

The highest consumption rate was found among the residence of Thengapattinam and the least was observed in Puttetti and Idindakarai.

Table 5-3: Annual intake rate (±1s) from 24h record method

	Annual Intake for DPS (kg y^{-1})		
	Children (4-11y)	**Adolescent (12-17 y)**	**Adults (>17 y)**
Puttetti	346 ± 62	467 ± 79	574 ± 96
Thengapattinam	703 ± 114	1113 ± 97	981 ± 139
Manavalakurichi	437 ± 91	583 ± 84	697 ± 103
Idindakarai	349 ± 91	407 ± 106	614 ± 133

According to marine fishery census 2005, the highest population involved in fishery in Tamilnadu is from Kanyakumari district [208]. Among the four villages considered in the study except for Thengapattinam, the main occupation of the population was fishery. Main occupation of the Idindakarai is fishery and the socioeconomic status is poor compared to other villages considered in the study. Thengapattinam has mixed population belonging to various religions and Muslims formed almost 40% of the population.

5.5 Activity concentration of ^{232}Th in DPS

Concentration of ^{232}Th in duplicate diets collected from four villages was estimated using INAA and are shown in Table 5-4. The basic statistic and normality test for the activity concentration in the samples (mBq kg^{-1}_{fresh}) was done using Minitab 18 and is presented in Fig. 5-2. The weighted average of ^{232}Th activity concentration in the Duplicate diet (DD) was 57.4 mBq $kg^{-1}_{fresh.}$

The data follows a normal distribution. P value >0.05 was obtained using Anderson Darling test for normality which indicates that the distribution of activity concentration in DD was normal. Anderson darling test for normality of individual villages was also analyzed using Minitab 18. The results indicated a normal distribution.

Table 5-4: Concentration of ^{232}Th (±1s)in diet samples

Location	Sample id	^{232}Th ($\mu g\ kg^{-1}_{Fresh)}$
Puttetti	Put-1	18.9 ± 0.6
	Put-2	11.3 ± 0.4
	Put-3	14.6 ± 0.5
	Put-4	14.4 ± 0.4
	Put-5	15.3 ± 0.5
	Put-6	10.2± 0.3
	Put-7	9.9 ± 0.2
	Put-8	14.3 ± 0.1
	Put-9	13.9 ± 0.6
Thengapattinam	Ten-1	17.8 ± 0.4
	Ten-2	19.5 ± 0.4
	Ten-3	8.1 ± 0.2
	Ten-4	8.9 ± 0.2
	Ten-5	13.6 ± 0.3
	Ten-6	19.1 ± 0.4
	Ten-7	19.5 ± 0.4
	Ten-8	10.7 ± 0.3
Manavalakurichi	Man-1	31.3 ± 0.9
	Man-2	18.5 ± 0.7
	Man-3	18.6 ± 0.7
	Man-4	17.5 ± 0.7
	Man-5	20.5 ±0.7
	Man-6	23.2 ± 0.7
	Man-7	25.5 ± 0.8
	Man-8	24.6 ± 0.7
Idindakarai	Idi-1	9.0 ± 0.1
	Idi-2	7.8 ± 0.1
	Idi-3	13.8± 0.2
	Idi-4	9.8± 0.1
	Idi-5	6.1±0.1
	Idi-6	8.2 ± 0.2
	Idi-7	13.4 ± 0.2
	Idi-8	4.1± 0.1
	Idi-9	7.6±0.1

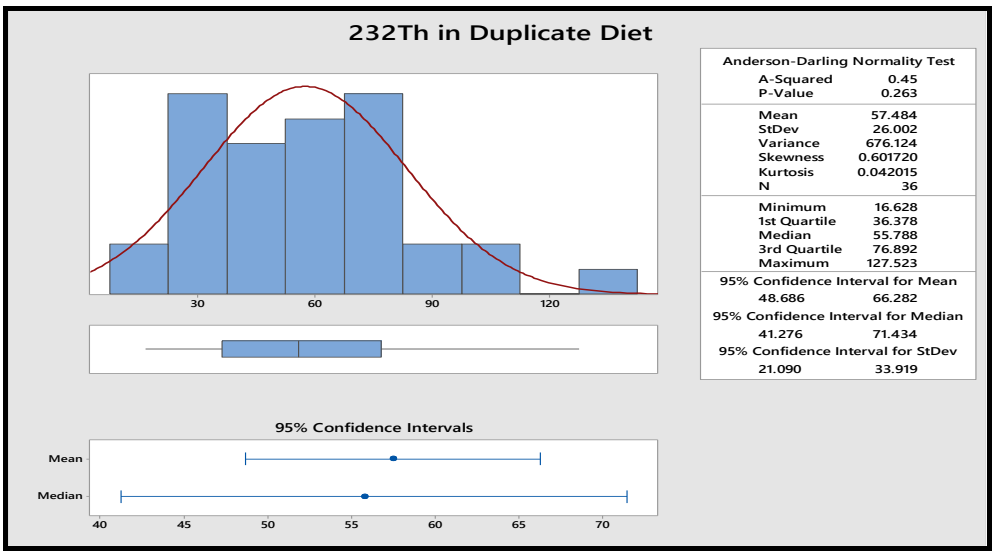


Figure 5-2: Summary of statistical analysis of ^{232}Th activity in duplicate diet

Table 5-5: Summary of ^{232}Th concentration in DDS in villages

Location	**Range (µg kg^{-1}$_{Fresh}$)**	**AM (µg kg^{-1}$_{Fresh}$)**	**SD (µg kg^{-1}$_{Fresh}$)**
Puttetti	9.9-19.9	13.4	2.9
Thengapattinam	8.1-19.5	*14.7*	4.9
Idindakarai	4.1-13.8	*8.3*	3.2
Manavalakurichi	17.5-31.3	22.5	4.7

Statistical cluster analysis, a form of multivariate analysis was conducted using the stats-graphic software package. The analysis was performed to evaluate the overall variation in the ^{232}Th in the DD with respect to villages.

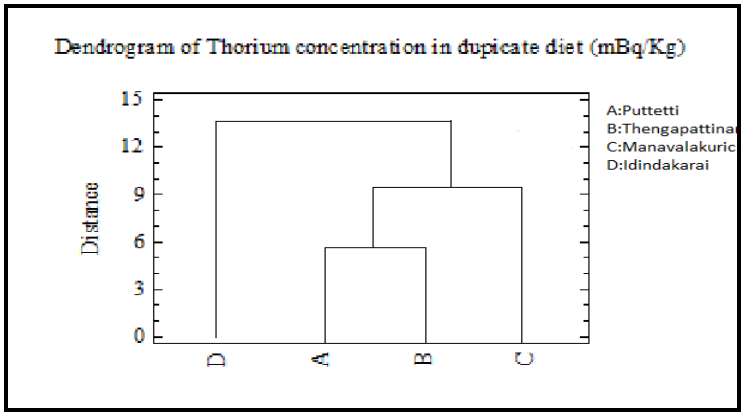


Figure 5-3: Dendrogram of cluster analysis of ^{232}Th concentration in duplicate diet for different villages

Using hierarchical cluster analysis (Fig. 5-3), it was observed that two main clusters were formed. The dendogram also shows a very distinct separation of the Idindakarai group, with all other villages and the group aggregates at a much lower level in the dendogram.

The highest concentration was found in DD collected from Manvalakurichi village (Table 5-5). This village had higher background radiation levels from the ground radiometric survey also. This variation in ^{232}Th content in the food may be due the food preparation methods. The village had a mixed population residing in concrete as well as thatched houses. People residing in the thatched houses cooked their food in open which could cause an extraneous addition of airborne soil activity to the food. Even in concrete houses, initial processing like washing and cutting is done at the backyard. Another observation made while collection of sample is that the certain food items like pulses, tapioca and tamarind were sundried in open during summer for preservation.

In a study conducted by Devajayanthi et al., ^{232}Th in cooked food, collected from ten villages located in the same area, was quantified using gamma spectrometry. They have reported that the activity concentration in the samples varied from 1.1 to 4.9 Bq kg^{-1}_{fresh} which is three orders higher than the values observed in this study. An average activity concentration of 25 mBq $kg^{-1}$was reported in Pakistani diet and is lower than the concentration evaluated in this study [209]. ^{232}Th in Korean total diet was also analyzed quantitatively using INAA by Chung et al., and they have reported a value of 1.3 mBq kg^{-1} which is much lower compared to the results in this study.

5.6 Daily intake of ^{232}Th by the population

The daily intake of ^{232}Th by three different age groups of the inhabitants of each village was evaluated using the average daily food consumption rate (Table 5-3) acquired using 24 h dietary record method and the average ^{232}Th activity in duplicate diet (DD) in respective village, is presented in the Table 5-6. The daily intake varied from 13.2 to 237.3 mBq d^{-1} with a geometric mean and standard deviation of 90.4 and 1.9 mBq d^{-1}, for adult population. The highest ingestion intake was observed among adult population residing in Manavalakurichi. The lowest was observed among children residing in Idindakarai village.

Table 5-6: Summary of daily intakes of thorium (in mBq) by inhabitants in various location

Location	Children (4-11y)	Adolescent (12-17 y)	Adults (>17 y)
Puttetti	51.7 ± 9.3	69.8 ± 11.9	85.7 ± 14.3
Thengapattinam	115.2 ± 18.7	182.4 ± 26.4	160.8 ± 21.8
Manavalakurichi	109.6 ± 21.8	146.3 ± 20.5	174.8 ± 25.3
Idindakarai	32.3 ± 8.8	37.7 ± 9.7	56.8 ± 9.7

Though the ^{232}Th concentration in DD collected from Thengapattinam was less compared to DD from Manvalakurichi, the daily intake by inhabitants of Thengapattinam is slightly higher compared to Manvalakurichi due to higher dietary consumption rate of food by Thengapattinam residents except in the case of adult population. In an earlier study, ^{232}Th intake by urban population residing in Mumbai was estimated using DPS by Dang et al., and have reported an activity concentration of 3.3-17.5 mBq d^{-1} with a mean of 9.1 mBq d^{-1} which is much lower than the values estimated in this study.

In another study by Dang et al., duplicate diet was collected from another monazite rich area, Chavara located in Kerala, India and ^{232}Th was evaluated in the diet and the

daily dietary intake of ^{232}Th varied from 35-253.9 mBq d^{-1} with a mean of 104 mBq d^{-1}which is higher than that observed in this study.

The intakes of thorium were studied in Greater Cairo Area using INAA (Akhter, Orfi, Kawamura, Ahmad, and Khaleeq-ur-Rahman, 2002). The highest daily intake was2.53 µg (10.3 mBq) and the lowest was 0.2 µg (0.8 mBq) which is very low compared to our results. The daily intake of thorium reported for New York residents by Fisenne et al. (1987) was 1µg (4.07 mBq), which is similar to the median of Greater Cairo Area intake value. A Japanese group, reported still lower daily intake of 1.7 mBq d^{-1} of thorium in their population. Thorium intake by this group was estimated on the basis of the analysis of duplicate diet. The daily dietary intake of ^{232}Th was estimated for Vietnamese adults using DPS. The daily intake of ^{232}Th in the DD varied from 0.7 to 23.3 mBq and is lower than that reported in the present study.

Table 5-7: Comparison of daily intake of thorium activity with the populations of other countries.

Country	**Daily intake (mBq d^{-1})**	**Method**	**Reference**
This study	**90.9**	**DPS**	
Bangladesh	21	MBS	Iyengar et al., 2004, [211]
China	22	MBS	Iyengar et al., 2004, [211]
Germany	4.1	DPS	Zingler et al., 2000, [212]
India	3.4	MBS	Dang et al., 2001, [177]
India (Kerala, HBRA)	104	DPS	Dang et al., 2000, [136]
India , Mumbai	9.1	DPS	Dang et al., 1986, [8]
Japan	2.7	MBS	Shiraishi et al., 2001, [92]
Japan	1.3	DPS	Shiraishi et al., 1992, [213]
Korea	2.7	TDS	Chung et al., 2002, [210]
NY, USA	4.1	DPS	Fisenne et al. 1987, [90]
Pakistan	10	MBS	Iyengar et al., 2004, [211]
Philippines	1.6	MBS	Iyengar et al., 2004, [211]
Poland	3.4	MBS	Pietrzak-Flis et al., 1997, [94]
Ukraine	4.4	DPS	Shiraishi et al. 1997, [45]
Vietnam	4.4	DPS	Giang et al., 2001, [214]
World wide	5.5	UNSCEAR 2000	

Duplicate diet samples were collected from adult male population from three different regions of Ukraine and ^{232}Th content was analyzed using ICP MS. The ^{232}Th daily intake varied from 0.37-10.5 mBq per person[210]. The comparison of thorium intake by the population in the study area with ICRP Reference Man value suggests that internal radiation dose from the ingestion of thorium incorporated in the diet is an order higher than what may be expected on the basis of an ICRP Reference Man intake value. A daily ^{232}Th intake in this study is compared with world values in Table 5-7.

The annual intake estimated by investigators who used gamma spectrometry for quantification of ^{232}Th in diet samples have reported a higher value.

5.7 Committed effective dose from annual intake of ^{232}Th by DPS

The weighted average annual effective ingestion dose to the adult using DPS was 7.7 μSv y^{-1}. A committed effective dose due to ingestion of ^{232}Th from duplicate diet consumed by the locals was also calculated and is shown in Table 5-8. The data shows that minimum radiation dose of 3.7 μSv is received by the population of Idindakarai and maximum radiation dose 14.3 μSv is received by the population of Manavalakurichi.

As expected the annual dose received by the adult population residing in Manavalakurichi is slightly high due to higher intake of ^{232}Th via diet. The dose received by the population is higher than the world average of 0.37 μSv. It can also be seen though the daily intake in children is less, the annual committed effective dose was high as the dose co-efficient for children is more compared to adolescent and adult group.

Table 5-8: Annual committed effective dose(μSv y^{-1}) of three age groups from intake of ^{232}Th

Location	Children (4-11y)	Adolescent (12-17 y)	Adults (>17 y)
Puttetti	6.4 ± 1.4	6.9 ± 1.4	7.4 ± 1.6
Thengapattinam	14.7 ± 2.9	15.3 ± 3.5	12.9 ± 2.8
Manavalakurichi	13.5 ± 2.8	13.0 ± 2.7	14.3 ± 2.1
Idindakarai	4.3 ± 0.6	3.4 ± 0.5	3.7 ± 1.1

It is interesting to note that the annual effective dose evaluated by DPS (7.7 μSv) using the weighted average of concentration activity in the DD samples, was higher than that was evaluated using MBS (3.4 μSv). The reason for the variation in the estimates may be because the in MBS the sample processing that included cleaning and cutting was done in a controlled environment in the laboratory whereas in DPS the sample processing involves only drying in the laboratory. Moreover, the raw materials, used by the household for preparation of food, are not cleaned thoroughly. It can be concluded that the daily dietary intake of ^{232}Th measured using DPS is more accurate compared to the MBS method.

The food consumption data used for evaluation of annual intake and dose for MBS method is based on the average consumption rate for a state. Whereas the annual consumption rate by individuals as observed using 24hr record method is a more accurate.

5.8 Thorium analysis using high resolution (HR) ICP MS in Water and Urine

Four drinking water samples (5 L) were collected from the households located across the village from the selected villages (Putteti, Thengapattinam and Manavalakurichi). 10 mL of conc. HNO_3 was added to the samples to prevent losses through microbial

activity and adsorption on the vessel walls. In case of urine, samples were collected from healthy individual volunteers belonging to two different villages in the study area, namely Putteti and Manavalakurichi. Care was taken not to include volunteers who had any history of previous occupational exposure. Volunteers were asked to collect total urine for 24 h under normal living habits in pre cleaned polyethylene bottles. 10 mL of conc. HNO_3 was added to the samples to avoid losses through microbial activity and adsorption on the vessel walls. The samples were spiked with ^{229}Th tracer. Thorium in the sample was co-precipitated with calcium phosphate precipitate. ^{232}Th was separated using an ion exchange procedure. The separated thorium was analyzed using HR ICP-MS. The radiochemical recovery of the procedure was determined using alpha spectrometry of ^{229}Th.

For quality control, trace Th determination was carried out using NIST SRMs: liquid Th reference standard (3159), spinach leaves (1570a) and orchard leaves (1571). Standard solution of thorium (10 ppm stock) was procured from SPEX Co. Ltd., USA, from which sub-solutions with concentrations 1, 10, 20, 30, 40 and 50 µg kg^{-1} were prepared for calibrating the instrument.

A sector field (SF) ICP MS, model Nu attom, manufactured by Nu instrument, UK was used to measure ^{232}Th in the samples. The sample eluent was diluted with deionized MilliQ water up to 10 mL and acidified to 2% HNO3. Prior to analysis, the instrument was optimized separately for ^{232}Th using 1 µg kg^{-1} solution, for nebulizer gas flow, flow rate, sensitivity, peak width, etc., and was allowed to stabilize. The samples were analyzed with sufficient washings in between to negate the memory of previous sample, and to obtain stable thorium peak representing the sample. Intensities in the form of counts per second (cps) were acquired for each sample which

were further treated with calibration plots for quantification by automated in-built processing software NuQuant®.

The detection limit L_D was determined according to the equation

$$L_D = \frac{3\sigma_b}{slope} \quad \textbf{(5.1)}$$

where σ_b represents the standard deviation of 10 blank measurements (cps) and slope is an equipment factor that relates the measured intensity of the ion to the element concentration in the solution. The detection limit was 0.006 ng L^{-1} for Th.

Because the response of the mass spectrometer in counts per second is directly proportional to the concentration of a given element in a sample, it is relatively easy to calibrate the system using the external standards of differing concentrations. Any sample entered into the mass spectrometer under exactly the same conditions will return a count rate, which can be converted directly to concentration for each element from a calibration curve.

Thorium concentrations were quantified from interpolating the intensities (cps) obtained for the samples on the calibration graphs using linear equation y = mx + c, where x is the concentration of thorium in µg kg^{-1}, y is the intensity, m is the slope and c is the intercept. Instrument was calibrated using 1, 10, 20, 30, 40 and 50 µg kg^{-1} Th solution prepared from stock solution., and a coefficient of correlation R^2 = 0.997 was obtained. The robustness of the calibration graph was validated using NIST SRMs and repeated analysis of 10 ng mL^{-1} of Th solution.

As there was no matrix matching reference material, precision and accuracy were calculated by repeated analysis of 10 µg kg^{-1} of the standard solution prepared from NIST reference standard solution and also using NIST SRMs.

The measured concentrations in NIST SRMs 3159, 1570a and 1571 in this work were in good agreement with the results are shown in Table 5-9.

Table 5-9: Thorium concentration in reference standard and biological standard reference materials (SRMs) from NIST

	Present work	**Certified value**	**U score**
Th standard sloution (3159) (ng L^{-1})	5.15 ± 0.1	5.0 ± 0.12	1.7
Spinach Leaves(1570a) (µg kg^{-1})	46.3 ± 1.4	48.0 ± 1.7	1.2
Orchard Leaves(1571) (µg kg^{-1})	63.1 ± 1.7	64 ± 6	0.5

The trueness of the proposed method was judged under the criterion of the u-test score using the Eq. 4.1. According to the accuracy test, our results were in agreement with the reference values for the thorium and showing good precision evaluated as the relative standard uncertainty.

Chemical recovery of the separation procedure was evaluated with ^{229}Th spiked to the samples. The absolute concentration of the ^{229}Th tracer in the column eluate was quantified using alpha spectrometry. The yield of electro-deposition was evaluated by preparing thin sources of known ^{229}Th activity concentration by electroplating on a stainless steel planchette. A typical spectrum of peaks of suitably separated thorium using ion exchange method is shown in Fig 5-4.

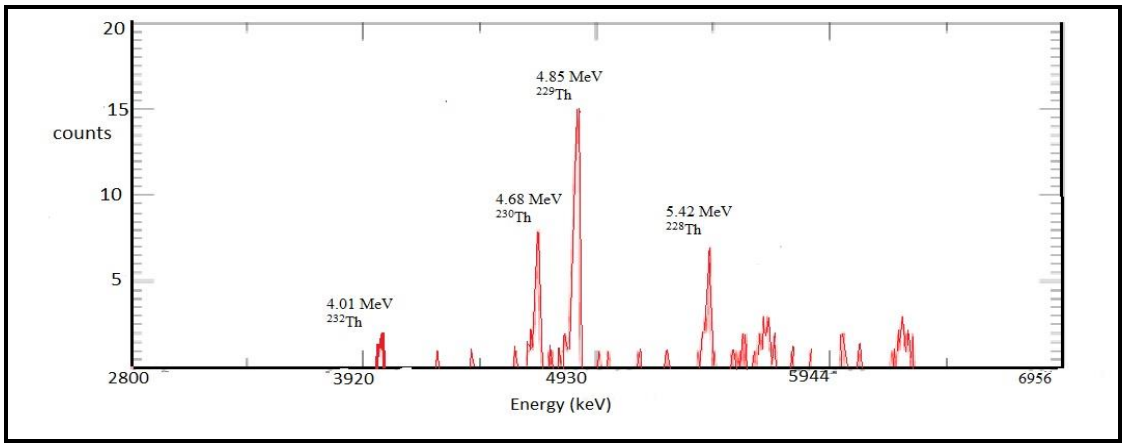


Figure 5-4: Typical alpha spectrum of radiochemically separated Th isotopes

Using this electro-deposition yield, activity of spiked ^{229}Th in the samples after successive co-precipitation and anion exchange column separation was calculated**.** The thorium chemical recovery varied from 89% to 93 %, with a mean of (92 ± 2) %. This average chemical recovery was applied for quantifying the ^{232}Th concentration in water and urine using SF-ICPMS.

5.8.1 Activity concentration of ^{232}Th in drinking water

Concentration of ^{232}Th in 12 water samples was determined using HR ICP MS after chemical separation. The concentration ranged from 2.4 to 18.3 ng L^{-1} and is presented in Table 5-10. The average concentration was 11.7 ± 4.9 ng L^{-1} (4.7×10^{-5} Bq L^{-1}). Value is similar to the international reference value of 5×10^{-5} Bq L^{-1}[1].

domestic bottled water samples, the concentrations ranged from 0.65 to 22.4 ng L^{-1}. Concentrations of ^{232}Th in imported bottled water ranged from 0.60 to 5.12 ng L^{-1}[93]. ^{232}Th was evaluated in drinking water samples of Buena, Brazil by Santos et al., and have reported a value ranging from 3.3- 4.9 x 10^{-5} Bq L^{-1}[215]. A higher concentration of 30 ng L^{1} and 100 ng L^{-1} was estimated in fresh water and river water respectively by Fuma et al., [216].

Table 5-10: ^{232}Th in drinking water, subsequent daily intake And annual effective dose

	^{232}Th (ng l^{-1})	***Intake rate (10^{-5}Bq d^{-1})***	***Dose (nSv y^{-1})***
Put1	2.4 ± 0.2	4.3 ± 0.4	3.6 ± 0.3
Put1	4.8 ± 0.3	8.8 ± 0.6	7.4 ± 0.5
Put1	8.9 ± 0.4	16.3 ± 0.7	13.7 ± 0.6
Put1	7.4 ± 0.3	13.5 ± 0.5	11.3 ± 0.5
Ten1	11.2 ± 0. 4	20.5 ± 0.7	17.2 ±0.6
Ten1	13.3 ± 0.5	24.3 ± 0.8	20.4 ± 0.8
Ten1	12.9 ± 0.6	23.7 ± 1.1	19.9 ± 0.9
Ten1	14.3 ± 0.7	26.3 ± 1.3	22.1 ±1.1
Man1	12.6 ± 0.5	23.1 ± 0.4	19.4 ± 0.8
Man1	11.8 ± 0.4	21.5 ± 0.9	18.1 ± 0.6
Man1	14.8 ± 0.5	27.1 ± 0.9	22.7 ± 0.8
Man1	18.3 ± 0.7	33.5 ± 1.3	28.1 ± 1.1

The lowest concentration was found in sample collected from Puttetti village and the highest concentration was obtained in water sample collected from Manavalakurichi village. Putteti is located in the hinterland and the radiometric survey also showed a lower exposure rate compared to the Manvalakurichi village. Another reason could be the extraneous contamination of water with micro sand particles in the water samples from beach sectors. Values for ^{232}Th in drinking water are scarce in the literature. Dang et al., estimated the ^{232}Th in water from Mumbai, India using RNAA and reported a concentration ranging from 0.7- 4 ng L^{-1} though low, is comparable to the levels observed in the study [8].

Shiraishi et al., have estimated the ^{232}Th content in water source from different resources namely drinking tap water, bottled water, and imported bottled water consumed by Japanese population using ICP MS. The concentration in drinking tap water ranged from 0.64 to 22.1 ng L^{-1} with arithmetic mean of 2.81 ng L^{1}. For The concentration of thorium in water samples collected from a reported HBRA in Malaysia was estimated using NAA and the estimated mean activity concentration of thorium in all water samples was 2.5 mBq L^{-1} which is much higher than the values observed in our study.

Fisenne et al., estimated the ^{232}Th in drinking water using alpha spectrometry in 50L of water and have reported an average concentration of 0.05 mBq l^{-1} which is comparable to the values observed in this study [91] . It was reported that thorium concentrations in groundwater in Austria, ranged from 0.05- 0.11 mBq L^{-1}[217].

^{232}Th in natural water Romania was estimated using gamma spectrometry as 8.3 mBq L^{-1} which is very high compared to results observed in this study.

The activity concentrations in the drinking water samples collected in Italy had a big variation and were in the range of 0.0007–0.0027 mBq L^{-1} for ^{232}Th, 0.0008–0.0053 mBq L^{-1} for ^{230}Th and 0.0014–1.32 mBq L^{-1} for ^{228}Th. The ^{230}Th/^{232}Th and ^{228}Th/^{232}Th ratios were in the range of 0.57–3.9 and 1.06–717, respectively. Above results indicated that the activity concentrations of ^{232}Th and ^{230}Th are almost similar but very low compared with that of ^{234}U, ^{238}U, ^{226}Ra, ^{228}Ra and ^{210}Po. They also have demonstrated that ^{228}Th concentration is much higher than ^{232}Th and ^{230}Th with an average ^{228}Th/^{232}Th ratio of 153 ± 192 which is a clear indication of disequilibrium between ^{228}Th and ^{232}Th [16].The authors have also clearly interpreted the reason for disequilibrium. The transport and removal rate of thorium in water is primarily controlled by the sediment re-suspension rate, mixing rate of the particle flux, the concentration of iron and manganese compounds in water, etc. The residence times for thorium with respect to removal by adsorption onto particles were reported to be short and may vary from 1 to 70 d [218]. If ^{228}Th is in equilibrium with ^{232}Th, activity of ^{232}Th and ^{228}Th should be similar. But the excess ^{228}Th in water is from the decay product of ^{228}Ra which exists in much higher concentration in water than its parent ^{232}Th due to higher solubility of radium. Therefore, the higher activity concentrations of ^{228}Th than ^{232}Th in water samples could be explained as there is new contribution from ^{228}Ra decay in water and removal of ^{228}Th from the water samples through suspended matter adsorption could be retarded. The higher concentration of Radium can be explained by the difference in solid–liquid distribution coefficients (K_d) for Th and Ra that results in differential mobility [16].

^{232}Th in mineral water was estimated using gamma spectrometry by many investigators. Amrani et al., in a study had evaluated ^{232}Th in Algerian drinking water

by measuring energy peaks of 911.2 keV from ^{228}Ac and have reported that activity of ^{232}Th ranged from 14 to 53 mBq. l $^{-1}$ with a mean value of 30 mBq. l $^{-1}$ [219]. In another study Olomo et al., have estimated ^{232}Th in Nigerian water using 583 keV gamma line of ^{208}Tl and reported that ^{232}Th ranged from 1 .9-4.1 Bq L^{-1} with a mean of 3.8 ± 1.3 Bq L^{-1} for surface water and those for drinking water ranged from 2.0-4 .6 Bq L^{-1} with a mean value of 3.4 ± 1.2 Bq L^{-1} [220].

The results obtained by Olomo and Amrani clearly indicate that gamma spectrometry cannot be used to determine ^{232}Th drinking water. Due to the reason explained in the above section, there is a disequilibrium between the parent and the subsequent decay products in the environment. Hence using gamma spectrometry for quantifying ^{232}Th in drinking water results in higher values and there from dose is overestimated.

The daily intake of ^{232}Th from drinking water was evaluated using a water consumption rate estimate of 3.6 l d^{-1} of for adult population [221]. The daily intake varied from 0.04 to 0.34 mBq d^{-1}. The annual effective dose due to intake of water varied from 3.6 to 28.1 nSv y^{-1} with average of 13.6 ± 0.6 nSv y^{-1}.

ICP MS is an effective method for determination of ^{232}Th in water samples even in a sample volume as low as 5 L compared to the samples volume of 50-100 L required for alpha spectrometry.

5.8.2 ^{232}Th daily urinary excretion

The daily excretion of ^{232}Th in the urine samples varied from 13.9 ± 0.18 to 197.1 ± 2.21 μBq d^{-1} with a mean value of 63.9 ± 8.7 μBq d^{-1}. Table 5-11 summarizes the daily urinary excretion data obtained in this study for population residing at Puttetti and Manavalakurichi regions.

Table 5-11: Range and average excretion (μBq d^{-1}) of thorium in urine

	Putteti			**Manvalakurichi**		
Age Group	0-17	17-60	>60	0-17	17-60	>60
No of subjects	4	5	2	6	6	3
Range	13.9-35.2	36.1-110.5	106.5-150.3	17.3-42.5	14.5-46.8	157.3-197.1
Geometric Mean	25.6	58.9	126.5	30.1	54.9	
Arithmetic Mean of the Total Subject				61.4 ± 38.1		
Geometric Mean of the total Subject				44.5		

Sunta et al., have investigated to measure the urinary excretion of thorium from three groups of persons, namely1) members of general public 2) office staff of thorium plant 3) occupational worker with 5-10 y service and 4) workers with 15-30 y service and reported a geometric mean of 3.5, 67.2, 339.8 and 371.9 μBq d^{-1} respectively [158].

The thorium excretion in the study area is slightly higher than that reported for an urban population with normal background radiation. The excretion rate is much less compared to occupational workers. The thorium excretion in the present study is much less compared to the excretion observed in Jordan population. They have reported a thorium removal in the urine of the unexposed subjects from 1.4 to 640 μBq d^{-1} with total average of 34.8 ± 11.4 μBq d^{-1}.

Table 5-12: Comparison of ^{232}Th urinary excretion rate (ng d^{-1})

Country	**No of samples**	**Range**	**Mean value**	**Method**
Russia [222]	-	-	105	NAA
India[223]	11	1.6-6.1	3.6	NAA
Australia [224]	5	12.6-28	12.6	NAA
Germany [225]	7	3.2- 12.4	-	α-spectrometry
Germany [226]	55	4.1-30	6.3	ICP MS
Germany[227]	31	0.44-5.76	0.39	ICP MS
Jordan [228]	60	1.3-157.2	8.6	ICP MS
Present Study	26	3.4-48.5	15.7	ICP MS

In another study conducted by Roth et al., for unexposed German population, the excretion ranged from 1.6 to 23.6 μBq d^{-1}. Table 5-12, compares the daily urinary excretion values of ^{232}Th (ng d^{-1}) obtained in the present study with report literature data. There is no significant variation in excretion rates between male and female subjects. Fig 5-5 gives the spread of daily ^{232}Th excretion with age. The average values were found to be proportional with age.

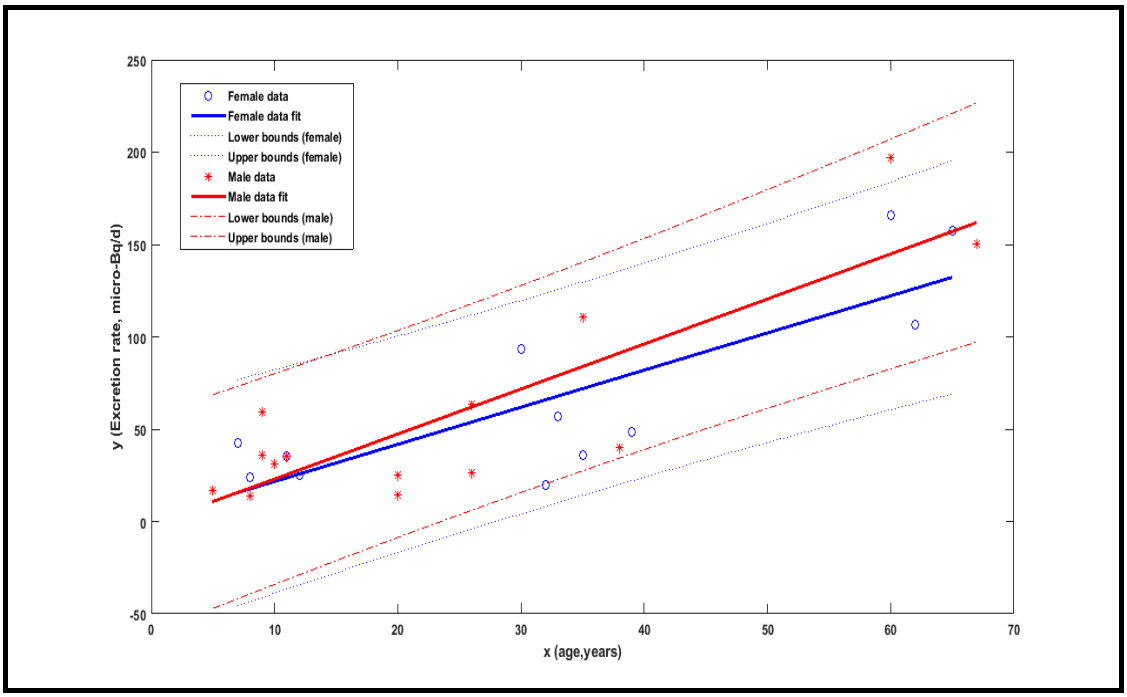


Figure 5-5: ^{232}Th excretion in 24 h urine as funtion of age

The increase in Th excretion with age can be related to accumulation of ingested thorium in bone. The excretion in urine for thorium is from the clearance of it from skeleton and other organs and soft tissue and from daily intake through diet. According ICRP Thorium biokinetic model, 70 % of thorium that enters the blood is transferred to bone. The thorium content in the bone increases with age and also the removal half-life of thorium from bone is 46 years. Hence as the age increases, there

is a steady removal of the accumulated thorium from bone into blood and hence more excretion.

There is an inter-individual variation of urinary thorium excretion at higher ages. As the individuals belong to the same study area, there is no geographical difference that can contribute to the variation. Instead the variation can be due to the change in dietary habits and differences in individual metabolism.

5.9 Comparison of annual effective dose from other radionuclides through external and internal exposure pathways received by inhabitants

The annual effective dose equivalent due to the inhalation of radon, thoron and progeny to the population of coastal Tamilnadu was calculated by Devajayanthi et al. and reported that the dose level varied from 2.59 to 8.76 mSv y^{-1} with an arithmetic mean of 4.72 mSv y^{-1}[25]. The authors have also evaluated the external dose due to gamma exposure using TLD and have reported a dose ranging from 1.2-4.8 mSv y^{-1}.

The exposure rate was measured using scintillometer by another group of researchers and showed radiation field ranging from 0.40 to 19.00 μGy h^{-1}. They have reported a similar external dose ranging from 1.2 to 5.8 mSv y^{-1}. The total dose (the internal: inhalation and external) estimated for the villagers residing in the NHBRAS, ranged from 4.47 to 8.38 mSv y^{-1} [30]. Sarojini et al., have studied the concentration of ^{226}Ra, ^{228}Ra and ^{232}Th in soil using gamma spectrometry and evaluated the external dose using the concentration of radionuclides in the soil. The annual effective dose ranged from 0.94 to 2.23 mSv y^{-1} [130]. High volume air Sampler with Whatmann 2000 special grade glass fibre micro-filter paper was used to collect particulates in the

ambient air of sampling station and were analyzed in a nuclear counter for gross alpha concentration in the air by Mini et al., and reported a dose of 0.07-0.8 mSv y^{-1} [229]. Lunch (food) samples were collected by Devajayanthi et al., and analyzed by means of gamma ray spectrometry to measure the activity concentration of ^{228}Ra, ^{40}K, ^{228}Th and ^{238}U. The daily intake of ^{228}Ra, ^{40}K, ^{226}Ra and ^{238}U activity ranged from 1.34 to 2.98 Bq kg^{-1}_{fresh}, 27.7 to 88.7 Bq kg^{-1}_{fresh}, 5.4 to 11.3 Bq kg^{-1}_{fresh} and 2.05 to 4.94 Bq kg^{-1}_{fresh}, respectively. Considering a daily consumption rate of 958 g d^{-1}, the authors have evaluated the annual effective dose received by the individuals to range from between 0.79 and 1.73 mSv y^{-1} [133].

^{210}Po was also estimated in diet samples collected in this study area and the mean activity was found to vary from 74 to 38 mBq kg^{-1}_{fresh}. The ingestion dose estimated for three different age groups for adults, adolescents and children in this region was 52, 53 and 109 μSv y^{-1}, respectively which is higher compared to the ingestion dose from ^{232}Th intake [6]. 7.7, 7.5 and 6.7 μSv y^{-1} annual effective dose was evaluated due to ^{232}Th intake for adults, adolescents and children respectively using an average food consumption rate of 585, 451 and 335 kg y^{-1} for adults, adolescents and children in this study.

Total dose received by the population residing in the study area both by external and internal (ingestion and inhalation) pathways, estimated using the data available in the literature from all NORMs, varied from 4.6 to 12.1 mSv y^{-1}. Though the ingestion dose from ^{232}Th evaluated in this study was higher compared to that reported by other regions of India, the contribution to the total dose is insignificant compared to total dose received by an individual from different sources.

CHAPTER 6

CONCLUSIONS AND FUTURE OUTLOOK

6.1 Conclusions

The main objective of this thesis work was to evaluate the ingestion intake of ^{232}Th and assessment of annual committed effective dose received by population residing in a naturally high background radiation area (HBRA) of Tamilnadu, India. Food materials and total diet (duplicate diet) samples were collected using standard protocols, stored for analysis by INAA method for low level Th (^{232}Th) concentration determination. INAA method using high flux reactor neutrons from CIRUS/Dhruva research reactor and high resolution gamma-ray spectrometry was optimized for ultra-trace (ng or below) determination of thorium in biological/food matrices utilizing daughter product of ^{233}Th: ^{233}Pa (half-life 27. 7 d, 312 keV gamma-ray). Method has been validated using synthetic samples as well as SRMs from NIST. As there is difficulty in irradiation of liquid samples for INAA, ICP-MS method was utilized for sub-trace Th concentrations in drinking water and urine samples from same area. Age dependent average annual intake and effective ingestion dose values were evaluated using both Market Basket Study (MBS) and Duplicate Portion Study (DPS) methods. Major contributors to dietary ^{232}Th intakes in the study group were found to be marine products and the lowest contribution was from obtained from fruits. It was observed that though the intake is slightly higher compared to another study conducted for evaluation of daily intake by an urban population, the contribution to total annual dose to the individual is insignificant from ingestion intake.

The activity concentration in dietary components in MBS was estimated using INAA and the concentration ranged from 0.2 to 550.3 mBq kg^{-1}_{fresh}. The highest was found in curated fish and the lowest in tomato. Vegetables (brinjal, plantain and drumstick) that were grown locally had higher concentration than those that were brought into the

market from other regions. Roots and tubers had the highest concentration in plant origin food items followed by green leafy vegetables. Where as in animal origin food items, concentration in the marine food is the highest. The highest contributor to daily intake was from curated fish, roots and tubers and rice in case of adult population. Whereas in children belonging to age group of 1-3 y, milk was found to be the highest contributor for Th. The total annual ingestion dose from ^{232}Th using MBS for adult was 3.4 μSv y^{-1}.

The radiation field survey demonstrated that the external radiation levels were higher along the beach sector compared to the hinterland. As established by previous works, the monazite is not present uniformly along the shore but occur in pockets. The highest external radiation dose was evaluated as 11.7 mSv y^{-1} in Manavalakurichi beach sector.

^{232}Th in duplicate diet (DD) was estimated from 24h diet samples collected from the selected villages. The concentration varied from 16.6 to 127.5 mBq kg^{-1}_{fresh} with a median of 60.33 mBq kg^{-1}_{fresh}. The highest concentration was found in DD of Manavalakurichi. The daily intake of ^{232}Th for adult population varied from 13 to 240 mBq d^{-1}. Annual effective dose from ingestion of ^{232}Th evaluated for adult men using DPS method was 7.7 μSv y^{-1}.

^{232}Th in consumable water samples collected from households in the study area was measured using ICP-MS. The concentration ranged from 2.4 to 18.3 ng L^{-1}. The dose received by adult population considering a daily water consumption estimate of 3.6 L varied from 3.6 to 28.1 nSv y^{-1} with average of 13.6 ± 0.6 nSv y^{-1}.

Another interesting observation is that annual effective dose evaluated using DPS method was higher than that evaluated using MBS. This indicates that DPS is a

preferred method for realistic biokinetic studies and MBS method gives us the indication of individual major contributor to the dose.

The results of this study will supplement to background data on terrestrial radioisotopes in this region and will also provide to evaluate the gut absorption fraction of thorium for Indian population. The evaluated ingestion intake of Th from food and diet will be helpful to assess the gut absorption fraction F_A. Due to lack of adequate data on ^{232}Th concentration in individual dietary components from normal background areas of India, our results couldn't be compared. Hence it was thus important to estimate ^{232}Th concentration in dietary component from different normal background areas of India, which will be treated as the base or control values. As the contribution to the total dose by ingestion pathway is very less, it can be concluded that the mining activities in the study area may not have influenced the ingestion dose.

Within the framework of the thesis work, it was demonstrated that INAA and ICP MS are powerful analytical methods of choice for the determination of Th (^{232}Th) at very low concentrations. The application of separation and co-precipitation techniques have shown to be adequate in order to access the extremely low concentration of ^{232}Th in drinking water and urine.

6.2 Scope for future work

Low level thorium determination using INAA and high resolution gamma-ray spectrometry is still a challenge and application of Compton suppressed anti-coincidence gamma-ray spectrometry is recommended for ultra-trace Th determination using high neutron flux irradiation of sample. Samples (food/diet) should be dried, ashed (so no moisture content) and then irradiation in high neutron flux for even 7 h for determining low concentrations of Th without any chemical

dissolution/separation. The study should aim at determining ingestion dose by calculating F_A from quantified ^{232}Th concentration, which was objective of the thesis when it was conceived. In this study, ^{232}Th in water and urine was measured by destructive method using ICP MS. Method can be standardised for determination of ^{232}Th in these matrix directly without any chemical separation using dilute and shot procedure, thereby reducing sample analysis time. The activity of other radionuclides mainly polonium, radium and ^{222}Rn needs to be measured in the underground drinking water and in tap water given by the municipality water supply as there are no reported detailed study. The ^{232}Th soil content in the study area is high and it was also observed that ^{232}Th in locally grown vegetables was higher, hence it is necessary to initiate studies on the factors influencing the transfer factor for uptake of plants. The important contribution to ^{232}Th ingestion dose to the inhabitants is from consumption of curated fish. As no information is available for consumption rate of curated fish, consumption rate of fish was used to evaluate the annual dose from ingestion. Hence it is necessary to determine the consumption rate of curated fish. Activity concentration of NORM is not available in curated fish which needs to be addressed to. The external and internal doses can be reduced by removing the monazite content present in the soil by mineral separation; which can be confirmed by estimation of NORM in food and water samples periodically to study the influence of mining in this region to build confidence among the residence. To have complete idea about dose due to inhalation, estimation of concentration of ^{232}Th in the air is necessary because air is least studied in Indian scenario. In order to have the idea about the effective 232Th in the body at any time, it is necessary to know the intake as well as loss through excretion (urine and fecal samples). In this way the contribution to total dose from

^{232}Th via inhalation can also be evaluated. The ^{232}Th ingestion data are also important from biokinetic point of view, in which inhabitants in the study area are chronically exposed to enhanced natural radiation hence serve a suitable group for study of behaviour of NORM in human body. The daily excretion rate of ^{232}Th via faeces can be used to assess the gut absorption fraction F_A with the dietary intake data generated in this study. Further body burden and organ retention fraction are necessary to be evaluated by quantifying ^{232}Th contents in various organ/tissue from accidental cadavers (inhabitant of this region) and the intake data from this study. Thorium ingestion data and related studies would be important input for our future departmental program towards thorium utilization in nuclear technology.

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