MEASUREMENTS OF HEAVY METALS AND NATURAL RADIOACTIVITY LEVELS IN SOILS AROUND THE TITANIUM MINING SITE IN KWALE DISTRICT

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Declaration

This is my original work and has not been presented in support of award of any degree or qualification of the University of Nairobi or any other University.

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List of Important Abbreviations

ADC	-	Analog Digital Converter
AQCS	-	Analytical Quality Control services
AXIL	-	Analysis Of X-Rays Using Iterative Least Square Method
BDL	-	Below Detection Limit
CES	-	Coastal Environmental Services
EDXRF	-	Energy Dispersive X-Ray Fluorescence
FWHM	-	Full Wave at Half Maximum
GANAAS	-	Gamma, Activity and Neutron Activation Analysis Software
Ge(Li)	-	Germanium-Lithium Drifted
GIS	-	Geographical Information System
HPGe	-	High Purity Germanium
IAEA	-	International Atomic Energy Agency
ICRP	-	International Commission on Radiological Protection
ICRU	-	International Commission on Radiological Units and Measurements
ILO	-	International Labour Organization
JICA	-	Japanese International Co-Operation Agency
KeV	-	Kilo Electron-Volt
LLD	-	Lowest Limit of Detection
MCA	-	Multi-Channel Analyzer
MDA	-	Minimal Detectable Activity
MPD	-	Maximum Permissible Dose
NCRP	-	National Council on Radiation Protection
NORM	-	Naturally Occurring Radioactive Material
NSRA	-	Nuclear Safety Research Association
QXAS	-	Quantitative X-Ray Analysis System
Si(Li)	-	Silicon-Lithium Drifted
SIPRI	-	Stockholm International Peace Research Institute
SRM	-	Standard Reference Material

TRMC	-	Taiwan Radiation Monitoring Center
UNSCEAR	-	United Nations Scientific Committee on the Effects of Atomic Radiation
WHO	-	World Health Organization

Abstract

This study was initially formulated specifically to provide data of radioactivity and elemental content of soils from two regions; Nguluku and Maumba, in Kwale District, that are earmarked for Titanium mining project. However, while radioactivity levels for both Nguluku and Maumba regions were assessed; elemental analysis for heavy metals was only carried out for Maumba. A total number of fifty samples were analyzed for heavy metals using energy dispersive x-ray fluorescence (EDXRF) system which consists of a radioisotope cadmium-109 source and a silicon-lithium drifted (Si(Li)) detector. Radioactivity levels of the samples were determined using a high purity germanium (HPGe) detector.

Iron and titanium were observed as the major elemental constituents of the Maumba soils with concentration levels of 1.21% and 1.57%, respectively. Zirconium and manganese levels were also found to be high, with mean levels of 1193.3 μg/g and 822.2 μg/g respectively. Niobium concentration level was found to vary between (13.77 - 79.24) μg/g with a mean of 31.81 μg/g in these samples. These levels were found to be lower than those reported earlier for Mrima Hill soil samples. Concentrations distribution of titanium and zirconium in the samples were found to have a strong correlation of r=0.97.

Activity concentrations of the three major primordial radionuclides – thorium-232, uranium-238 and potassium-40 – in the fifty samples from Maumba and seven samples from Nguluku were assessed. High contributions from Th-232 and U-238 determined as 72.0 and 50.2 Bq/kg in Maumba and 178 and 162 Bq/kg in Nguluku soil samples. These levels are much higher than the world average of 25 Bq/kg. Contribution from K-40 was found to be negligible in all the samples analysed.

Elemental concentrations of titanium, iron, zirconium and niobium were found to correlate significantly with the activity concentration levels of radionuclides in the Th-232 and U-238 series.

Using an occupancy factor of 0.2, annual effective dose to an adult due to gamma rays, in air 1 m above the ground was estimated to be 156 μSv in Nguluku. This level exceeds the world average effective dose (< 70 μSv) by a factor of two. Results for Maumba samples have been presented for three sub-regions – Miembeni, Maumba Central and Maumba ya Chini. The annual effective dose levels for the three sub-regions are 84, 44 and 23 μSv respectively.

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Chapter 1

Introduction

1.0 Background

Naturally occurring radioactive materials (NORMs), under certain conditions, can reach radiologically hazardous levels. The natural radioactivity in soil comes mainly from the radionuclides in the U-238 and Th-232 series, and K-40. The radiological implication of these radionuclides is external radiation exposure by gamma rays and internal exposure due to inhalation of radon and its daughters. (UNSCEAR, 1988).

Measurements of radiation exposure by gamma rays from NORMs, and consequently the determination of the respective dose rate are needed to implement radiation safety measures. Over time, the exposure of human beings to natural sources of radiation have been carefully evaluated and constitutes about 80% of the dose received by an average person (WHO, 1972).

According to UNSCEAR report (1993), the tendency towards an increase in radioactivity at the global level must be closely monitored. This is particularly important in connection with the disposal of radioactive wastes into the sea and elsewhere in isolated areas and also from the peaceful use of nuclear energy development. The development of nuclear technology for national defense and generation of power, and the applications of radionuclides in medicine, industrial research, and consumer products result in the release of radioactive material into the environment. Other activities that have led to increase in radioactivity in the environment include production of non-nuclear fuels such as coal, oil

and gas; production of industrial minerals like phosphate and clay materials and also failures in the waste containment systems (IAEA, 2003). Testing of nuclear weapons, including the use of depleted uranium, has also led to widespread radioactive contamination in the environment.

Monitoring of radiation is done both on global or national scale, and on local scale around installations such as nuclear plants or research institutions. According to WHO (1972), environmental radiation monitoring systems were first organized in a number of countries to monitor radiation fallout from nuclear weapon tests. At a later stage, these systems were developed to monitor the radiation levels around nuclear installations, nuclear power stations and research reactors. In the recent past, monitoring has also been extended to non-nuclear industries involving natural radioactivity (Botezatu *et al,* 1999) such as mineral mining and processing plants. Originally, these monitoring systems were under the responsibility of national atomic energy commissions, and it was only later that public health authorities in some countries became involved in the monitoring of radioactivity levels in the environment (WHO, 1972).

Processing of earth minerals for economic purposes may expose miners and the general public to additional natural radiation exposure when these minerals, or their by-products, contain above-average concentration levels of naturally occurring radionuclides. According to UNSCEAR report (2000), very little information is available to assess these additional exposures and hence the related exposure dose estimates are highly uncertain

.1 Natural Source of Ionising Radiation

The main natural sources of ionizing radiation are extra-terrestrial; comprising cosmic radiation and cosmogenic radionuclides, and terrestrial radiation due to the primordial radionuclides (SIPRI, 1981). The exposures from these sources vary very slightly with time. The magnitude of exposures to cosmic is largely dependent on the geographical location and altitude. For instance, the higher the altitude, the higher the exposure. Cosmogenic radionuclides are those formed as a result of interaction of the primary cosmic ray with earth's atmospheric elements. Examples are C-14, H-3 and Be-7. Primordial radionuclides are those that are thought to have occurred since the creation of the earth. They include U-235, U-238, Th-232, and K-40. These are often characterized by long half-lives in the order of hundreds of thousands of years.

The other category of exposures is the technologically enhanced natural exposure. These are exposures to natural sources of radiation that are caused by human activities. Examples of technologically enhanced exposures include exposures to cosmic radiation during air and space travels. For example, at 10 km height, aircraft crews and frequent travellers are subjected to 1 to 2.5 μSv/h near the equator and 4 to 6 μSv/h above 50^0N (Kraus and Kendall, 1999). Additional cases of enhanced exposures include mining activities in phosphate industry, processing of monazite sands for rare earths extraction, oil and gas industry and coal-fired work stations.

.2 Ionizing Radiation

Ionizing radiation may be divided into two main groups: the electromagnetic radiation (x-rays and gamma rays) and the corpuscular radiation, some of which (alpha particles, beta particles, and protons) are electrically charged whereas others (neutrons) have no electric charge. The corpuscular or the particulate type may be regarded as projectiles whose energy is greater than that binding the atoms in chemical compounds. They are thus capable of breaking chemical bonds and dividing the electrically neutral molecules into positively and negatively charged ions.

When x-rays and gamma rays are absorbed, high-energy electrons are released in the irradiated materials, and it is these electrically charged particles that are the effective ionizing agents. The action of the neutrons is more complex. When they collide with the nuclei of hydrogen atoms, these nuclei (or protons) are set in motion and produce ionization. Neutrons may also enter the atomic nuclei, causing such instability that the atoms themselves disintegrate and emit radiation that, in turn, produces ionization. Mechanisms of radiation interaction with matter are discussed in details by Knoll (Knoll, 1979). The common characteristic of all the types of radiation, whether electromagnetic or corpuscular, is that charged particles are produced and are responsible for the ionization effects they ultimately produce.

The biological effects of these types of radiation, which are related to the ionization that they are capable of producing in living tissue, are essentially similar. However, the distribution of damage they cause in the body will vary according to the type, energy and

penetrating power of the radiation involved. According to IAEA report (1974), alpha particles, for example, have ranges of only about 0.01 to 0.07 mm in soft tissue and less in bone. Beta particles have ranges in soft tissues of the order of several millimetres, that is, much greater than those of alpha particles in such tissues.

In human beings, radiation exposure may cause such diseases as blood cancer and may also cause somatic and genetic effects. In the somatic effects, the victim carries the hazard whereas in the case of genetic effects, it is the offsprings of the irradiated victim, or the future descendants that may suffer the consequences. To avoid such negative effects, various organizations worldwide have come up with standards on radiation safety guidelines. Among them are: International Commission on Radiological Protection (ICRP), International Atomic Energy Agency (IAEA), International Labour Organization (ILO), International Commission on Radiological Units and Measurements (ICRU) and the United States' National Council on Radiation Protection and Measurements (NCRP). These organisations recommend that the guidelines they produce may be adopted or improved on by national regulatory organisations. As such, practically all countries have such organisations; in Kenya, the Radiation Protection Board is the organisation responsible for matters relating to radiation uses, monitoring and protection.

1.3 Monitoring of Natural Radiation

As a result of effects from ionizing radiation on human beings, monitoring of natural radiation has been a concern of the scientific community for several decades. The oldest of the scientific organisations in this area is the International Commission on

Radiological Protection (ICRP) formed in 1928. ICRP has maintained continuous studies in radiation monitoring and protection problems that are of special relevance to the radiation control programs. UNSCEAR, established 1955, presents to the United Nations General Assembly, and thereby to the world community, its latest evaluation of the sources of ionizing radiation and effects of its exposures. IAEA was set up in 1957 within the United Nations family as the world's center of cooperation in the nuclear field to promote safe, secure and peaceful nuclear technologies. IAEA, in its part, while responding to the needs of its member states, recently launched an environmental remediation project dealing with problems of radioactive contamination worldwide (IAEA, 2006b). Its aim is to collate and disseminate information concerning the key problem affecting the environment and remediation of contaminated sites.

The techniques employed globally in radiation monitoring include periodic physical examinations and estimation of internally deposited radioactivity by bioassay and total body counting. Personnel monitoring, radiation and contamination surveys, and continuous environmental monitoring are other approaches utilised in radiation monitoring.

1.4 Monitoring of Radioactivity in Kenya

Over time, various surveys to monitor the levels of radioactivity have been carried out in Kenya by researchers in the universities and also by the Radiation Protection Board. In the year 2000, a South African private firm, contracted by Tiomin (Kenya) to do an

environmental impact assessment of the proposed Titanium mining area reported on the radioactivity levels (CES, 2000).

Mangala (1987) reported that the high radiation levels at Mrima Hill, about 60 Km Southeast of the Mombasa Island and about 30 Km South of Kwale Township, was due to occurrence of thorium and uranium. Titanium was also reported as one of the major constituents in rocks samples from Mrima Hill; its concentrations were observed to be in the range of 1- 9% with a mean value of 4.7% for most samples analysed.

Mustapha (Mustapha, 1999) and Mustapha *et al* (1999*)* carried out an assessment of human exposures to natural radiation in Kenya, mainly in Nairobi, Kiambu, Kwale Mombasa, Machakos, Bungoma and Trans Nzoia, and reported an average effective dose of 3.79 $mSv.y^{-1}$. This value is above the world average of 2.4 $mSv.y^{-1}$ and therefore dictates further assessments of even smaller regions of the studied areas.

The Kenyan coastal region, in particular, has been a concern to many researchers as a region of high background radiation. Austromineral, an Austrian minerals prospecting company, in collaboration with the government of Kenya, carried out a mineralization study of the South Coast in 1978 (Austromineral, 1978). It was found the sediments containing zircon ore and some concentrations of radioactive isotopes of lead and zinc were distributed in the region. Niobium and rare earths were found to be concentrated in Mrima-Jombo areas leading to the high alkalinity of the partially dominant igneous rocks in the regions. According to Patel (1991a & b), gamma radiation levels were found to be

usually high at and around Mrima hill area, in addition to the cosmic content, which may expose the residents beyond world average limit of 2.4 mSv annually.

According to Radiation Protection Board report (RPB, 1999), some patterns of high radioactivity were reported in some areas of the South Coast area mainly due to the high levels of radiation from the Mrima Hill confirming the results of Patel (Patel, 1991b). The Radiation Protection Board carried out external radiation measurements at Mrima Hill and along the roads known to have been gravelled using radioactive materials from Mrima. Other places such as Mombasa Island, where there was no effect of the radioactive gravelling materials, were also surveyed for comparisons. Radiation levels from Mombasa Island were found to be very low, about 90 Bq/kg of Th-232 on average, as compared to Likoni-Lunga Lunga highway, the stretch from Msambweni to Kenya - Tanzania border point (Figure 1.2), where along this stretch, an average activity of 600 Bq/kg of Th-232 was recorded on the tarmac 15 mm deep, and as high as 1200 Bq/kg (Th-232) at the base gravel, 500 cm deep. However, from Lunga Lunga to Msambweni Hospital still along this highway, where no gravel from Mrima Hill was used, values recorded averaged 70 Bq/kg(Th-232). Other areas like Mwangwei-Majoreni-Jego road, a loose gravel road, recorded 1200 Bq/kg of Th-232. From these measurements, the annual effective dose rate from outdoor terrestrial radiation, was determined to be 6.1×10^{-5} Sv/a and for the indoor exposure, using an occupancy factor of 0.8, the annual effective exposure dose equivalent was determined to be 2.9×10^{-4} Sv/a, which is within the UNSCEAR 1993 recommendations of an annual effective dose not exceeding 3.5×10^{-4} S/a.

According to a report by Coastal and Environmental Services (2000), a South-African consulting firm, the physical environment at Kwale proposed titanium mining site is composed of two large sand dunes separated by the Mukurumudzi River. This river serves as a source of water for domestic purposes to the neighbouring households. Owing to its vicinity to the proposed titanium site, high contamination of the water is highly inevitable in future once the mining process commences.

According to Wamicha *et al* (2000), rutile and zircon, two titanium bearing ores, were found to contain appreciable concentrations of uranium and thorium for samples from Msambweni titanium mineral deposits. Rutile was found to have about 28 μg/g of uranium and 24.7 μg/g of thorium. Zircon was found to contain about 309 μg/g of uranium and 143 μg/g of thorium. Ilmenite was found to contain no concentrations of these two radioactive elements.

Other studies which have been carried out on natural radiation measurements in the country include Maina *et al* (2002) on indoor radon (Rn-222) in Coastal and Rift Valley regions of Kenya and Agola (2006) on natural radiation levels in (Olkaria) Geothermal region and Nderito (unpublished) on natural radiation study in Kerio Valley.

The mentioned studies, which have been discussed further in Chapter 2, have largely contributed to the continuous radiation monitoring program in Kenya. This is especially important to the government of Kenya in general and in particular to the radiation monitoring section of the Ministry of Health which is responsible for radioactivity

mapping, monitoring and protection in the country. This study aims at contributing further to the ministry efforts in and gathering more information on possible enhancement of radiation exposure in Kenya and particularly at the titanium mining sites in the southern coastal region.

1.5 Area of the Study

1.5.1 Location

The study area is located in Kwale district, in the coastal region of Kenya, and lies between longitudes $38^{o}31'$ and $39^{o}31$E and latitudes $3^{o}30'$ and 4^{0} 45S. The region borders the Taita Taveta district to the northwest, Kilifi district to the north, Mombasa district to the northeast, Indian Ocean to the south east and Tanzania to the South as shown in Figure 1.1.

1.5.2 Geology and Titanium Mineralization of Kwale

The coastal region of Kenya, along the Indian Ocean, is generally characterized by sediments of Triassic to Jurassic ages, igneous rocks of Cretaceous age and the unconsolidated sediments of Tertiary to Quaternary ages (JICA, 1993). Triassic to Jurassic sediments are mainly comprised of sandstone beds. Igneous rocks are widely observed in the form of intrusive of alkaline rocks of varied type. The unconsolidated sediments are observed to be composed of Tertiary sediments and the alluvial and colluvial residues of Quaternary age (JICA, 1993). A detailed discussion on the geology of the area is presented by Caswell and Baker (1993).

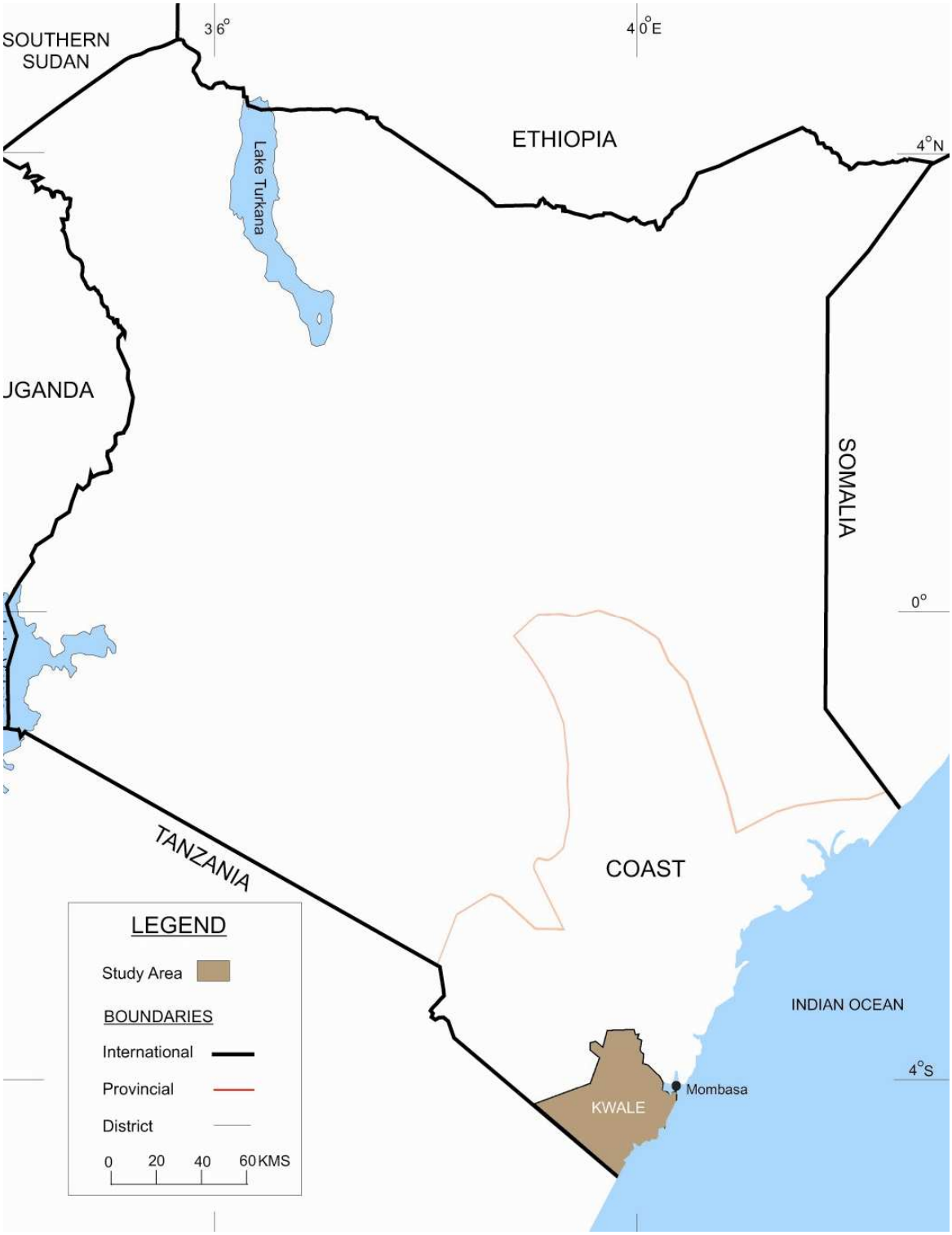

Figure 1.1: Map of Kenya showing the location of Kwale District in the Coast Province

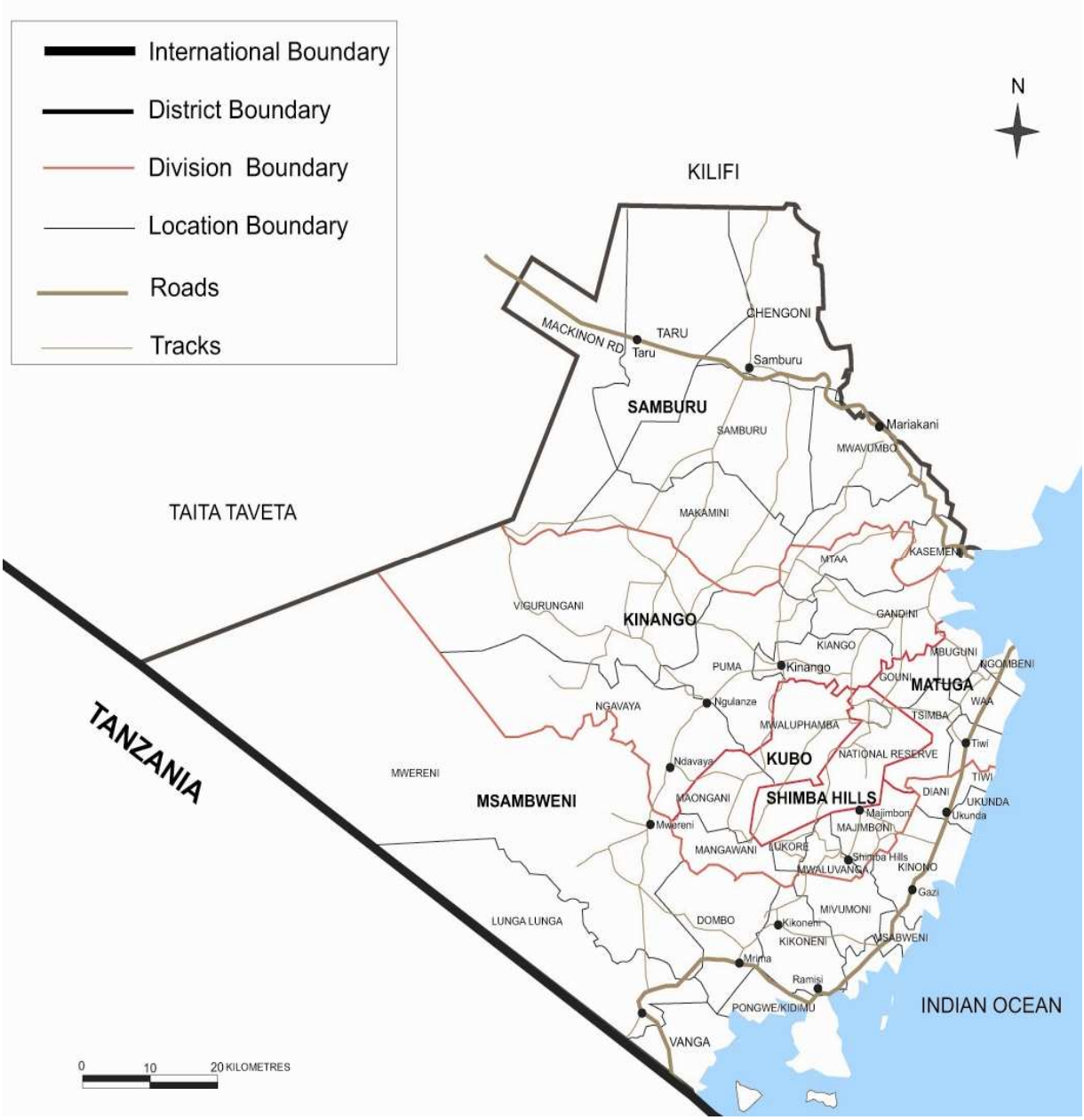

Figure 1.2: Map of Kwale District showing the administrative boundaries and the roads network

1.5.3 Nguluku Region

According to Austromineral report (Austromineral, 1978) on Kenya's coastal mineralization, Nguluku area is mainly comprised of Maji-ya-Chumvi Formation and Igneous rocks both of Duruma Group of Formations. The other members of Duruma

Group are Mariakani Formation, Mazeras Formation, and Magarini Formation. The geological arrangement is such that Nguluku Body is considered to be of a vent by igneous activities of alkaline rock composed of the so-called “agglomerate”. Niobium and rare earths can be expected to be the main components of the alkaline igneous rock. The same mineralization was reported in Mrima-Jombo area under the same alkaline igneous conditions. Post-reef sediments and the coral reef sediments were associated with zircon and limestone respectively.

In the JICA report (1993), the Maji-ya-Chumvi Formation is divided into such three members as Upper, Middle, and Lower members in upward grading. Lower and Middle members are dominated by shale and siltstone beds while the Upper member consists of sandstone beds. In the same report, a high content value of salt has been reported in shale beds of lower member to pose a sedimentary probability under arid environmental condition hence the name “Maji-ya-Chumvi”, which means “saline water” in Swahili language. Sandstone beds in Upper Member are massive and are comprised of silty sandstone beds with flaggy texture and well-developed joints.

1.5.4 Maumba Region

Rutile (TiO_2), ilmenite ($FeOTiO_2$) and zircon ($ZrSiO_4$) minerals appear in Maumba and Nguluku with respective specific gravities of 4.72, 4.2 to 4.3, and 3.9 to 4.7 (CES, 2000). This shows that they are heavy sands (specific gravity beyond 2.9). They are therefore deposited at similar sites through sedimentation in riverine and marine waters. Ilminite and rutile are titanium-bearing (titaniferous) minerals while zircon belongs to zirconium

and zirconia-bearing minerals. Rutile and ilmenite are used to make titanium metal or titanium dioxide (TiO_2) pigment, a white non-toxic substance. Zircon is used mainly in the manufacture of tiles and in the refractory and foundry industries. Thus, rutile, ilmenite and zircon are targets for titanium-mining project in the near future of this region under study.

According to CES (2000) the geological arrangement in Maumba region is actually expected to greatly alter in the process of extracting these minerals. As such, this may expose the environment to the suspected radionuclides in the affected regions. Information in the same report indicates that in the Maumba area, the titanium mineral deposits constitute about 5.7% of the Magarini sediments. The concentrations reduce southwards to about 3% in the Nguluku area. Coral reef deposits give high existence of limestone whereas a lead/zinc mineralization appears about 3 Km Northeast of Kwale Township. Other minerals in the Southern Coast are gypsum and Kimberlitic Diatremes, a diamond mineral (Ausrolmineral, 1978). Monazite, a rare earth bearing mineral, is one of the principal sources of radioactivity of mineral sands deposits. However, according to CES (2001), Kwale deposits contain very low concentrations of monazite. This results in very low contaminations of ilminite, rutile and zircon hence low activity levels of 1.5, 5.2 and 49.8 Bq/g. Typical activity ranges encountered worldwide in such minerals are estimated to be 3 – 30, 3 – 20 and 30 – 65 Bq/g respectively (CME, 2000).

1.6 Statement of the Problem

Exposure to the naturally occurring radioactive materials (NORMs) is actually enhanced through mining/excavation works and the processing of minerals. According to UNSCEAR report (1993), communities living near mineral sands mining operations may be exposed to about 100 times the normal background levels (approximately 2.4 mSv per year). Heavy mineral sands usually contain high concentrations of uranium and thorium compared to the average levels in normal soils and rocks (UNSCEAR, 1993).

One of the ways in which the mining operations cause exposures of the general public is the use of mine by- or waste-products for building and road construction. For example, the use of gravels from Mrima Hill in the construction of the Likoni – Lunga Lunga road increased the external dose due to gamma emission. Dust generation and re-settling or suspended particles may also lead to changes in the distribution of the naturally occurring radionuclides in the environment around the mines (Patel, 1991b). The use of the titanium by/waste-products, e.g. in roads construction may enhance exposure to radiation. (Mangala, 1987).

It was also noted (UNSCEAR, 1993) that information on exposures of members of the public resulting from the mining and milling of mineral sands is extremely scarce. This is also true in Kenya, and one of the reasons that there are often no pre-operational baseline data on the environmental radioactivity levels around mines. Therefore, it is difficult to determine the radiological implications once the mining operations have commenced.

This project is intended to provide baseline values of the radioactivity levels in soil around the proposed titanium mines.

1.7 Objectives of the Study

The main aim of this study is to provide information and data on the pre-operational status of the elemental and radionuclides concentrations in soil and rocks around the titanium mining project site, Kwale district.

The specific objectives are:

1. To determine the elemental concentration in the soil samples of Nguluku and Maumba,
2. To determine the activity concentrations of Th-232, U-238 and K-40 in soil samples from the above areas,
3. To determine outdoor gamma dose rate in air above ground in these areas,
4. To compare the obtained results with data from other parts of the world.

1.8 Hypotheses of the Study

Null Hypothesis

Radioactivity levels are low and hence radiation dose in the regions of Nguluku and Maumba are below or equal to the world average levels.

1.9 Justification and the Significance of the Study

The minerals found in the proposed mining areas include ilminite and rutile and sometimes occur together with monazite, a rare earth mineral that usually contain thorium and uranium (Binge and Mason, 1996). The proposed mining project therefore poses a potential radiation exposure risk.

This study endeavours to determine the specific radiation levels around the proposed mining site. This study, therefore, will be important especially to the Radiation Protection Board in designing radiation protection control guidelines. It is therefore of primary importance that radioactivity data that is collected for such regions earmarked for mining, forms a basis for protection guidelines.

The results obtained in this study, together with data from other studies done earlier, will enable projections on the possible levels of radioactivity enhancement due from the radioactive sands extraction.

Chapter 2

Literature Review

2.0 Contributions to Global Data on Radiation Measurements

In this chapter, various studies reported globally and their scopes of coverage in respective regions are discussed. It has been observed that most studies have largely dwelled on exposure levels and their equivalent dose. To formulate the world average radionuclide content in soil in the year 2000, UNSCEAR (2000), for instance, considered various studies done world over. The regions reported by the UNSCEAR (2000) include 2 in Africa, 2 in North America, 1 in South America, 12 in East Asia and West Asia and 25 in Europe.

According to the UNSCEAR (2000) report, from Africa, only Algeria and Egypt were considered to contribute data to the world average radionuclide concentrations in soil and other materials. In the formulation of the world average radionuclide concentrations and the associated external exposure rates in the UNSCEAR 2000 Report, there were contributions from only two African countries – Algeria and Egypt. In the formulation of population-weighted averages due to external exposure rates from terrestrial gamma radiation in the same report, contributions from Sudan and Namibia were also considered together with Algeria and Egypt. In Kenya, various studies have been carried out country wide in areas suspected to be of high background radiation levels. In order to contribute to global data on natural radiation levels, comprehensive studies need to be done.

2.1 Global Monitoring of Natural Radiation

It has been established that, on average, the effective background radiation dose rate is about 2.4 mSv per year (UNSCEAR, 1993) and 1.1 mSv of this dose is due to background radiation and an equal contribution due to radon exposure. This is an average value for people living near sea level; with increasing altitude, there is a slight increase in natural radiation due to the more intense cosmic radiation. In a few small regions of the world, where the radioactive component of the earth's crust is large, the terrestrial component is enhanced, giving a natural background of 10-20 times greater (SIPRI, 1981).

Radiation exposures resulting from the extraction and processing of earth minerals have also been studied. These exposures are relatively low in comparison to the overall exposure from the natural sources of ionizing radiation. The average annual effective dose worldwide arising from the extraction and processing of earth minerals, according to UNSCEAR (1993) is estimated to be about 20 μSv. It is reported that (UNSCEAR, 1993), in an assessment of an Australian mineral mining plant, members of the public who worked on the property adjacent to the plant site were estimated to receive a dose slightly greater than 1 mSv/a attributed mainly to external irradiation from heavy minerals spilled on the property. Away from the site, the main contribution to the dose received by members of the public resulted from the inhalation of dust from the plant; the highest doses were estimated to be about 2.5 mSv/a for five persons located 1.5-2 km from the plant.

In Africa, levels of terrestrial gamma radiation in some parts of Sudan with mean concentrations of 20.11 Bq/kg from U-238, 19.10 Bq/kg from Th-232 and 280.30 Bq/kg from K-40 were reported to be within tolerable limits. The respective mean concentrations were also below the world average values of 25 Bq/kg for both U-238 and Th-232, and 370 Bq/kg for K-40 (UNSCEAR, 1988). The world average values for both U-238 and Th-232 were further revised to 40 Bq/kg (UNSCEAR, 1993) on the basis of higher levels reported in China and the United States. However, a more recent country-wide survey carried out in China by Pan (1999) with communication to UNSCEAR Secretariat (UNSCEAR, 2000) indicated lower values. World median values 400, 35, and 30 Bq/Kq and the population weighted values of 420, 33 and 45 Bq/kg for K-40, U-238 and Th-232 have been suggested by UNSCEAR (2000). The population weighted values give an average absorbed dose rate in air outdoors from terrestrial gamma radiation of 60 nGy/h with a median range of 50-59 nGy/h.

After regular global and national studies on natural and occupational radiation exposure and its implications to man, various organizations worldwide have formulated the radiation protection standards and guidelines. ICRP recommendations are as shown in the Table 2.1. The dose limits for members of the republic are intended to be applied to the effective dose equivalents to the members of the critical group which should be a representative of those individuals in the population expected to receive the highest dose equivalent. According to IAEA guidelines (IAEA, 1990), limit for the annual dose equivalent is 5 mSv. However, if the exposure of the same individual extends over many years, the average annual effective dose equivalent should not exceed 1 mSv.

Table 2.1: Values of Maximum Permissible Dose (MPD) and Dose Limits for Specified Organs and Tissues as Recommended by ICRP and IAEA

Organ or tissue	MPD for adults exposed in the course of their work	Dose Limits for members of the public (average for groups of individuals)
Whole body (in case of uniform irradiation), gonads and red bone marrow	50 mSv in a year, 30 mSv in 13 weeks	5 mSv in a year *1 mSv in a year for a prolonged exposure
Skin, bone & thyroid	300 mSv in a year, 80 mSv in 13 weeks	20 mSv in a year
Other single organs	150 mSv in a year, 40 mSv in 13 weeks	14 mSv in a year
Hands and forearms	750 mSv in a year, 200 mSv in 13 weeks	75 mSv in a year.

Source: WHO, 1972; *IAEA, 1990

According to Lin et al (1996), the indoor gamma dose rate in Taiwanese houses was found to be 72 nSv/h, a level found to be higher than in other countries. Indoor radon level, however, was much lower than most other countries. The annual effective dose for adults in Taiwan which was found to be 1.56 mSv comprised of 0.25 mSv from cosmic rays, 0.58 mSv and 0.28 mSv from terrestrial external and internal radiations respectively, and 0.36 mSv from inhalation of Rn-222. According to the study, other minor components such as cosmogenic radionuclides, inhalation of Rn-220, and ingestion of Rn-222 were estimated to be comparable to the world average. In Taiwan, therefore, the natural radiation dose level by year 1995 was reported to be only about two-third of the global average of 2.4 mSv reported by UNSCEAR report of 1993 but very close to Japanese level of 1.48 mSv (NSRA, 1992).

On dose assessment, Lin et al (1996), considered the major items as cosmic radiation, cosmogenic radionuclides, terrestrial external exposure, and the terrestrial internal exposure including radon. Exposure levels were found to be 25.7 nGy/h at sea level and 26.9 nGy/h at ground level. According to Lin et al (1996), the exposure levels at 2100 m high (Mt. Alishan) were found to be double the value at sea level. Lin *et al* (1996) also measured the shielding effect of cosmic radiation in a 20-storey building. At 155 g/cm^2 concrete wall thickness, equivalent to 14 cm of lead, the cosmic component was almost completely attenuated. In Taiwan, most people live in reinforced concrete buildings. According to study done by Lin a decade earlier (Lin et al, 1986), two layers of 12 cm concrete (56 g/cm^2) could absorb 20% of cosmic rays. The indoor cosmic ray intensity was estimated to be 21.5 nGy/h and its annual equivalent dose to be 0.2 mSv. Annual effective dose was later determined to be 0.25 mSv including 0.015 mSv neutron component and an ionizing component of 0.235 mSv.

In terms of dose, the four most important cosmogenic radionuclides are C-14, Na-22, Be-7 and H-3. The four nuclides according to Lin et al (1996) have been measured routinely by Taiwan Radiation Monitoring Centre (TRMC). However, it has been difficult to distinguish whether they came from cosmic rays, nuclear detonation, or nuclear facilities. Annual dose level from C-14 of 0.012 mSv/y reported by UNSCEAR (1993) has been adopted since variability of dose from C-14 is not radiologically significant and that contribution from the other radionuclides is negligible.

Miah et al (1998) determined the distribution of radionuclides in soil samples in and around Dhaka city, Bangladesh. Concentrations of uranium, thorium and of K-40 and a fission product Cs-137 were determined by gamma-ray spectrometry; the values compared were with other global radioactivity measurements. Concentration values of Cs-137 found in near-surface samples ranged from 5 to 10 Bq/kg greater than levels obtained from samples of greater depths. The K-40 concentrations ranged from 402 to 750 Bq/kg with an average value of 574 Bq/kg, Ra-226 (uranium series) varied from 21 to 43 Bq/kg while concentrations of Th-228 ranged from 9 to 22 Bq/kg. The concentrations of Ra-228 (thorium series) were found to range from 34 to 81 Bq/kg.

In India, Kumar et al (1999) analysed conventional building materials and by-products from coal power plants for natural radiation due to Ra-226, Th-232 and K-40 using gamma ray spectroscopy. According to the study, conventional building materials such as clay bricks, sand, cement, fly ash and slag were found to have radioactivity levels below the world averages. The concentration of primordial radionuclides in soil samples of Gudalore Taluk in the Udagamandalam district of India was determined by Selvasekarapandian et al (2000). The mean activities of Th-232, U-238 and K-40 were found to be 75.3 ± 44.1 Bq/kg, 37.7 ± 10.1 Bq/kg and 195.2 ± 85.1 Bq/kg respectively. The average outdoor absorbed dose rate in air at a height of 1 m above the ground was found to be 74.3 ± 27.8 nGy/h, corresponding to an annual effective dose equivalent of 455.6 μSv. The dose equivalent ranged from 168.3 to 1,250 μSv. In comparison with world average activity values of 25 Bq/kg for Th-232 and U-238 and 370 Bq/kg for K-40

(UNSCEAR, 1988), levels in Gudalore were found to be 3, 1.5 and 0.53 times the world averages (Selvasekarapandian et al, 2000).

Bajwa et al (2003) studied natural radioactivity in some water and soil samples of Punjab State in India. Uranium concentration in Amritsar and Bathinda cities were determined using Solid State Nuclear Track Detectors which employs a plastic-etch technique. The values obtained varied from 0.61 μg/g to 1.27 μg/g. Activity levels of Ra-226, Th-232 and K-40 were determined by use of a gamma spectroscopic technique; 43.9, 55.9 and 101.7 Bq/kg, respectively were obtained.

In the barren and cultivated soils of Bio-saline Research Station in Pakka Anna, Pakistan radioactivity levels due to Th-232, U-238 and K-40 were determined by Akhtar et al (2005). In the barren soils radioactivity levels due to Th-232, U-238 and K-40 were found to be in the range of 50 – 55, 26 – 31 and 500 – 610 Bq/kg, respectively. Similar results were found in fertilised soils; 50 – 64, 30 – 38 and 560 – 635 Bq/kg, respectively. The results from the two soils segments were found to be within the world median ranges of 11 – 64, 17 – 60, 140 - 850 Bq/kg respectively (UNSCEAR, 2000).

Dose rate was calculated (Akhtar et al, 2005) from the activity concentration values and were found to be in the ranges of 20.8 – 25.4, 12.0 – 14.3 and 30.2 – 33.2 nGy/h from K-40, U-238 and Th–232 in barren soils respectively, and 23.5 – 26.3, 13.8 – 17.5 and 30.2 – 39.2 nGy/h from K-40, U-238 and Th–232, respectively in fertilised soils. The total dose rates from the two soil segments were found to be in ranges of 63 – 73 and 68 – 83

nGy/h which were within the world median range of 18 – 93 nGy/h (UNSCEAR, 2000). In the same study, effective dose rate values for the virgin saline and the fertilised saline soils were found to be 82 μSv/y and 90 μSv/y respectively, far below world average. According to UNSCEAR (2000), the worldwide annual effective dose is within 0.3 – 0.6 mSv range with an average of 0.48 mSv.

In Southern Italy, Bellia et al (1997) performed gamma ray measurements for U-238, Th-232 and K-40, on rocks and soils of the island of Ustica. The concentrations obtained ranged from 15 - 164, 16 - 174 and 201 - 1,350 Bq/kg respectively. The gamma activity levels were compared to the mineralogical and chemical data obtained by XRD and XRF analyses and what was observed. The observed levels of the primordial radionuclides corresponded to the magmatological features of the rocks.

Sroor et al (2002) calculated the dose rate due to naturally occurring radioactive materials (NORMs) in North Tushki area of the Egyptian south western desert from the radioactivity levels obtained from the study. The activity concentrations due to Th, U and K were found to be higher than the international recommended limits as shown earlier in this section. The study indicated averages of 35.75 to 4576.61 Bq/kg for U-238, 36.66 to 93,824.18 Bq/kg for Th-232 and 427.17 to 10,203.18 Bq/kg for K-40. Elemental analysis of the soil samples was also carried out for the three nuclides and the contents ranged form 2 to 370.8 μg/g for U-238, 3.7 to 23221.6 μg/g for Th-232 and 6.3 to 335 μg/g for K-40.

In Kuwait, Saad and Al-Azmi (2002) carried out measurements of radioactivity concentrations in sediments and their correlation to the coastal structure. The average activity concentrations obtained for U-238, Th-232, Ra-226, K-40 and Cs-137 for the southern coastline were 13.5±6.2, 2.3±0.8, 18.4±7.5, 110.3±40.7 Bq/kg respectively and 66.5±19.25, 11.2±4.0, 59.8±5.9, 384.4±133 and 2.16±1.25 Bq/kg respectively for the northern region of Kuwait coastline. Activity concentration due to Cs-137 was found to be below the detection limit for the southern coastline. According to Saad and Al-Azmi (2002), Table 2.2 compares mean activity concentrations, in Bq/Kq, of different countries with the world averages.

2.2 Studies on natural radioactivity in Kenya

Mustapha (1999) reported high concentrations of Ra-226 and Th-232 in soils samples from various parts in the country. In that study on the assessment of human exposure to natural radiation in Kenya, samples (geological materials and water) from different geological terrain, particularly the more densely populated areas; Nairobi, Kiambu, Kwale, Mombasa, Machakos, Bungoma and Trans Nzoia districts were in the study. The overall mean activity concentrations of K-40, Ra-226 and Th-232 in the geological materials were found to be 705, 65 and 163 Bq/kg respectively. The estimated effective dose due to external exposure to terrestrial gamma radiation varied from 0.06 to 2.00 mSv/y with an average of 0.76 mSv/y. Radon concentrations in various water sources were reported to be higher than the accepted world average of 37.1 Bq/kg.

Table 2.2 The mean activity concentrations of U-238, Th-232, Ra-226, and K-40 for different countries, Bq/kg

No	Country	Activity concentration (ranges), Bq/kg				References
		U-238	Th-232	Ra-226	K-40	
1	China	62 (26-119)	90 (35-228)	50 (18-135)	524(281-711)	Ziqiang et al (1988)
2	USA – Lousiana	34	36	64	472	Delune et al (1986)
3	Turkey	75 (15-224)	24 (5-63)		(220-3202)	Kemru (1997)
4	Republic of Ireland	37 (8-120)	26 (3-60)	60 (10-200)	350 (40-800)	McAulay and Moran (1988)
5	Spain		49 (7-204)	45 (13-165)	650 (48-1586)	Baeza et al (1992)
6	Netherlands	(19-17)	(22-77)		(290-700)	Koster et al (1988)
7	Japan		(5-185)	(5-130)	(75-1400)	Megumi et al (1988)
8	Belgium		(9-47)	(13-43)	(170-610)	Deworm et al (1988)
9	Norway		(26-50)	(720-1760)	(700-1400)	Stranden and Strand (1988)
10	Italy		(16-62)	(17-630)	(398-649)	Buttaglia and Bramati (1988)
11	Greece	214 (15-1049)	43 (18-66)	212 (24-764)	1130 (258-2464)	Travidon et al (1996)
12	France	37 (9-62)	38 (16-55)	38 (9-62)	599 (120-1026)	Lambrechts et al (1992)
13	Banglandesh	38 (20-90)	66 (51-88)	36 (18-85)	272 (217-320)	Mantazul et al (1999)
14	Bulgaria	(10-77)	(5-110)	(9-77)	(11-760)	Strezov et al (1998)
15	Portugal		(60-85)		(42-51)	Carreira and Sequeira (1998)
16	Taiwan	18 (0.87-35)	28 (0.4-66)		479 (16-970)	Chu et al (1992)
17	Egypt	17 (5-64)	18 (2-96)		316 (26-653)	Ibrahiem et al (1993)
18	Algeria			(27-133)	(184-632)	Noureddine et al (1998)
19	Kuwait	36 (5-115)	6 (2-17)	36 (8-72)	227 (41-492)	Saad and Al-Azmi 2002)
20	***World Averages**	**25 (10-50)**	**25 (7-50)**		**370 (100-700)**	**UNSCEAR (1988)**
21	**World Averages (population weighted values)**	**33**	**45**		**420**	**UNSCEAR (2000)**

* The world average values are also presented for comparison purposes with the world average values. Ranges are given in parentheses (Saad and Al-Azmi, 2002).

According to Maina *et al* (2002) and Nderito (unpublished), a number of samples analysed had reportedly higher values of ^{238}U and ^{232}Th gamma activity concentrations than the world average of 40 Bq/kg for the two radionuclides. Agola (2006) also reported mean activity concentrations of U-238 series, Th-232 series, Ra-226 series and K-40 as 73.72 ± 7.4, 149.33 ± 17.0, 163.81 ± 18.6, and 1,095.20 ± 53.2 Bq/kg respectively in the Olkaria geothermal area. Radon (Rn-222) mean activity concentrations in water ranged from 1.95 ± 0.4 to 8.63 ± 0.1 KBq/m^3 with an overall mean value of 5.56 ± 0.5 KBq/m^3. The radon values obtained from water sources (Agola, 2006) were therefore within the recommended level of 10 KBq/m^3 in water (UNSCEAR, 1993). The overall mean concentration for radon in water was also far below the US-EPA, 1993 permissible level of 11 KBq/m3. Radon activity concentration for the indoor environments ranged from 5.13 ± 0.7 to 83.47 ± 0.1 Bqm^3 with a mean value of 41.05 ± 3.2 Bq/m^3 with a value below the reference levels of 200-600 Bq/m^3.

Agola (2006) computed absorbed dose rate in air and annual effective dose as 213.89 nGy/h and 0.53 mSv/y respectively. Comparing with the world average values of 57 nGy/h and 0.46 mSv/y respectively, the area of study, according to Agola (2006), was classified to be high background radiation area. A total mean effective dose due to Rn-222 activity in water was obtained as 46.55 nSv/y assuming dose to adults only and a water consumption rate of 0.5 litres per day. Effective dose for indoor radon activity was 0.09 mSv/y due to radon gas and 1.87 mSv/y due to short-lived radon decay products dissolved in soft tissues assuming equilibrium factor of 0.4. The geothermal are was

therefore deduced to have significant levels of natural radiation that pose some heath risks to the residents.

According to Maina et al (2002) radon levels in 42 mud constructed houses of Soi region in Kenya's province of Rift Valley, were all below the action level of 200 Bqm^{-3} recommended by IAEA. In Taita and Taveta regions of the country's coastal province, however, more than half of similar houses exceeded the IAEA limit. Thirteen houses exceeded 400 Bq/m^3, the limit given by UNSCEAR 1993 report. Annual effective dose was also computed and ranged from 3.1 – 3.6 mSv/y in the coastal region and 0.4 – 2.6 mSv/y in Rift Valley. Based on the African cultural norms, outdoor occupancy factors of 0.6 and 0.5 for men and women respectively from these regions were used to compute the effective dose.

Chapter 3

Experimental Procedures and Sample Preparation

3.0 Introduction

In this chapter, the procedures followed for sampling, sample preparation, measurement instruments and data evaluation are presented.

3.1 Sampling

Samples of the heavy sands were randomly obtained from two separate regional dunes namely: Nguluku and Maumba (Figure 3.1). Bulk samples weighing between 500 g and 1000 g, and considered to be representatives of the radioactive heavy sands, were obtained. At each sampling point, two samples were obtained as follows; one sample of sand at up to 30 cm - depth and the other obtained at a depth below 30 cm. During sample collection, the following factors were put into consideration;

i. Cleanliness of the tools used was ensured against any possible contaminants,
ii. Care was taken to obtain soils above 30 cm separately from that of below this depth,
iii. Samples were collected from the entire cross section of each pit to ensure proper presentation,
iv. The top humus and other vegetation were removed from the sampling point prior to sample collection,
v. All the samples collected were labelled and stored in polyethylene bags that were in turn put in a shielded container to minimize radiation exposure level during transportation.

Sampling Regions

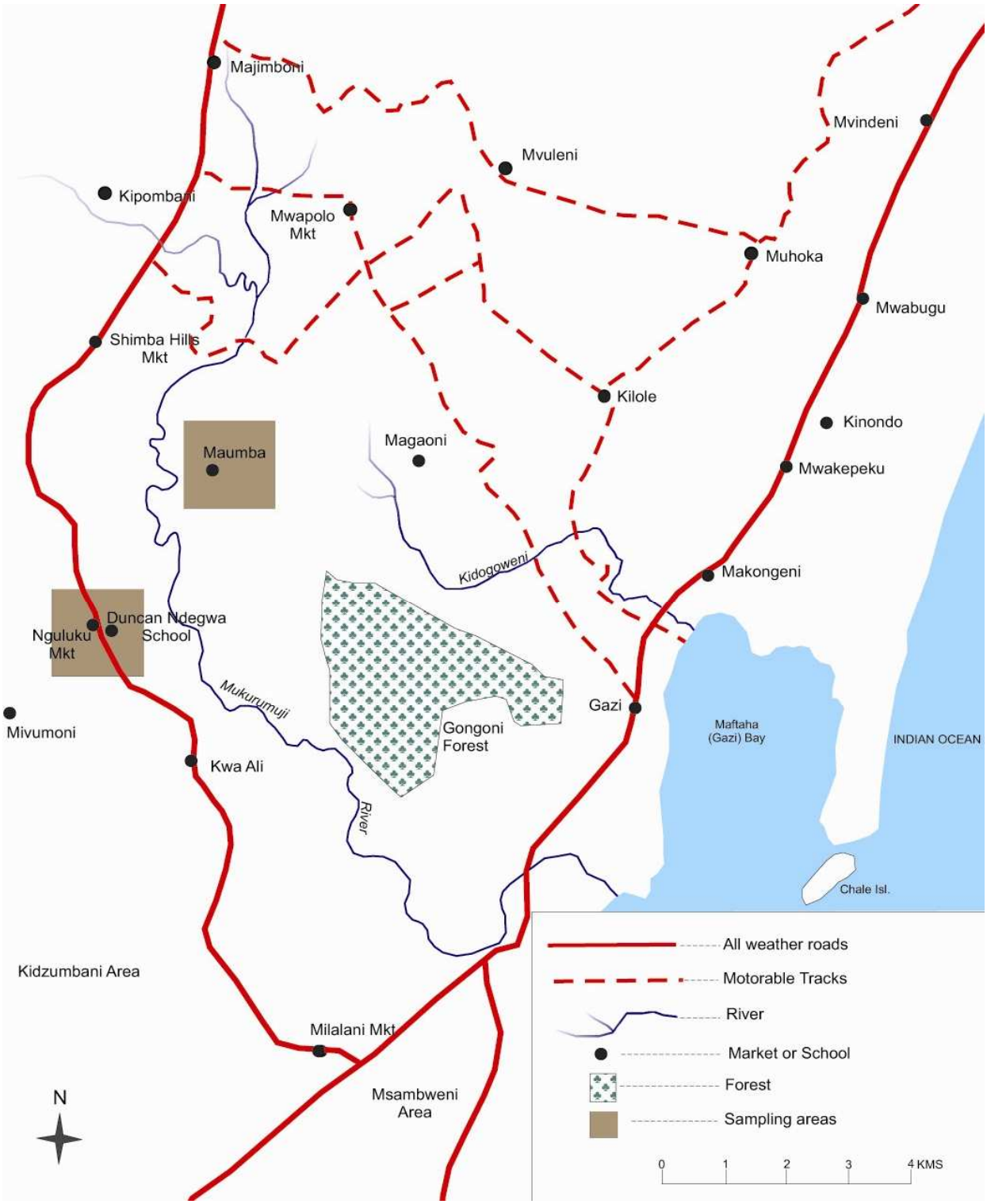

Figure 3.1 **Map showing the sampling sites of Nguluku, Maumba and their environs in Kwale District.**

3.1.1 Nguluku Samples

In the Nguluku region, only seven samples were obtained for radioactivity measurements. A summary of samples description is presented in Table 3.1.

Table 3.1 Samples Descriptions – Nguluku Samples

Sample	Description
Ngu1	Topsoil along the road, approx. 1.5 Km from Shimba Hills Border
Ngu2	Subsoil, along the road, approx. 1.5 Km from Shimba Hills Border
Ngu3	Surface run-off deposits, along the road (surface), approx. 0.5 Km from Nguluku Ctr towards Shimba Hills
Ngu4	Topsoil, along the road (surface), approx. 0.5 Km from Nguluku Ctr towards Msambweni
Ngu5	Topsoil, along the roadside, approx. 0.5 Km from Nguluku Ctr towards Msambweni
Ngu6	Topsoil, Noma Centre
Ngu7	Subsoil, Noma Centre

3.1.2 Maumba Samples

Maumba region is geographically divided into three sub-regions namely; Miembeni (also known as Mwaweche), Maumba Central and Lower Maumba (known 'Maumba ya Chini'). In these three regions the surface soils were generally observed to be sandy and pale brown in colour with some mix of black colouration. Intense black colouration could be observed along the vertical profile of gulley and at various erosion deposits. It is important to note that the titanium plant was initially erected at Miembeni.

Samples were collected from the farms where the residents spend most of their time during the day and along the roadsides where soils were not disturbed. This was done during and after the rains. Random sampling was the most applicable method of sample

collection due to various limitations during fieldwork. Inadequate resources and lack of appropriate tools, like Geographical Information System (GIS), could not enable application of modern sampling methods on the grid system. At every point, one sample was collected at an approximate depth of 30 cm and then labeled as sample A; the second at a depth below 30 cm and labeled as sample B. Since a GIS was not available during sampling, further labeling of the samples was considered important by noting the names of the farm owners where sampling was done for purposes of future reference. A total of 50 samples were collected in all and labeled numbers 1A, 1B, …, to 25A, 25B. A summary of description of Maumba samples is presented in Table 3.2.

Table 3.2 Samples Descriptions – Maumba Samples

Sample	Location of sampling point
1 to 10	Miembeni
11 to 13	Maumba Centre
14 to 17	Maumba Centre, Duncan Ndegwa Pry. Sch
18 to 20	Maumba Centre
21 to 24	Maumba ya Chini
25	Miembeni, Surface run-off deposits

3.2 Sample Preparations for Radioactivity Measurements

The samples collected from the two regions were transported to the Institute of Nuclear Science & Technology, University of Nairobi, for radioactivity analysis. The samples were oven-dried for 48 hours to constant weight, before preparation. Storage of the samples for a minimum period of one month was allowed to enable equilibrium of Ra-

226 with its decay products in the uranium series and Ra-228 with its daughters in the thorium series.

The samples were crushed using a pestle and a mortar to reduce the particle sizes and ensure homogeneity. This was followed by sieving (size of mesh) to ensure particles sizes less than less than the mesh. For each sample, mechanical grinding was then carried out using a Fritsch Pulverisette type 120 for about 20 minutes each to further reduce the particle size and hence the interparticle sizes. Samples weights between 400-700 g were portioned in a Marinelli beaker for gamma ray analysis.

To avoid detector contamination and sample cross-contamination every Marinelli beaker used was cleaned with a solution of EDTA, dried and counted empty to confirm the absence of any residual activity before putting in a new sample. To enable calculation of activity concentration using the intercomparison method, the background spectrum, standard reference material spectrum and the samples spectra were collected.

The background spectrum was collected by counting an empty Marinelli beaker for 20 hrs. Spectra acquisition for the samples and the standard reference material was carried out by counting a known mass of material for a minimum period of 5.6 hrs. However, a spectrum for the standard material was collected daily for use in the activity calculations, with sample spectra collected on any particular day. The collected spectra were then stored in a PC for further analyses. Each sample was analysed once.

3.3 Sample Preparations for X-ray Fluorescence Analysis

In the preparations for EDXRF analysis, a small fraction of every sample was obtained by way of coning and quartering method. After the sample was ground, it was poured on a clean sheet of paper in a small cone-like heap. The cone was then flattened and divided into four equal parts. Two opposite quarters were stored separately while the other two were further ground and sieved through a 200 mesh to attain particles size of not more than 75 μm. The remains after sieving were further ground until all the two quarters passed through the 200 mesh. The fine samples were then dried in an oven at 100^0 C for 48 hours to constant weight. The coning and quartering procedure was repeated on the dried samples so as to obtain a 25-g representatives of the whole sample which were then stored in Petri-dishes.

The 25-g samples were further ground in a mortar to reduce the particle sizes. Further, they were diluted and homogenised using cellulose, with dilution factors of 1- 2, in order to reduce matrix effects and improve pellet formation. Due to the sandy nature of mineralised soils, cellulose in the sample increased the cohesiveness of the soil particles that is needed in pelletizing. Small amounts of the fine soil samples were pressed into pellets of 2.5 cm in diameter using a hydraulic press at pressure of 2-3 kPa. Two pellets were made from each sample, weighed and analysed. The mass of the pellets was used in the determination of elemental concentrations. For each sample analysed, three determinations were done.

3.4 EDXRF Instrumentation and Measurements

The x-ray fluorescence detector system used consisted of a Canberra Si(Li) detector crystal model 2008 with 6 mm active diameter, 5 mm sensitive depth, and a beryllium window thickness of 0.025 mm. The detector was operated at a negative bias of 1500 V through an Ortec 456 high voltage bias supply, and had a resolution of 200-230 eV at the Manganese K_α spectral line of 5.9 KeV at a time shaping constant of 10 μs. Other spectrometer electronics include a Canberra 2026 spectroscopy amplifier with a pile-up rejector (PUR) for pulse shaping and an interface of a Canberra 8075 ADC and an S-100 PC based multi-channel analyser (MCA) for spectral data acquisition storage and analysis. Energy calibration of the detector's multi-channel analyser was carried out using Cd-109 and Fe-55 radioactive excitation sources.

The pellets of the prepared samples were irradiated for a period of 1500s using a Cd-109 excitation source using the geometry shown in Figure 3.2. A PC based MCA was used spectral data collection and storage and the data deconvolution was done using AXIL program. The program enables for calculation of background subtraction by fitting a polynomial function to the actual spectrum and determines net peak areas of the elements of interest present in the sample. Typical spectra of titanium bearing ore samples from Kwale district are shown in Appendices V and VI.

For each pellet, three measurements were done; sample alone for 1500 s to acquire the spectrum of interest and sample with multi-element target on top for 500 s, and the target alone for 500 s for the purposes of absorption correction. The multi-element target used

was a thick pellet of pure cellulose mixed with titanium, manganese, zinc, bromine, and niobium compounds of high purity. The energies of characteristic x-rays of these elements cover the energy of the multi-channel analyser calibration.

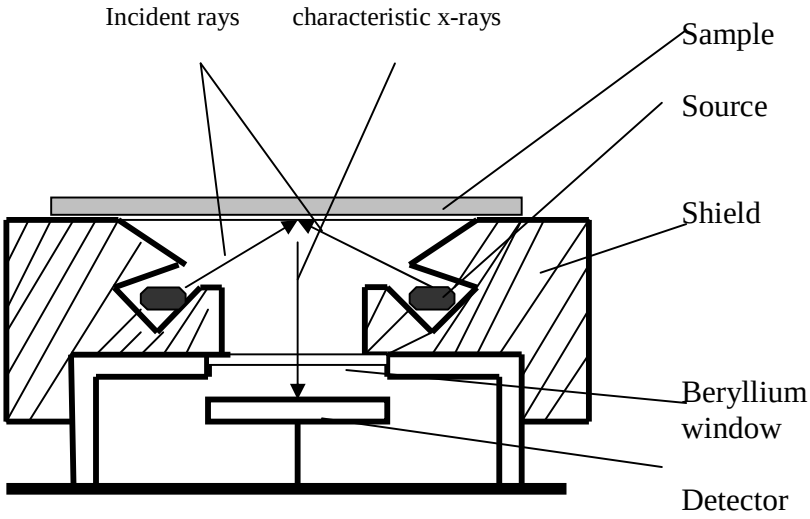

Figure 3.2 Direct samples excitation with annular cadmium-109

3.4.1 Accuracy of EDXRF by the Fundamental Parameter Method

A soil reference material (Soil 7 SRM) was analysed and the results compared to the certified values to indicate the accuracy of the method used for quantitative analysis.

3.4.2 Lower Limits of Detection, LLD

The expression used for determining the lower limit of detection for an element of interest is given by

$$LLD = \frac{3}{m} \bullet \sqrt{\frac{R_b}{T_b}} \quad \text{..... 3.1}$$

where $\mathbf{R_b}$ is the background count rate, $\mathbf{T_b}$ is the background count time, and **m** is the sensitivity expressed in count rate per unit concentration of element of interest. Lower limit of detection values in EDXRF analysis were obtained from the analysis of a reference material; Soil – 7 SRM; which has a similar matrix to the samples collected for analysis

3.4.3 Calculations of Elemental Concentrations

The fundamental parameter method was used for the evaluation of elemental concentrations in soil samples. The computation method is programmed and available for PC use at the Institute of Nuclear Science ant Technology laboratory and depends on input results of AXIL (Analysis of X-rays using Iterative Least square method) software. This is a modular program of the IAEA QXAS software that allows for analysis of the spectra for the element of interest. A typical summary of EDXRF results from the analysis tool, AXIL, is shown in Appendix III.

3.5 The Gamma-ray Spectrometric Instrumentation and Measurements

The most important naturally occurring radionuclides and the gamma lines used are given below:

- The U-238 series (half-life of 4.5 billion years): Pb-214 (242.0, 295.2 and 351.9 KeV lines) and Bi-214 (609.3 and 1120.3 KeV lines)
- The Th-232 series (half-life 14 billion years): Ac-228 (338.3, 911.2 and 969.0 KeV lines), Pb-212 (238.6keV line) and Tl-208 (583.2keV)
- Potassium (K-40), half-life 1.3 billion years: K-40 (1460.8keV line)

3.5.1 Apparatus and Spectral Collection

The gamma detector is a coaxial high purity germanium detector model CPVDS30-30185 from Oxford was used for gamma ray spectroscopy in this work. Spectral collection was done using a fixed geometry by placing a 500 ml Marinelli beaker with the sample over the vertically mounted coaxial HPGe detector. The spectrometer consists of the following specifications:

i. Crystal characteristics

- Diameter – 57.4 mm
- Length – 56.9 mm
- Active volume – 144 cubic mm
- Germanium dead layer thickness – 600 microns
- Detector-to-window distance $\leq$ 5 mm

ii. End Cap Characteristics

- Outside diameter – 76 mm, Aluminium 1mm thick
- Front window – 1 mm thick Aluminium

iii. Performance specifications

- Operating HV supply bias – 3200 V
- Polarity - positive

iv. Bias

- Gain setting to give 0.3 keV/channel for 1.33 MeV performance
- Gain setting to give 0.04 keV/channel for 122 keV

v. Pulse Height Analyzer

- PCA-8000 with 8192 channels.

The following schematic diagram illustrates the electronic set up of HPGe gamma spectrometer.

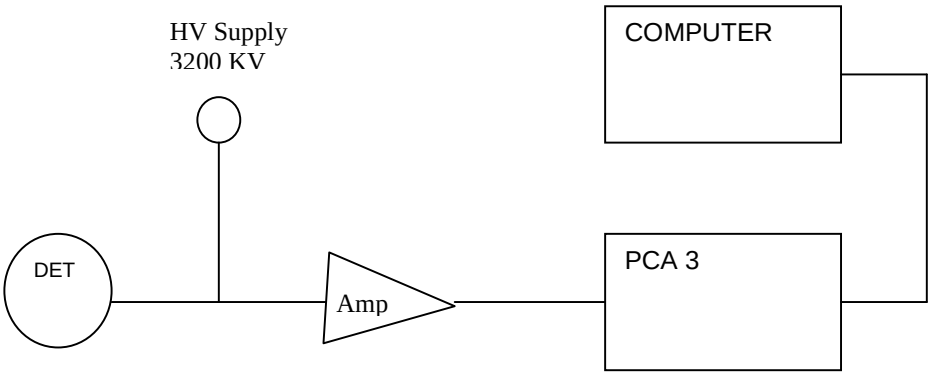

Figure 3.3 Schematic diagram of an HPGe detector system

Other important parameters of the detector are summarized as per Table 3.3

Table 3.3 Some Important HPGe Detector Parameters

	Expected	**Measured**	
		June 12, 1995*	**June 14, 2007****
Efficiency	30%	29.7%	Not measured
1.33 MeV (Co-60) FWHM	1.85 KeV	1.80 KeV	3.94 KeV
FWTM/FWHM	1.90 KeV	1.83 KeV	1.78 KeV
Peak to Compton ratio	58:1	64:1	Not measured
122 KeV (Co-57) FWHM	875 eV	850 eV	Nuclide (h=270.5 d), concentration in the std negligible
277 KeV (Ba-133) FWHM (a low energy close to Co-57)			2.70 KeV

***The measurements done by the suppliers, Oxford Instruments Inc., Analytical Systems Division, according to the IEEE standard ANSI/IEEE Std 325-1986.

****The measurements done at the Institute of Nuclear Science and Technology, University of Nairobi.

3.5.2 Detector Calibration

This process was carried out using four energy lines in a spectrum of a liquid standard reference material, SRM-1 from Poland containing three radionuclides: Am-241 (59.54 eV line), Cs-137 (661.66 eV line), and Co-60 (1173.24 eV and 1332.50 eV lines). The spectrum of the standard was used to determine energy, FWHM and photoefficiency calibration parameters by regression method through submodule of Gamma, Activity and Neutron Activation Analysis Software, GANAAS (Zaman, et al, 1993). The energy and FWHM functions are polynomials of the second degree while the photoefficiency function used was a logarithmically transformed power series of the form given by the equation

$$\varepsilon = \frac{1}{E}\sum_{i=0}^{n} a_i (\ln(E))^n \quad \text{..... 3.2}$$

where ε is the detector photoefficiency, ln(E) is the natural logarithm of photon energy E and a_i is the sought regression parameters. In this work, n=2 or n=4 gave a good fit.

3.5.3 Standard Reference Material for Intercomparison

In this experiment, an IAEA SRM 375 Standard was used. The standard was a soil sample whose radioactivity concentrations of the various radionuclides commonly found in geological materials have been predetermined. The values of radioactivity concentrations for this particular reference material were determined on December 31, 1991 as shown in the Table 3.4. The material was collected in Chernobyl region in 1990 and donated to the IAEA by the former USSR (AQCS, 1998/99). Among the radionuclides whose concentrations were determined and recorded are K-40, Th-232 and U-238, which are of major concern in this work.

Table 3.4 Activity concentration levels of radionuclides under investigation in the standard reference material as at December 31, 1991

Radionuclide	Activity Concentrations (Bq/kg)
Th-232	20.5
U-238	24.4
K-40	424.0

Source: AQCS (1998/99)

3.5.4 Calculation of Radionuclide Concentrations

The concentrations of the radionuclides of interest were computed using the Intercomparison Method.

$$\frac{A_S M_S}{I_S} = \frac{A_R M_R}{I_R} \quad \text{..... 3.3}$$

where,

A_S = activity concentration of a radionuclide ***i*** in the sample, Bq/kg,

M_S = mass of the soil sample, in g,

I_S = intensity of a radionuclide I in the sample, in c/sec,

A_R = activity concentration of a radionuclide i in the standard reference material, in Bq/kg ,

M_R = mass of the standard reference material, in g, and

I_R = intensity, in counts per second, of a radionuclide i in the standard reference material, in c/sec.

from which activity concentration, A_S, as defined above, is calculated.

The results obtained are further compared to the world average as reported by UNSCEAR (2000). Samples collected and their preparation, analytical procedures, measurements of radionuclide in food and activity in the environment, in the UNSCEAR (2000) report, were done according to procedures provided by IAEA in its technical and quality control reports (IAEA, 2006b; IAEA, 2001; IAEA, 1989; AQCS, 1998) and safety guidelines (IAEA, 2000a; IAEA, 2000b; IAEA, 1996a; IAEA, 1996b).

3.6 Determination of Dose Rate and Exposure

The gamma dose rates D in outdoor air at 1 m above the ground was calculated using equation 3.4 and the conversion factors published by UNSCEAR (2000).

$$D = A_C \times C_F \quad \text{.....} \quad \textbf{3.4}$$

where

D is the dose rate in nGy/h,

A_C is the activity concentration in Bq/kg and,

C_F is the dose conversion factor in nGy/h per Bq/kg (absorbed dose rate in air per unit of activity concentration).

For an adult person, the absorbed dose rates were converted to effective dose rates by using the following relationship given by UNSCEAR report of 2000:

$$H_E = D \times T \times F \quad \text{.....} \quad \textbf{3.5}$$

where

H_E is the effective dose in μSv/y,

D is the estimated absorbed dose rate in nGy/h,

T is the outdoor occupancy time factor (0.2 ×24 h×365.25 d ≈ 1753 h/y) and,

F is the adsorbed-to-effective dose conversion factor (0.7×10^{-3} μSv per nGy).

Chapter 4

Results and Discussions

4.0 Introduction

In this chapter, the results of the study are presented and discussed. First, the accuracy of the analytical techniques is determined using standard reference materials from International Atomic Energy Agency (IAEA). The elemental analysis results of the fifty (50) soil samples from Maumba are then presented and discussed. Concentration levels of titanium, vanadium, manganese, iron, cobalt, copper, zinc, thorium, yttrium, uranium, zirconium, niobium and molybdenum are presented and discussed for the three smaller subdivisions of the Maumba area sampled. The results have also been compared to a similar study on Mrima Hill soil.

Also discussed in this chapter are the activity concentrations of Th-232 and U-238 in the fifty samples from Maumba and the seven samples from Nguluku. The discussion is limited to the two radionuclides owing to low activity concentration values of K-40 present in these samples.

Elemental concentrations distribution of the three major constituents of Maumba samples; titanium, iron and zirconium, and that of niobium, a minor constituent, have been compared to the distribution of Th-232 and U-238 activity concentrations. Finally, dose rates due from exposure to the two radionuclides, is estimated using conversion factors from the UNSCEAR (1993) and (2000) reports; as 0.0417, 0.462 and 0.604 respectively, for K-40, U-238 and Th-232. To convert dose rate to Sv, a factor of 0.7

Sv/Gy was used. This was adapted the UNSCEAR (2000) report and Selvasekarapandian study (Selvasekarapandian et al, 2000). The results obtained are further compared to the world average as reported by UNSCEAR (2000).

4.1 EDXRF Analysis

In this section, the accuracy and the detection limits of the method used are presented and discussed.

4.1.1 Accuracy of the Si(Li) Detector in determination of Elemental Concentrations

The results obtained after carrying out elemental determination of the standard reference material, IAEA Soil 7 using the Si(Li) detector are presented in Table 4.1. The measured values of most of the elements of interest are found to be within the certified limits whereas a slight deviation is observed for manganese, iron and zinc. However, using two-tailed student t-test, the difference between the measured mean from the certified mean is found to be insignificant at 95% confidence limit.

Table 4.1 Results of EDXRF Analysis of Certified Reference Material, IAEA Soil 7

Element	Measured concentration	Certified concentration
Ti	0.28 %	0.30 %
Mn*	558 μg/g	631 μg/g
Fe*	2.28 %	2.57 %
Zn*	79.4 μg/g	104 μg/g
Sr	111 μg/g	108 μg/g
Y	18.2 μg/g	21 μg/g
Zr	193 μg/g	185 μg/g
Nb*	20.3 μg/g	12 μg/g

* Elements whose measured concentrations are not within the certified intervals

4.1.2 Detection Limits of Si(Li) Detector for the Elements of Interest

The lowest limits of detection of the method used for the elements of interest were obtained by applying Equation 3.1 and the results obtained after analysis of the pellet form samples are presented in Table 4.2.

Table 4.2 Lower Limits of Detection of Si(Li) Detector for the Elements of Interest

Nuclide	Detection limits (units in µg/g unless otherwise stated)
Titanium	0.13 %
Vanadium	616.0
Manganese	253.8
Iron	196.1
Cobalt	104.0
Copper	74.50
Zinc	66.70
Yttrium	17.30
Zirconium	13.81
Niobium	13.70
Molybdenum	13.01
Thorium	8.90
Uranium	8.87

It can be deduced from Table 4.2 that the detection limit improves with increasing atomic number. Lowest limits of detection (LLD) for the elements of interest were found to be considerably higher than is usual the case. This was attributable to the detector resolution (220-230 eV) during the time when these measurements were done. Typical resolution values of 180 – 200 eV yield much lower LLD values.

4.1.3 Maumba Samples

The EDXRF analysis results of Maumba samples are presented in Tables 4.3 to 4.5. Sample numbers 25A and 25B, which had been collected from black erosion deposits had significantly high elemental concentrations and were therefore excluded when computing mean concentration values.

4.1.4 Occurrence and Distribution of Elemental Concentrations of Maumba Samples

The occurrence of the major elements in the soil samples was determined through calculations of mean concentrations at 95 % confidence level. The major constituents in Maumba samples are titanium, manganese, iron and zirconium (Table 4.4). This is partially comparable to Mangala (1987), where Mrima Hill samples, soil sediments of carbonatite, exhibited iron as the major constituent despite the alkalinity of their origin. Other constituents, in lower concentrations include; zinc, vanadium, cobalt, yttrium, thorium, niobium and molybdenum.

Low concentrations of copper, thorium, zinc and molybdenum are observed in very few samples from Miembeni region of Maumba. Copper is observed only once (sample 25A) with a level of 138.8 ± 30.09 μg/g. Zinc and molybdenum appear twice with concentration levels of 109.1 ± 23.26 & 155.1 ± 30.96 μg/g and 22.17 ± 5.09 & 58.01 ± 9.90 μg/g in samples 25A and 25B respectively. Thorium appears in three samples – 7B, 10A and 25B – in respective levels of 22.47 ± 3.64, 16.33 ± 2.81 and 40.93 ± 7.22 μg/g. Uranium concentrations are observed below the detection limits in all samples analysed.

Titanium

This element is one of the major constituents and occurred in all the fifty (50) samples analysed with a concentration range of 0.13 % to 2.81% and a mean range 1.21 ± 0.21%. These values are significantly lower (95% confidence level) than the levels reported for Mrima Hill samples analysed by Mangala's study (1987), from which the element was found to be one of the major constituent with an uneven distribution in the concentration range of 1.00 % to 9 % and a mean concentration of 4.69 %.

In this study, occurrence of titanium has been found to be very strongly correlated to iron, zirconium and niobium and weakly to manganese with respective coefficients of 0.96, 0.97, 0.90 and 0.25 as presented in Table 4.4. Its distribution in the samples has been found to correlate strongly with the activity concentrations of Th-232 and U-238 with respective coefficients of 0.88 and 0.83.

Other Elements

It was observed that concentration levels of copper, zinc, thorium, uranium, niobium and molybdenum were very low (<LLD) for most soil samples from Maumba. However, zinc, molybdenum and thorium were observed in two samples with highest levels registered as being 155.1, 58.01 and 40.93 μg/g, respectively. Concentration levels of yttrium and uranium were below detection limits in all the samples analysed.

Table 4.3 **Elemental concentrations for soil samples from Miembeni, Maumba** (in µg/g unless otherwise stated) $\overline{X} \pm 1STD$; n=2

Sample	Ti (%)	V	Mn	Fe (%)	Co	Y	Zr	Nb
1A	2.35 ± 0.64	< 616	(0.15 ± 0.03) %	2.87 ± 0.49	< 104	19.4 ± 3.7	(0.23 ± 0.04) %	29.7 ± 6.4
1B	1.65 ± 0.47	920 ± 175	(0.11 ± 0.02) %	2.34 ± 0.37	333 ± 90	18.0 ± 2.8	(0.20 ± 0.030 %	26.6 ± 7.5
2A	1.33 ± 0.05	< 616	889 ± 182	1.90 ± 0.45	< 104	<17.3	(0.13 ± 0.02) %	17.2 ± 2.9
2B	2.51 ± 0.70	704 ± 122	(0.17 ± 0.04) %	2.98 ± 0.75	186 ± 52	<17.3	(0.24 ± 0.06) %	41.9 ± 9.6
3A	1.72 ± 0.41	640 ± 98	679 ± 126	1.90 ± 0.31	136 ± 31	<17.3	(0.19 ± 0.04) %	31.2 ± 3.3
3B	1.35 ± 0.37	< 616	375 ± 87.7	1.58 ± 0.29	< 104	<17.3	(0.12 ± 0.02) %	28.2 ± 4.8
4A	0.93 ± 0.23	< 616	824 ± 169	1.08 ± 0.22	< 104	<17.3	870 ± 139	17.0 ± 2.4
4B	0.47 ± 0.14	< 616	922 ± 213	1.18 ± 0.28	< 104	<17.3	547 ± 115	< 13.7
5A	0.58 ± 0.16	< 616	801 ± 160	0.89 ± 0.24	< 104	<17.3	594 ± 107	< 13.7
5B	0.93 ± 0.19	< 616	652 ± 115	1.21 ± 0.37	< 104	<17.3	850 ± 167	16.5 ± 3.0
6A	0.88 ± 0.20	< 616	647 ± 131	0.92 ± 0.21	< 104	<17.3	843 ± 156	15.5 ± 3.0
6B	1.34 ± 0.25	< 616	634 ± 125	1.38 ± 0.26	< 104	<17.3	(0.15 ± 0.03) %	< 13.7
7A	0.92 ± 0.16	< 616	697 ± 122	1.62 ± 0.43	< 104	<17.3	(0.11 ± 0.02)%	< 13.7
7B	1.42 ± 0.32	(0.11 ± 0.02)%	820 ± 174	1.99 ± 0.51	295 ± 53	<17.3	(0.15 ± 0.03) %	22.7 ± 3.8
8A	1.51 ± 0.45	(0.11 ± 0.03)%	957 ± 223	1.98 ± 0.43	< 104	<17.3	(0.14 ± 0.03) %	30.4 ± 2.3
8B	2.05 ± 0.41	875 ± 138	(0.11 ± 0.02) %	2.60 ± 0.53	485 ± 88	<17.3	(0.17 ± 0.03) %	37.6 ± 6.5
9A	1.26 ± 0.27	< 616	(0.16 ± 0.03) %	2.02 ± 0.32	190 ± 40	<17.3	(0.12 ± 0.03) %	< 13.7
9B	2.78 ± 0.77	908 ± 148	(0.16 ± 0.04) %	3.11 ± 0.81	281 ± 46	19.6 ± 5.0	(0.26 ± 0.06) %	43.9 ± 7.8
10A	2.81 ± 0.49	(0.10 ± 0.02) %	(0.25 ± 0.06) %	2.98 ± 0.69	282 ± 51	22.8 ± 5.1	(0.33 ± 0.07) %	52.2 ± 10.2
10B	1.61 ± 0.38	917 ± 168	(0.12 ± 0.03) %	2.17 ± 054	< 104	19.8 ± 4.3	(0.18 ± 0.03) %	57.0 ± 9.8
25A	11.61 ±1.78	(0.59 ± 0.10)%	(0.14 ± 0.03) %	7.89 ± 1.69	675 ± 117	67.3 ± 0.4	(0.97 ± 0.17) %	184 ± 31.4
25B	16.6 ±3.44	(1.14 ± 0.21)%	(0.18 ± 0.04) %	13.76 ± 2.61	< 104	86.2 ± 5.3	1.86 ± 0.31 %	337 ± 60.9

Table 4.4 Correlation Matrix Table for EDXRF Results of the Major Constituents

	Ti	Mn	Fe	Zr	Nb
Ti	1				
Mn	0.25	1			
Fe	0.96	0.33	1		
Zr	0.97	0.22	0.95	1	
Nb	0.90	0.19	0.88	0.90	1

Table 4.5 Elemental concentrations for soil samples from Maumba Central (in μg/g unless otherwise stated), $\overline{X} \pm 1STD$; n=2

Sample	Ti (%)	V	Mn	Fe (%)	Co	Zr	Nb
11A	2.52 ± 0.65	752.1 ± 127.5	(0.15 ± 0.03) %	2.89 ± 0.47	220 ± 52	(0.18 ± 0.04) %	42.6 ± 7.0
11B	2.18 ± 0.31	< 616	718 ± 140	2.62 ± 0.53	< 104	(0.18 ± 0.03)%	63.5 ± 14.0
12A	1.51 ± 0.37	< 616	702 ± 129	1.75 ± 0.46	291 ± 78	(0.12 ± 0.04)%	26.3 ± 5.0
12B	1.34 ± 0.24	< 616	519 ± 112	1.77 ± 0.42	225 ± 61	(0.11 ± 0.02) %	28.5 ± 5.1
13A	1.53 ± 0.25	< 616	754 ± 152	1.61 ± 0.35	127 ± 28	(0.13 ± 0.03) %	25.9 ± 6.2
13B	1.98 ± 0.41	< 616	948 ± 190	2.71 ± 0.71	268 ± 68	(0.18 ± 0.04) %	36.7 ± 7.8
14A	0.95 ± 0.21	< 616	375 ± 80	1.35 ± 0.43	106 ± 19	884 ± 180	19.4 ± 2.8
14B	0.71 ± 0.2	< 616	250 ± 57	1.37 ± 0.35	222 ± 41	738 ± 137	39.2 ± 7.9
15A	1.09 ± 0.23	< 616	360 ± 76	1.31 ± 0.23	< 104	929 ± 177	27.6 ± 6.1
15B	0.88 ± 0.13	< 616	411 ± 80	1.36 ± 0.29	< 104	891 ± 140	17.0 ± 3.4
16A	1.29 ± 2.21	< 616	449 ± 78	1.64 ± 0.03	132 ± 22	(0.11 ± 0.02) %	18.5 ± 3.6
16B	0.96 ± 0.15	862.3 ± 145.4	370 ± 97	1.53 ± 0.37	158 ± 40	933 ± 163	29.9 ± 5.8
17A	0.55 ± 0.12	(0.11 ± 0.03) %	388 ± 81	0.97 ± 0.22	< 104	479 ± 79	45.5 ± 7.1
17B	1.34 ± 0.27	< 616	373 ± 62	1.67 ± 0.31	< 104	(0.11 ± 0.02) %	20.2 ± 4.6
18A	1.22 ± 0.27	< 616	772 ± 91	1.75 ± 0.41	196 ± 41	776 ± 124	93.01 ± 17.9
18B	0.96 ± 0.24	< 616	996 ± 114	1.61± 0.33	253 ± 42	685 ± 124	13.8 ± 3.2
19A	1.74 ± 0.47	(0.12 ± 0.02) %	(0.13 ± 0.02) %	2.07 ± 0.56	187 ± 41	(0.14 ± 0.03) %	28.6 ± 5.2
19B	0.90 ± 0.19	< 616	987 ± 133	1.48 ± 0.29	< 104	747 ± 121	< 13.7
20A	1.06 ± 0.23	(0.15 ± 0.03) %	364 ± 69	1.36 ± 0.23	< 104	980 ± 213	16.7 ± 3.2
20B	1.05 ± 0.21	< 616	282 ± 65	2.14 ± 0.48	148 ± 32	(0.16 ± 0.03) %	26.5 ± 4.3

Table 4.6 Elemental concentrations for soil samples from 'Maumba ya Chini' (in μg/g unless otherwise stated), $\overline{X} \pm 1STD$; n=2

Sample	Ti (%)	Fe (%)	Zr
21A	0.18 ± 0.05	0.37 ± 0.09	353 ± 61
21B	0.30 ± 0.08	0.29 ± 0.08	625 ± 111
22A	0.13 ± 0.03	0.15 ± 0.03	361 ± 67
22B	0.28 ± 0.06	934.1 ± 210.3	741 ± 124
23A	0.18 ± 0.04	0.15 ± 0.03	367 ±73
23B	0.19 ± 0.04	0.17 ± 0.04	278 ± 49
24A	0.23 ± 0.06	0.15 ± 0.03	536 ± 109
24B	0.23 ± 0.05	0.14 ± 0.03	601 ± 103

Manganese

The concentration levels of this element is found to range from 249.6 μg/g to 0.25 % in forty-four (44) samples and a mean of 822.2 μg/g. Out of the eight samples from Maumba ya Chini, however, the element appears only twice with the highest value of 261.9 μg/g. Manganese is weakly correlated to titanium, iron, zirconium and niobium as shown in Table 4.4. This is in agreement with Mangala (1987), where the concentration distribution of manganese was found to be weakly correlated to titanium and iron. The concentrations of the element in Mrima Hill varied from 3556 μg/g to 17.1 % with a calculated mean of 6.3 %. This difference is explained by the fact that Mangala mainly considered rock samples as opposed to the fine soil samples.

Iron

Iron occurs in all the samples analysed with a range of 0.09 % to 3.11 % and a mean of 1.57 %. When compared to other elements of interest, a strong correlation to zirconium

and niobium is evident and is also comparable to the correlation to titanium. According to Mangala (1987) study in Mrima Hills, the concentration of the element varied from 5.00 % to 30.00 % with a mean of 21.25 %. This is much higher than the results in this study. Like titanium, this element is also found to correlate strongly with the activity concentrations of Th-232 and U-238 as shown in Tables 4.2 and 4.3. However, a weak correlation with manganese is observed in this study and which is in agreement with Mangala (1987).

Table 4.7 Correlation Matrix Table for Activity Concentrations of Th-232 and U-238 and the Elemental Concentrations of Titanium, Iron and Zirconium

	Ti	**Fe**	**Zr**	**Nb**	**Th-232**	**U-238**
Ti	1					
Fe	0.96	1				
Zr	0.97	0.95	1			
Nb	0.90	0.88	0.90	1		
Th-232	0.88	0.82	0.83	0.74	1	
U-238	0.83	0.78	0.77	0.68	0.92	1

Zirconium

All the samples exhibit moderate levels of zirconium. It occurs with a range of 278.4 μg/g to 0.33 % with a mean of 1189.3 μg/g. These concentration distributions of the element correlate strongly to those of titanium, niobium and iron and weakly to manganese. These values have been found to be slightly higher than the values of Mrima Hill reported by Mangala. According to Mangala, the values reported were between 94 μg/g and 720 μg/g and a mean of 251 μg/g. The correlation coefficients to the elements and to the activity

concentrations of Th-232 and U-238 have been presented in Tables 4.2 and 4.3.

Niobium

Niobium occurs in small quantities compared to titanium, iron and zirconium ranging from 13.8μg/g to 79.2 μg/g in 38 samples. Similar to the case of Manganese, out of the eight samples from Maumba ya Chini, the element appears only twice above detection limit with the higher value of 34.69 μg/g. The element occurs below detection limit in the rest of the 12 samples. The trend is similar with Mangala's study (1987) where the element was also reported as one of the minor constituent within concentration range of 1000 μg/g to 9000 μg/g. A mean of 31.81 ± 2.71 μg/g was obtained from the 38 samples compared to a mean of 4068 μg/g reported by Mangala (1987). Its concentration values correlated strongly to the concentrations of titanium, zirconium and iron with a weak correlation to that of manganese as shown in Tables 4.4. A fairly strong correlation with activity concentrations of Th-232 and U-238 is demonstrated in Table 4.7. Typical EDXRF spectra obtained from the titanium-bearing samples of Kwale are presented in Appendices VI and VII.

Cobalt

This element appears in some selected samples in concentrations ranging from of 106.0 to 485.3 μg/g. It is normally masked by Fe-β line a fact that interferes with the results if not well taken care of. In this study, a model spectrum which contained cobalt lines was used to fit all the samples spectra thus giving room for accurate reporting.

4.2 Results of Gamma Ray Analysis

In this study, a high-purity germanium detector spectrometer was used for the analysis. A comparative method using standard reference materials was used for evaluating concentrations. It is important therefore to present, in this section, the accuracy and detection limits of the method and the results of analysis of the standard reference material.

4.2.1 Accuracy of the Gamma Analysis Method Used

The degree of agreement of measured values and the certified values for the reference materials represents the accuracy of the analytical method. Accuracy of the gamma ray spectroscopy method was confirmed using the standard reference material, SRM 375 soil. A spectrum of the standard sample was collected on daily basis and used for spectral analysis for the sample, using the equation 4.1.

$$\varepsilon_\gamma = \frac{I}{A_t P_r} \times \frac{1}{M}, \qquad \text{..... 4.1}$$

where $\boldsymbol{\varepsilon_\gamma}$ is the detector efficiency at energy, **T**, ***I*** is the intensity, in counts per second, of a radionuclide ***i*** in the SRM, $\mathbf{A_t}$ is the activity, in Bq/kg, of the radionuclide **i**, $\mathbf{P_r}$ is the emission probability of the radionuclide **i** and **M** is the mass of the SRM in Kg. The results of the analysis of the certified reference material (IAEA, Soil 375) are presented in Table 4.8. The measured values for the three radionuclides are found to be within the IAEA certified limits.

Table 4.8 Results of Gamma Analysis of Certified Reference Material, IAEA Soil 375.

Radionuclide	Activity Concentrations in Bq/kg		Confidence interval (certified)
	Measured	Certified	
Th-232	18.6 ± 2.0	20.5	19.1 – 22.1
U-238	24.3 ± 5.0	24.4	18.6 – 31.4
K-40	438.0 ± 6.0	424.0	417 - 432

4.2.2 Detection Limits for Gamma Analysis for Th-232, U-238 and K-40

Detection limit is a term used to express the detection capability of a measurement system under certain conditions. An estimate for the lowest amount of activity of a specific gamma-emitting radionuclide that can be detected at the time of measurement can be calculated from several different expressions. A generally accepted expression for the estimate of the detection limits, which is frequently referred to as the lower limit of detection (LLD) and which contains a pre-selected risk of 5% of concluding falsely that activity is present and a 95% degree of confidence for detecting the presence of activity, is as follows:

$$LLD = \frac{4.66 S_b}{\in P_\gamma} \quad \text{.....4.2}$$

where S_b is the estimated standard error of the net count rate,

$\in$ is the counting efficiency of the specific nuclide's energy; number ≤ 1

P_γ is the absolute transition probability by gamma decay through the selected energy as for $\in$, number ≤ 1.

LLD of the above equation provides a means of determining the operating capability of a gamma measuring system without the influence of a sample and is applicable on the assumption that the count rate in the energy area taken for the specific nuclide and the count rate in the region(s) taken for background are independent.

A certified reference material, Soil 375, was used to obtain the detection limits of Th-232, U-238 and K-40 by applying Equation 4.3. According to IAEA (IAEA, 2000b), detection limit is defined as the true signal level which may be expected to lead to detection. The parameter, LLD, of a radionuclide by a gamma ray detector and according to IAEA (IAEA, 1974), is mathematically given by equation 3.1 discussed earlier as

$$LLD = \frac{3\sqrt{B_G}}{P_A} \times C \text{ , } \ldots\ldots\ldots\ldots \textbf{4.3}$$

where

B_G is the background counts obtained from gamma spectrum,

P_A is the peak area or the net area of the gamma spectrum, and

C is the activity concentration in Bq/kg of the specific radionuclide of interest.

Lower limits of detection for Th-232, U-238 and K-40 are presented in Table 4.9. The values for U-238 have been found to be two times that of Th-232 while that of K-40 was twenty times higher. However, decay energies and probability for decay also play a very critical role in gamma ray detection limits. Emission probability of K-40 (1460.81 KeV line only) is about 10.67% where as the emission probabilities for Th-232 (Tl-208, 583.1 KeV line) and U-238 (Bi-214, 609.3 KeV line) are 30.6% and 44.6% respectively.

Another factor likely to contribute to the detection limits is the efficiency of the detector. The higher the efficiency, the better the detection limit is likely to become.

Table 4.9 Lower Limits of Detection of the HPGe Detector for the Radionuclides of Interest

Radionuclide	Detection limits (Bq/kg)
Th-232	2.04
U-238	4.78
K-40	44.97

4.2.3 Activity Concentrations of Th-232, U-238 and K-40 in Soil Samples from Maumba

Samples from this region were sub-divided into three groups: Miembeni, Maumba Central and Maumba ya Chini. The results of analysis obtained are presented in Tables 4.10 to 4.12.

Miembeni Samples

The activity concentrations of samples from this region range from 49.2 ± 0.1 Bq/kg to 209 ± 1 Bq/kg for Th-232; 11.40 ± 0.15 to 134 ± 1 Bq/kg for U-238 means of 106 ± 21 and 73.1 ± 15.8 Bq/kg respectively. The K-40 concentrations levels are below the detection limits (<45 Bq/kg) for all the samples analysed as shown in Figure 4.1.

Samples 25A and 25B which had been collected from erosions deposits show high levels of activity concentrations in comparison with the other samples. These were 588 and 367 Bq/kg for Th-232 and U-238 respectively for sample 25A and 616 and 358 Bq/kg

respectively for sample 25B. This is evidence enough that radioactive ores exist uphill of Miembeni.

Table 4.10 Activity concentrations of Th-232 and U-238 K-40 - Miembeni

Soil sample	Activity Concentration in Bq/ Kg for:	
	Th-232	U-238
1A	204 ± 1	107 ± 2
1B	209 ± 1	109 ± 2
2A	156 ± 1	88.4 ± 1.4
2B	144 ± 1	84.6 ± 1.5
3A	138 ± 1	84.8 ± 0.2
3B	119 ± 1	76.9 ± 0.2
4A	49.2 ± 0.1	31.3 ± 0.2
4B	49.9 ± 2.0	32.1 ± 0.1
5A	55.7 ± 0.1	33.5 ± 0.2
5B	61.7 ± 0.9	35.1 ± 0.1
6A	102 ± 1	52.9 ± 0.2
6B	102 ± 1	104 ± 3
7A	97.9 ± 0.1	134 ± 5
7B	93.4 ± 0.1	128 ± 3
8A	79.5 ± 0.1	65.3 ± 0.2
8B	82.2 ± 0.1	67.4 ± 0.2
9A	80.2 ± 0.1	11.4 ± 0.1
9B	77.5 ± 0.1	60.1 ± 0.2
10A	112.3 ± 0.1	77.9 ± 0.2
10B	110 ± 1	79.4 ± 1.2
25A	587± 1	367± 4
25B	616 ± 0.1	358 ± 6

∗K-40 is below detection limit in all the samples

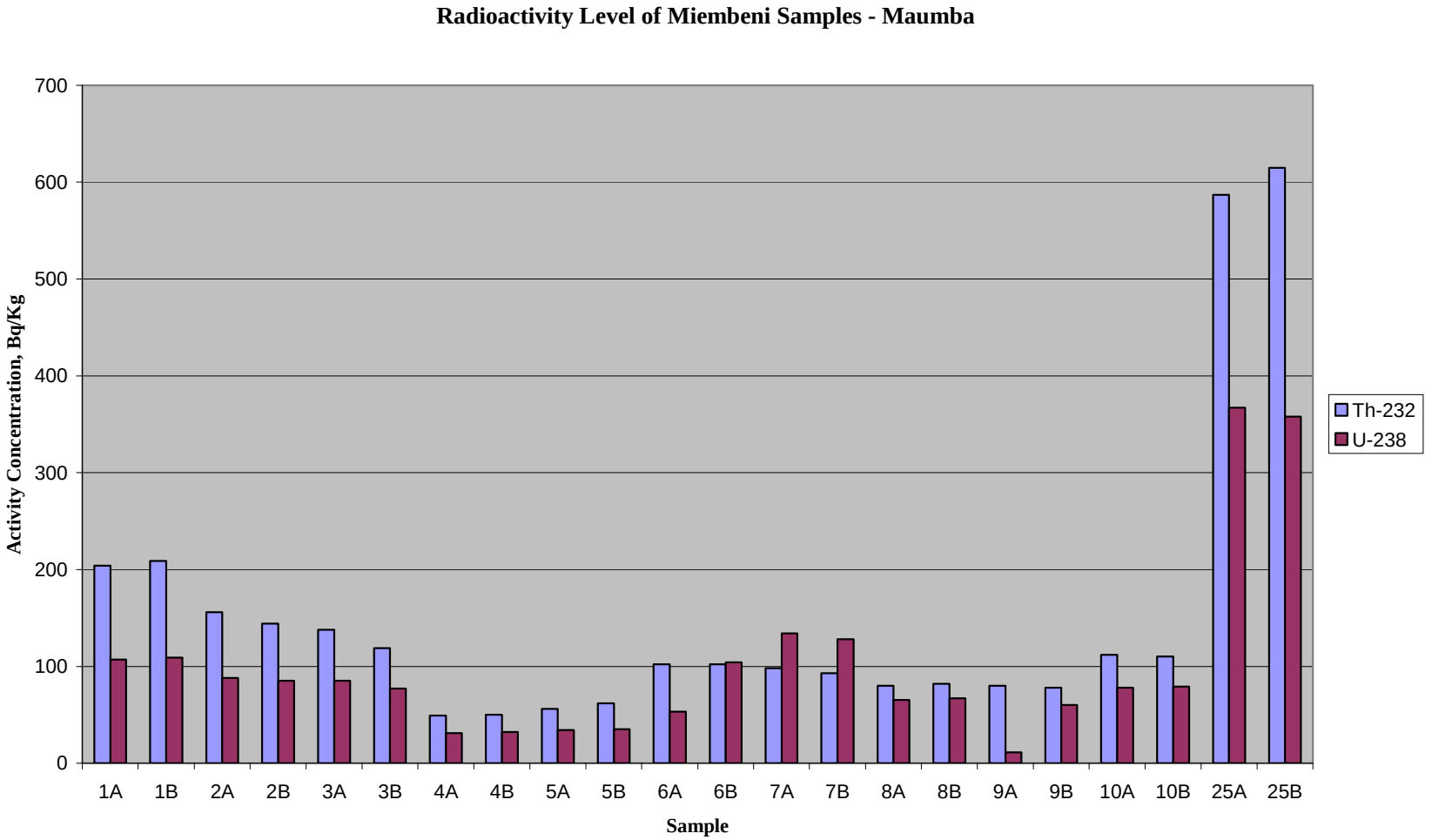

Figure 4.1 Activity levels of Th-232 & U-238 in Miembeni samples

Maumba Central Samples

The activity concentration in samples collected from Maumba Central, range from 30.6 - 107 Bq/kg with mean value 55.1 Bq/kg for Th-232 and 25.7 - 100 Bq/kg and mean value of 39.5 Bq/kg for U-238. Activities of levels for K-40 are below detection limit in all the samples (Table 4.11 & Figure 4.2).

Table 4.11 Activity concentrations of radionuclides in soil samples from Maumba Central

Soil sample	Activity Concentration in Bq/ Kg for:	
	Th-232	U-238
11A	70.29 ± 0.08	100.23 ± 0.44
11B	63.56 ± 0.06	52.82 ± 0.13
12A	51.25 ± 0.06	45.79 ± 0.12
12B	51.63 ± 0.08	43.46 ± 0.16
13A	34.53 ± 0.06	31.56 ± 0.13
13B	34.35 ± 0.05	31.66 ± 0.11
14A	30.63 ± 0.06	28.03 ± 0.07
14B	32.19 ± 0.08	26.56 ± 0.10
15A	37.99 ± 0.09	32.77 ± 0.11
15B	40.83 ± 0.06	25.71 ± 0.07
16A	46.18 ± 0.08	28.07 ± 0.09
16B	48.47± 0.06	28.90 ± 0.06
17A	42.35 ± 0.05	29.75 ± 0.05
17B	46.84 ± 0.05	26.81 ± 0.06
18A	106.77 ± 0.11	55.58 ± 0.11
18B	82.57 ± 0.10	42.48 ± 0.13
19A	92.78 ± 0.06	47.50 ± 0.06
19B	65.01 ± 0.08	44.01 ± 0.09
20A	62.52 ± 0.10	35.64 ± 0.13
20B	60.32 ± 0.07	32.54 ± 0.09

∗K-40 is below detection limit in all the samples

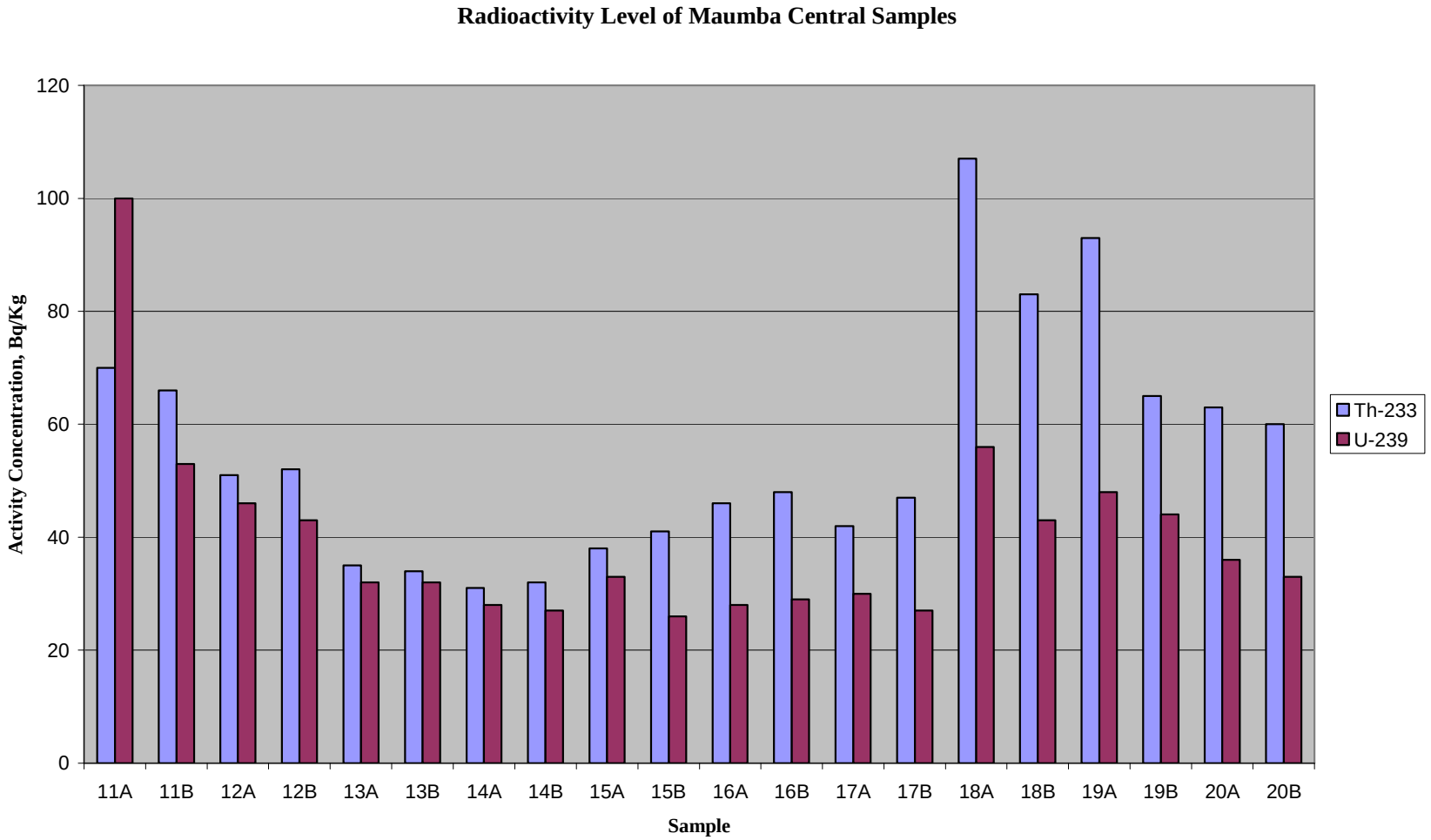

Figure 4.2 Activity levels of Th-232 & U-238 in Maumba Central

Maumba ya Chini Samples

The activity concentrations in samples collected from 'Maumba ya Chini', range from 24.3 - 35.3 Bq/kg with mean value of 29.2 Bq/kg for Th-232 and 16.2 - 24.6 Bq/kg for U-238 and mean value of 19.5 Bq/kg (Table 4.12 & Figure 4.3).

Table 4.12 Activity concentrations of radionuclides in soil samples from 'Maumba ya Chini'

Soil Sample	Activity Concentration in Bq/ Kg for:	
	Th-232	U-238
21A	24.3 ± 0.	17.1 ± 0.1
21B	26.5 ± 0.1	18.7 ± 0.1
22A	35.3 ± 0.1	24.6 ± 0.1
22B	33.8 ± 0.1	23.5 ± 0.1
23A	27.6 ± 0.1	17.5 ± 0.1
23B	32.1 ± 0.1	18.3 ± 0.1
24A	28.8 ± 0.1	20.1 ± 0.1
24B	25.4 ± 0.1	16.2 ± 0.1

∗K-40 is below detection limit in all the samples

4.2.4 Activity concentrations of Th-232, U-238 and K-40 in soil samples from Nguluku

The activity concentrations of radionuclides of interest are presented in Table 4.12. Activity values range from 14.5 - 57.9 Bq/kg with a mean of 29.6 Bq/kg for Th-232 for six samples and 11.0 - 35.3 Bq/kg with a mean of 27.1 Bq/kg for U-232. Sample Ngu3 was a top soil collected from surface run-off deposits. It was found to be highly radioactive in comparison with levels of Th-232 and U-238 (502.43 ± 3.87 and 292.19 ± 4.06 Bq/kg respectively). The results of this sample show that the soils uphill are mineralised with the two nuclides. None of the samples analysed had K-40, except for samples Ngu2 and Ngu3 where activity concentrations for K-40 were 78.9 Bq/kg and 52

Bq/K. Figure 4.4 shows the variation of the activity concentrations for the samples from Nguluku.

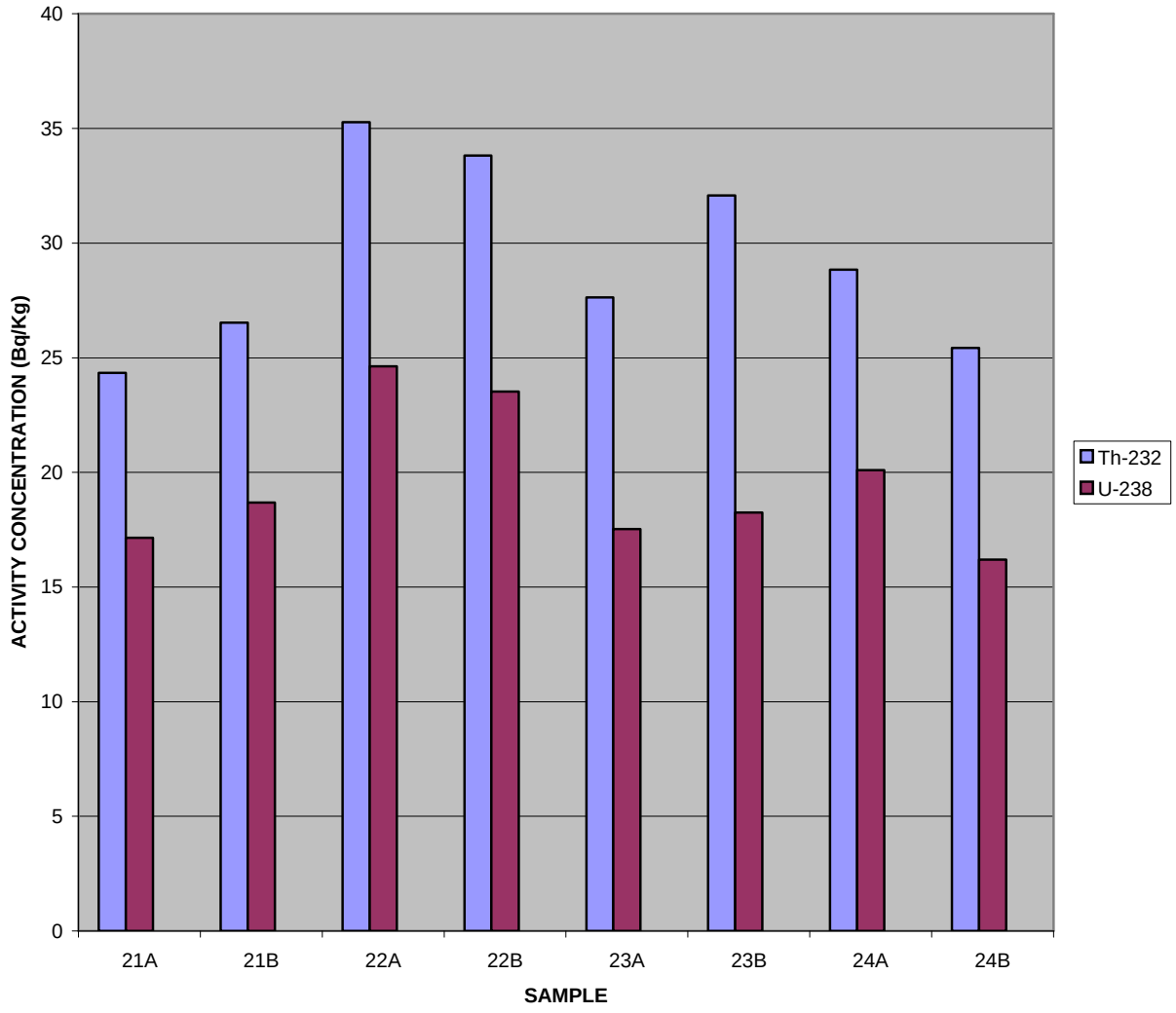

Figure 4.3 Activity levels of Th-232 & U-238 in Maumba ya Chini

Table 4.13: Activity concentrations of Th-232, U-238 and K-40 - Nguluku

Soil sample	Activity Concentration in Bq/ Kg for:		
	Th-232	U-238	K-40
Ngu1	37.59 ± 0.98	28.33 ± 1.04	< 45
Ngu2	57.89 ± 0.37	29.88 ± 0.36	78.88 ± 1.40
Ngu3	502.43 ± 3.87	292.19 ± 4.06	51.98 ± 10.01
Ngu4	18.34 ± 1.11	35.25 ± 1.21	< 45
Ngu5	15.04 ± 0.77	29.14 ± 0.82	< 45
Ngu6	14.46 ± 1.06	10.97 ± 1.17	< 45
Ngu7	34.16 ± 0.44	28.89 ± 0.65	< 45

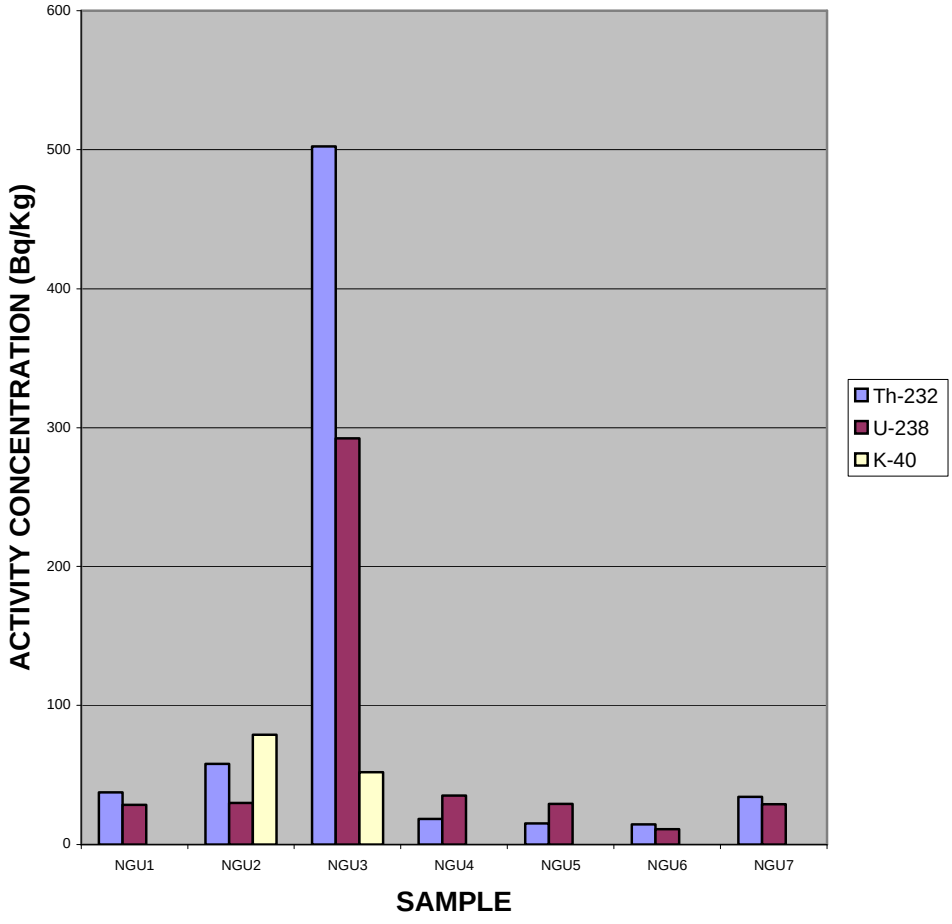

Figure 4.4 Activity levels of Th-232, U-238 & K-40 in Nguluku samples

For most of the samples analysed, the activity levels for the three nuclides namely U-238, Th-232 and K-40 are < 100 Bq/K except for sample Ngu3 (300 – 500 Bq/K) from a partially mineralised area.

4.3 Outdoor Gamma Dose Rate Levels in Maumba

The gamma dose rates D in outdoor air at 1 m above the ground was evaluated from the results of radionuclides concentrations of samples analysed. Dose conversion factors for K-40, U-238 and Th-232 used were 0.0417, 0.462 and 0.604, in nGy/h per Bq/kg respectively (UNSCEAR, 1998). The dose rates for an adult person compared to global averages (Table 4.14).

Table 4.14 Outdoor Dose rate and Annual Effective Dose for Maumba

Radionuclide	Mean activity concentration (Bq/ Kg)	Exposure (nGy/h) (E-09 Gy/h)	Dose (nSv)	Annual effective dose (µSv/y)
Miembeni				
Th-232	106.1 ± 21.26	64.08 ± 12.84	44.86 ± 8.99	55.05 ± 11.03
U-238	73.14 ± 15.78	33.79 ± 7.29	23.65 ± 5.10	29.02 ± 6.26
	Totals	97.87	68.51	84.07
Maumba Central				
Th-232	55.05 ± 9.71	33.25 ± 5.86	23.28 ± 4.11	28.57 ± 5.04
U-238	39.49 ± 7.96	18.24 ± 3.68	12.77 ± 2.57	15.67 ± 3.15
	Totals	51.49	36.05	44.24
'Maumba ya Chini'				
Th-232	29.24 ± 4.58	17.66 ± 2.77	12.36 ± 1.94	15.17 ± 2.38
U-238	19.51 ± 2.56	9.01 ± 1.82	6.31 ± 0.83	7.74 ± 1.02
	Totals	26.67	18.67	22.91

The outdoor annual effective doses for the three subdivisions of the larger Maumba sand dune – Miembeni, Maumba Central, and Maumba ya Chini – are found to be 84.07, 44.27 and 22.91 μSv/y respectively. According to UNSCEAR (2000), the worldwide annual total effective dose due to external radiation is within 0.3 – 0.6 mSv range with an average of 0.48 mSv, for the outdoor component limit 70 μSv while for the indoor component is 410 μSv. In comparison to the world averages only samples from Miembeni exceed the required limit (<70 μSv).

4.4 Outdoor gamma Dose Rate Levels in Nguluku

The total outdoor dose rates are estimated for Th-232 and U-238 and are summarised in Table 4.15 where activity from K-40 was found to be insignificant. Based on the mean value of dose exposure rate for the entire Nguluku, annual outdoor effective exposure dose rate to an adult person was estimated to be 155.88 μSv: double the world average.

Table 4.15 Outdoor Total Dose Rate and Annual Effective Dose Rates for Nguluku region

Radionuclide	Mean activity concentration (Bq/ Kg)	Exposure (nGy/h)	Dose (nSv)	Annual effective dose (μSv/y)
Th-232	177.5 ± 17.05	107.21 ± 10.30	75.05 ± 7.21	92.09 ± 8.85
U-238	162.5 ± 8.28	75.08 ± 3.83	52.56 ± 2.68	63.79 ± 3.29
Total Dose due from Th-232 and U-238		182	128	156

Chapter 5

Conclusions and Recommendations

5.0 Introduction

In this chapter, the conclusions and suggestions for further studies are presented based on the objectives of the study. Elemental concentration distribution has been summarised for the major constituents where thorium and uranium, though major contributors to radioactivity, have not been reported as major constituents of Maumba and Nguluku sands.

5.1 General Conclusions

The following conclusions have been drawn:

i. The major elements in soil from Maumba area are iron, titanium and zirconium with mean concentrations of 1.57 %, 1.21 % and 1189.3 μg/g.

ii. The activity concentrations of Th-232 and U-238 are higher than world average of 25 Bq/kg, apart from concentration levels for Maumba ya Chini.

iii. Annual effective doses to adults due to gamma dose in air 1m above the ground, are below the world average value (< 70 μSv) for two sub-regions of Maumba (44 μSv for Maumba Central and 23 for Maumba ya Chini) and slightly higher (84 μSv) than the world average value for the third sub-region of Maumba (Miembeni). An annual dose level for Nguluku was estimated as 156 μSv, higher than the world average value by a factor of two.

5.2 Recommendations and Suggestions for Further Research

A similar but more detailed study is highly recommended for entire Kwale district and the environs. This should be extended to cover activity levels in plants and water. Various plants used for food or otherwise should be considered for this study. Sources of water used for drinking and cleaning purposes, such as wells and boreholes and Mukurumudzi River should also be investigated.

Further study should also be carried out, especially in the neighbouring areas, to determine levels of the indoor component of annual effective radiation exposure dose.

On the method of elemental analysis used, EDXRF, lowest limits of detection (LLD) for the elements of interest were found to be considerably higher than is usual the case. This was attributable to the detector resolution (220-230 eV) during the time when these measurements were done. Typical resolution values of 180 – 200 eV yield much lower LLD values. There should be an endeavour therefore to bring down the detector resolution to within the typical range.

It has been observed that variation in the depths at which samples were did not bring out significant difference in both the elemental contents and radioactivity concentrations. It would therefore be important that further research be carried out for soil samples of depth 1 – 2 metres or even at expected mining depths for further investigation on the variation of the two parameters with depth.

The Government of Kenya, through Radiation Protection Board should ensure a continuous radiation monitoring of Kwale district and the environs especially following excavation from currently on-going titanium mining activities. This would ensure that the enhanced radioactivity level does not put the workers and the public at risk, and to provide protective measures where and when radiation levels are found as a threat to human health.

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APPENDICES

Appendix I Uranium-238 Decay Series

Radionuclide	Half-life	Mode of Decay[a]	Gamma energy[b] (KeV)
U-238	4.468 x 10^9 a	Alpha	
Th-234	24.10 d	Beta	63.29 (4.8%), 92.38-92.8 (5.6%),
Pa-234m	1.17 min	Beta	1001.03 (0.837%)
U-234	245 700 a	Alpha	
Th-230	75 380 a	Alpha	
Ra-226	1600 a	Alpha	186.211 (3.59%)
Rn-222	3.8235 d	Alpha	
Po-218	3.10 min	Alpha	
Pb-214	26.8 min	Beta	351.932 (37.6%)
Bi-214	19.9 min	Beta	609.312 (46.1%)
Po-214	164.3 μs	Alpha	
Pb-210	22.20 a	Beta	46.539 (4.25%)
Bi-210	5.012 d	Beta	
Po-210	138.376 d	Alpha	
Pb-206	Stable		

[a]Only major modes of decay are shown
[b]Some important gamma emissions

Appendix II Thorium-232 Decay Series

Radionuclide	Half-life	Mode of Decay[a]	Gamma energy[b] (KeV)
Th-232	1.405 x 10^{10} a	Alpha	
Ra-228	5.75 a	Beta	
Ac-228	6.15 h	Beta	911.204 (25.8%)
Th-228	1.912 a	Alpha	
Ra-224	3.66 d	Alpha	240.986 (4.1%)
Rn-220	55.6 s	Alpha	
Po-216	0.145 s	Alpha	
Pb-212	10.64 h	Beta	238.632 (43.6%)
Bi-212	60.55 min	Beta 64.06% Alpha 35.94 %	727.330 (6.67%)
Po-212	0.299 μs	Alpha	
Tl-208	3.053 min	Beta	583.191 (84.5%), 2614.533 (99.16%)
Pb-208	Stable		

[a]Only major modes of decay are shown
[b]Some important gamma emissions

Appendix III Typical AXIL computer generated elemental concentrations report (in g/g)

*** RESULTS ***

MPLE: 261 MATRIX: [A0= 11440] WEIGHT [G/CM^2]: 0.04519

	E [KEV]	INT [C/S]	S	T	CONC [FRAC]	ERROR
	4.508	4.601	2.20E+04	0.0381	2.31E 02	1.52E 03
	4.949	0.200	3.40E+04	0.0474	6.08E 04	7.62E 05
	5.895	1.442	6.41E+04	0.0701	1.54E 03	1.06E 04
	6.400	39.322	8.33E+04	0.1176	2.75E 02	1.79E 03
	6.925	0.524	1.06E+05	0.1275	1.82E 04	2.56E 05
	8.041	0.024	1.47E+05	0.2003	7.44E 06	LDL
	8.631	0.148	1.75E+05	0.2420	3.47E 05	4.08E 06
	10.540	0.074	2.20E+05	0.3758	1.37E 05	2.29E 06
	13.375	0.037	4.44E+05	0.5876	2.30E 06	LDL
	14.142	0.063	5.06E+05	0.6445	3.44E 06	1.20E 06
	12.760	0.077	3.85E+05	1.0275	7.78E 06	1.64E 06
	14.933	0.258	5.53E+05	0.7004	1.20E 05	1.54E 06
	15.800	0.019	4.07E+05	1.1163	1.20E 06	LDL
	15.746	47.071	5.02E+05	0.7554	2.10E 03	1.42E 04
	16.504	0.877	6.30E+05	0.8578	3.60E 05	2.92E 06
	17.443	0.027	7.09E+05	0.8686	1.02E 06	LDL

hen analyzing the same sample with Fe 55 source please consider:

bsorption intercept: A0= 0799
Absorption slope: Ai= 2.020

ESIDUAL MATRIX is characterised by:

Absorption intercept: A0= 7125
Absorption slope: Ai= 2.020

esidual matrix characterised by: INORGANIC ORIGIN and
composed of MIXTURE of ALUMOSILICATES, OXIDES, CARBONATES
or NITRATES of measured elements!

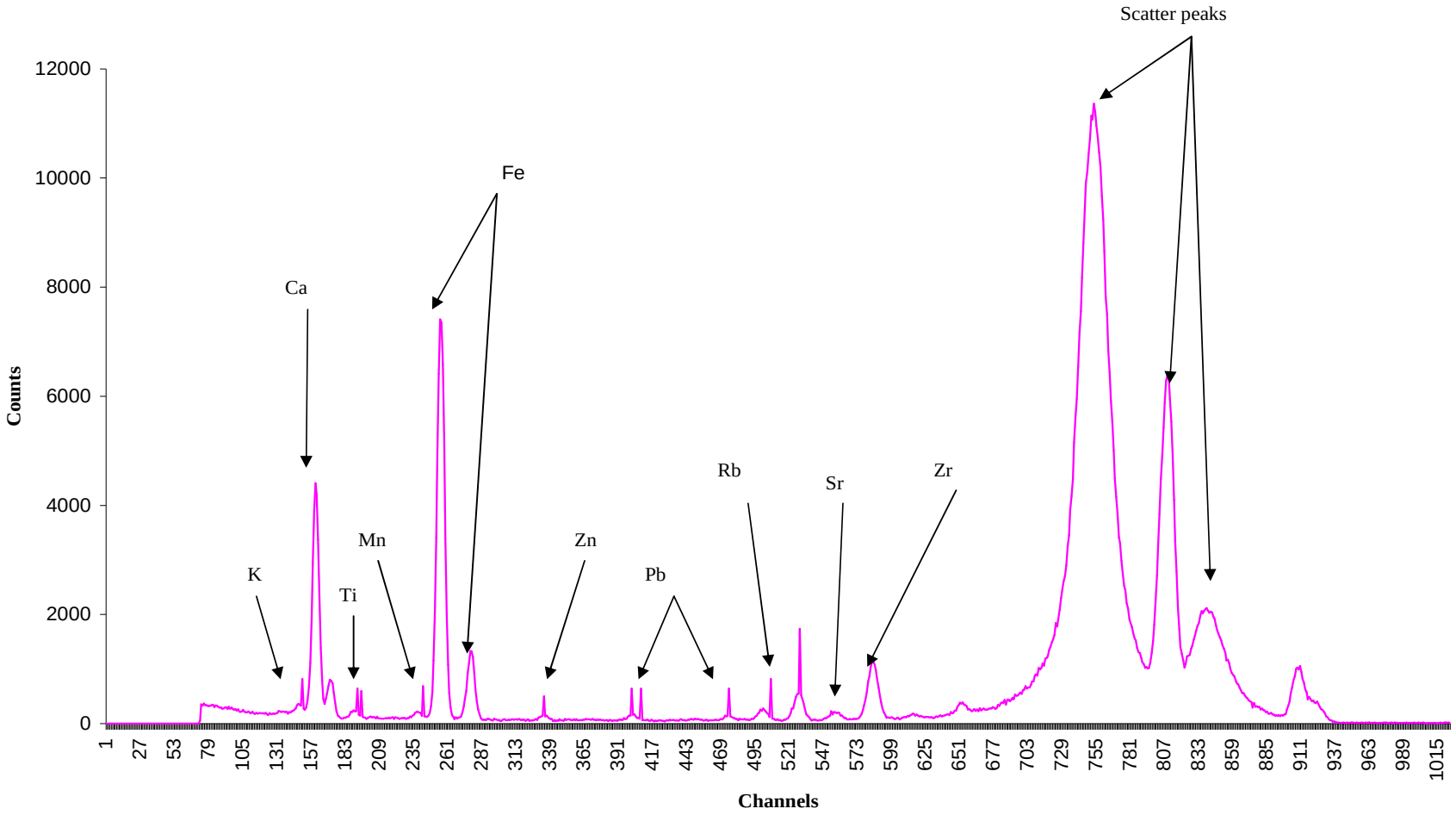
*** RESULTS ***

SAMPLE: 262 MATRIX: [A0= 7060] WEIGHT [G/CM^2]: 0.06153

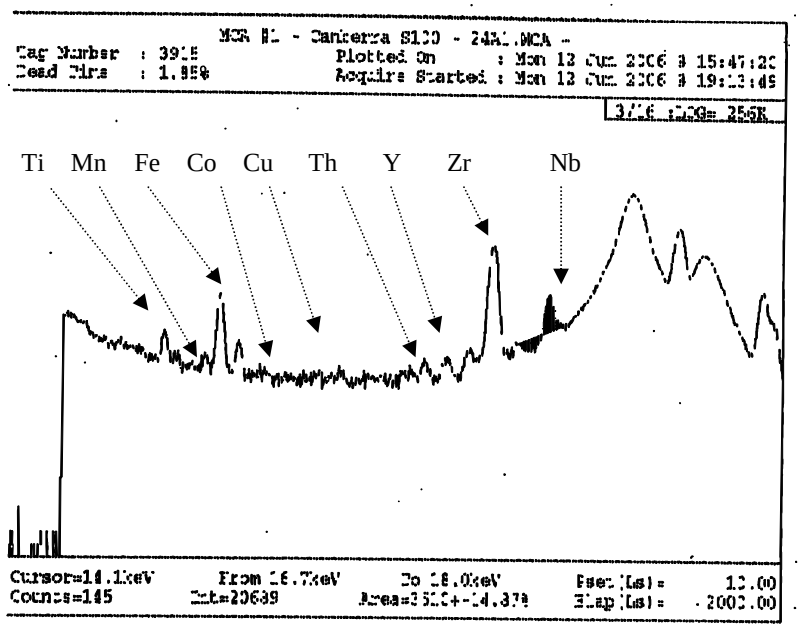
EL	E [KEV]	INT [C/S]	S	T	CONC [FRAC]	ERROR
TI	4.508	4.673	2.20E+04	0.0292	1.55E 02	1.02E 03
V	4.949	0.237	3.40E+04	0.0366	4.75E 04	6.92E 05
MN	5.895	1.486	6.41E+04	0.0715	1.06E 03	7.29E 05
FE	6.400	40.050	8.33E+04	0.0751	1.83E 02	1.19E 03
CO	6.925	0.205	1.06E+05	0.1036	1.04E 04	1.71E 05
CU	8.041	0.015	1.47E+05	0.1675	2.43E 06	LDL
ZN	8.631	0.106	1.75E+05	0.2008	1.52E 05	2.70E 06
PB	10.540	0.137	2.20E+05	0.3270	1.10E 05	1.56E 06
RB	13.375	0.071	4.44E+05	0.5541	2.54E 06	7.75E 07
SR	14.142	0.129	5.06E+05	0.6095	3.70E 06	7.70E 07
TH	12.760	0.121	3.85E+05	0.7619	5.60E 06	1.04E 06
Y	14.933	0.301	5.53E+05	0.6661	8.20E 06	9.62E 07
U	15.800	0.021	4.07E+05	1.0515	8.00E 07	LDL
ZR	15.746	56.041	5.02E+05	0.7211	1.40E 03	9.47E 05
NB	16.504	1.127	6.30E+05	0.8207	2.65E 05	1.77E 06
MO	17.443	0.051	7.09E+05	0.8343	1.05E 06	LDL

When analyzing the same sample with Fe 55 source please consider:

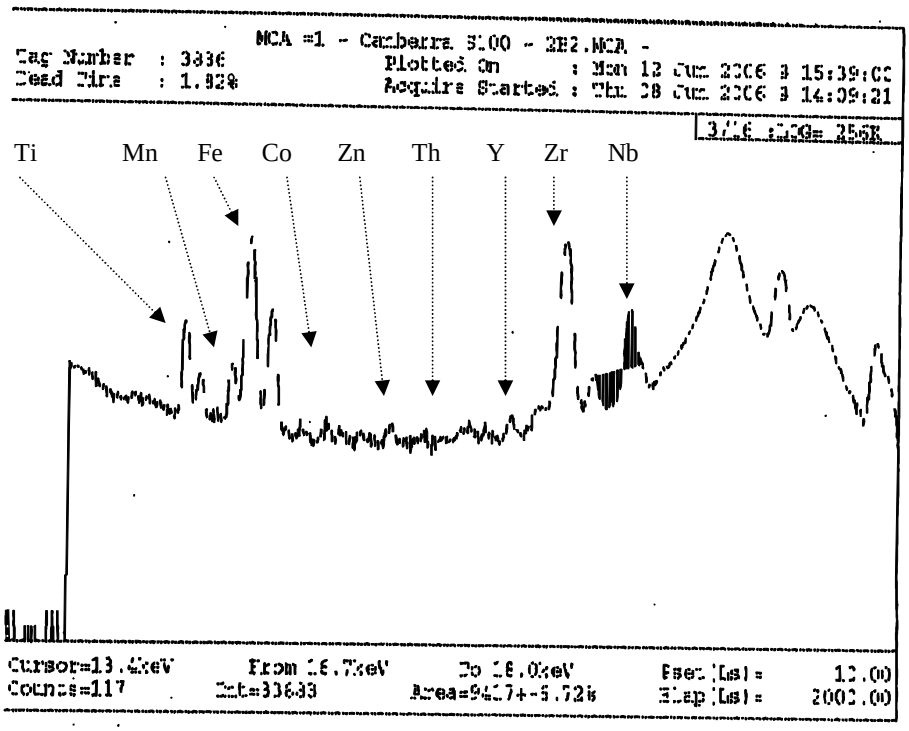
Appendix IV Typical EDXRF Spectrum - Standard Sample, Soil-7



Appendix V A typical spectrum from titanium bearing ore samples of Kwale – sample 24A1



Appendix VI A typical spectrum from titanium bearing ore samples of Kwale – Sample 2B2



Appendix VII A Typical Gamma Spectrum