



Evaluation of Naturally Occurring Radioactive Materials and Toxic Heavy Metals in the Surface Soil Around Serule Prospective Mining Area in Botswana

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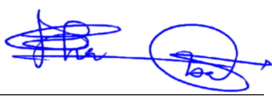
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Certification

The undersigned certify that they have read and hereby recommend for acceptance by the Faculty of Sciences a dissertation titled **Evaluation of Naturally Occurring Radioactive Materials and Toxic Heavy Metals in the Surface Soil Around Serule Prospective Mining Area in Botswana**, in fulfillment of the requirements for the degree of Master of Science (Physics) of the Botswana International University of Science and Technology.

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Abstract

Human exposure to Naturally Occurring Radioactive Materials (NORMs) and toxic heavy metals has been a concern for the entire history of mankind since they are commonly found in the environment. Their increased levels are a result of anthropogenic activities such as mining. A-cap Resources Ltd, now A-cap Energy Ltd company discovered that there were large uranium deposits in the underlying rocks of Serule. It was given licensing to start mining in 2016 with a lease of about 144 km². Uranium mining results in large disruptions of surface soils which causes radionuclide and metal contamination thus affecting soil quality and human and environmental health. As a result, this work focused on evaluating NORMs and toxic heavy metal concentrations in the surface soil around Serule prospective mining area as well as their health risk to members of the public. From a depth of about 15 cm, 29 soil samples were randomly collected using an auger and analysed for natural radionuclides and selected toxic heavy metals using a High-Purity Germanium (HPGe) detector and Inductively Coupled Plasma Mass Spectrometer (ICPMS), respectively. A control sample was also collected and analysed in the same manner. All measurements obtained were compared to the control and reference standards.

The HPGe detector with a relative efficiency of 60 % and a 2.0 keV resolution was used to identify and measure activity concentrations of radionuclides found in samples. Average activity concentrations of ²²⁶Ra, ²³⁸U, ²³²Th, ⁴⁰K and ²¹⁰Pb in areas with high activity of ²³⁸U were 1126.26 ± 6.49 , 498.21 ± 10.01 , 71.39 ± 1.27 , 284.18 ± 21.74 and 1490.20 ± 28.77 in Bq/kg, respectively. These activities were higher in comparison to the world average values as reported by UNSCEAR (2000), where average activity concentrations of ²²⁶Ra, ²³⁸U, ²³²Th and ⁴⁰K were 32, 33, 45 and 420 in Bq/kg, respectively. The world average activity concentration value of ²¹⁰Pb is still not published.

The radiological risk to members of the public in the study area was calculated using radiological parameters from UNSCEAR (2000). Areas with high activity of ^{238}U had higher concentrations of radiological parameters in comparison to the world average, areas with low activity of ^{238}U and the control. This showed that areas with high activity of ^{238}U pose a radiological risk to residents.

Following an acid digestion of method 3051A, toxic heavy metals were analysed using an Agilent (7500 series) ICP-MS. This was used to determine mass concentrations of these heavy metals. In areas with high activity of ^{238}U , toxic heavy metal concentrations decreased in the order $\text{Cr} > \text{Pb} > \text{As} > \text{Cd} > \text{Hg}$ with values 101, 26.4, 9.56, 0.133 and 0.00475 in mg/kg, respectively. These concentrations were compared to the maximum permissible limits of World Health Organisation (WHO) guidelines, where the maximum permissible limits for Cr, Pb, As and Cd were 10, 100, 20 and 3 in mg/kg, respectively. The maximum permissible limit for Hg is not yet published. Cr was the only toxic heavy metal greater than the recommended World Health Organisation (WHO) value for areas with high activity of ^{238}U . Using these concentrations, the total non-carcinogenic risk for adults and children was determined and results showed that they both have a close to zero non-carcinogenic risk due to toxic heavy metals in the study area. Toxic heavy metals from all locations of the study area showed a carcinogenic risk that was within the allowable limit of 1×10^{-4} , therefore, the carcinogenic threat to residents due to toxic heavy metals is negligible.

Dedication

To my family and friends.

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List of Abbreviations

- NORMs: Naturally Occurring Radioactive Materials
- HPGe: High Purity Germanium detector
- MCA: Multichannel Analyser
- IAEA: International Atomic Energy Agency
- PVC: Polyvinyl Chloride
- GPS: Graphical Positioning System
- ICP-MS: Inductively Coupled Plasma Mass Spectrometry

Introduction

1.1 Problem statement and motivation

Research into exposure to radiation and toxic heavy metal pollution has attracted public attention around uranium mining areas worldwide [1, 2, 3, 4]. Radiation is energy transmitted in wave forms or energized particles. It can be classified into ionizing and non-ionizing. Ionizing radiation is the type that has so much energy to eject electrons from an atom thereby leaving it positively charged. The charged ions are unstable, therefore, they de-excite in a bid to attain stability. During this process, radiation is emitted. Depending on the branching ratio (intensity), a nuclide that decays undergoes alpha, beta and gamma decay modes. On the other hand, non-ionizing radiation is less energetic and does not charge atoms, hence it does not change matter [5]. In general, the term radiation is normally used for ionizing radiation. Nuclear radiation is a part of our everyday lives and is found everywhere in the environment [6]. Three main known sources of radiation can be identified, as follows, Naturally Occurring Radioactive Materials (NORMs), Anthropogenic radiation and Cosmic radiation.

NORMs are radioactive materials or radionuclides that were present since the big bang and usually have long half lives e.g. ^{238}U , ^{235}U , ^{232}Th and ^{40}K [7]. These can be detected even up to today because they have half lives that are larger than the earth's age (4.543×10^9 years) whereas NORMs like ^{237}Np cannot be detected because it has long decayed. Radiation dose from NORMs in a local area is affected by soil or rock composition, therefore, different soil or rock types have different radiation levels [8]. Major contributors of outdoor natural radiation are radionuclides in soils that belong to decay series of ^{238}U and ^{232}Th and of radioisotope of ^{40}K [9]. The National Council on Radiation Protection and Measurements of the United States of America

states that the major radiation exposure to humans is produced by natural radiation in the environment which gives about 85% of the annual radiation exposure dose to the world population [10]. Anthropogenic radiation comes from human activities like isotope production, manufacturing and usage of nuclear reactors or accelerators. Examples include ^{137}Cs , ^{90}Sr and ^{97}Tc .

Cosmic rays interact with atoms in the earth's atmosphere producing radioisotopes that result in cosmogenic radiation. ^{14}C , ^{14}N and ^3H are examples of the radioisotopes produced by cosmic rays. The amount of cosmic radiation reaching the earth's surfaces depends on altitude, hence, people living at high elevations are more open to elements of cosmic radiation than people who live in low elevations.

Conversely, any radiation dose has a potential health risk to humans and chronic exposure can lead to long term health effects. Above certain levels of radiation, tissues and organs can be impaired depending on absorbed dose, radiation type and their sensitivity. Malfunctioning of these can result in acute effects such as radiation burns, skin redness, hair loss and cellular and genetic damage which can eventually induce cancer [11]. Since radiation cannot be eliminated from the environment, controlling our exposure to it can lessen the risks to human health.

On the other hand, high concentrations of heavy metals are both of environmental and health concerns due to their persistence and cumulative trend. These are metals that are non degradable, have high density (more than 5 g/cm^3) and mass number above 40. Heavy metals in a particular region can be facilitated by mining, soil erosion, soil/rock weathering, industrial activities and many others [12]. At high doses, all substances are toxic/dangerous although some metals are still toxic at low doses; these are called toxic heavy metals. Lead, chromium, cadmium, arsenic and mercury are regarded the most toxic heavy metals to the public even at low concentrations [13]. Studies have shown that heavy metals can also be harmful to vegetation and animal life. Plants typically have a large metal uptake, as a result, toxic heavy metals are eventually consumed by animals and humans. Toxic heavy metals hinder essential biochemical processes and cause a threat to living organisms. Their high level of toxicity can result in multiple organ damage and fatality [14].

Between August-November 2014, an Australian company named A-cap Energy Ltd discovered the existence of uranium in Serule area. As a result, a shallow open pit mine based in Serule is expected to commence in the near future. This poses a poten-

tial increase in natural background radiation levels and toxic heavy metal disruptions in the area.

Since studies on baseline radiation levels and toxic heavy metal concentrations are at an infant stage in Serule, Botswana, there was a need for a comprehensive study aimed at establishing a reference guide on environmental radiation and toxic heavy metal levels in the area.

In this study, activity concentrations of the radionuclides, absorbed dose rate, annual effective dose equivalent, radium equivalent, external hazard index as well as excess lifetime cancer risk have been determined and discussed in detail. This has led to a better understanding on the amount of natural radiation exposure to humans due to Serule soils. After random soil sample collection, a High-Purity Germanium detector (HPGe) was used to conduct high resolution laboratory based radiation measurements. In order to establish the possible risk due to toxic heavy metals exposure in Serule soils, hazard identification, exposure assessment and risk characterisation were evaluated. An Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to identify specific mass elemental concentrations of toxic heavy metals. In addition, correlation between radionuclides and toxic heavy metal concentrations were discussed in detail. This study could establish a reference guide on environmental natural radiation levels and toxic heavy metals in Botswana.

1.2 Hypothesis

Serule soils are expected to have elevated activity concentrations of natural radionuclides due to the presence of uranium that was discovered by A-cap resources company [15]. Uranium mining gives rise to the concentrations of toxic heavy metals in soil [12], therefore, the baseline concentrations have to be studied. Due to currently undisturbed soils in the study area, toxic heavy metal concentrations are expected to be within the regulatory limits.

1.3 Aim and objectives

The aim of the study was to identify Naturally Occurring Radioactive Materials (NORMs) and toxic heavy metals in the surface soil around Serule prospective mining area in Botswana.

The objectives of this study were to;

- determine activity concentrations of radionuclides,
- measure elemental mass concentrations of toxic heavy metals,
- investigate correlations between toxic heavy metals and radionuclides,
- estimate the radiological and toxicological risk to people living in the vicinity of the study area.

1.4 Justification of the study

There is a rising demand for baseline soil data since it is used in officiation processes in relation to public health, land use and the environment [16]. Since there is limited or no environmental data on natural radiation and toxic heavy metal levels in Serule, the results of this study will not only be beneficial to academia but also the Radiation Protection Inspectorate of Botswana (RPI) may use it to enforce public and environmental exposure control for protecting the public. Sensitivity and reactivity to radiation and toxic heavy metals differs from one plant to another, therefore, the Department of Agriculture can use this baseline data to help them identify which plants will sustain the amount of natural radiation or toxic heavy metals in Serule hence advising farmers on which plants can be of good harvest in their area [17]. Ministry of health may also find this research helpful when looking at a patient's background history which will increase the chances of more accurate diagnosis. Moreover, this study will provide baseline data on levels of natural radiation and toxic heavy metals in Serule area. This will enable thorough environmental monitoring during the mining period and executable preparation or repatriation alternatives subsequent to mining.

This dissertation is divided into 5 chapters, viz;

- Chapter 1: introduction to the research problem, the main aim of the project, objectives and hypothesis are stated,

- Chapter 2: a discussion on background information and theoretical framework of radiation and radioactivity, toxic heavy metals and equipment used in this research project,
- Chapter 3: discussion of experiments carried out and techniques followed in the present study,
- Chapter 4: a detailed discussion of findings obtained from both HPGe and ICP-MS are interpreted in the form of graphs and tables under this chapter,
- Chapter 5: conclusions on the main points of the research and answers to the aim and objectives are stated. An outlook is also put forward.

Theoretical Considerations

This chapter gives a detailed discussion on background information of the present study. Literature on theoretical framework of radiation and radioactivity, NORMs, toxic heavy metals as well as equipment used in this study is also explained.

2.1 NORMs and toxic heavy metals in the environment

In general, NORMs in the environment exist in levels that do not cause potential harmful effects to human life; On the other hand, existence of toxic heavy metals in the environment can be harmful to humans even at low exposure levels. However, there is need for concern since levels of NORMs and toxic heavy metals are elevated due to natural hazards like earthquakes and human practices such as uranium mining [12]. Large amounts of waste material emanating from uranium mining can affect the environment and human life negatively. In radiation protection, radionuclides from the decay series of ^{238}U , ^{232}Th and the non-series ^{40}K are the most important NORMs to be studied as they lead to major radiation exposure to humans in the environment [9]. Their concentrations are dependent on local geological conditions. In decay processes of these NORMs, ionising radiation is emitted which can potentially cause biological damage to the human tissues and organs [18]. On the other hand, heavy metals have a slow metabolism leading to bioaccumulation in living organisms which makes them toxic. Some of the most toxic heavy metals include Pb, As, Cd, Cr and Hg. Toxic heavy metals can be transported from one place to another but cannot be eliminated from the environment. Both NORMs and toxic heavy metals can reach humans through dermal contact, inhalation and ingestion pathways. They both pose a human health risk.

2.2 Radioactivity

Radioactivity is the process of spontaneous emission of energetic particles (α , β and neutron) or photons (γ) as a result of nuclear instability. It is also referred to as nuclear decay. As a nucleus decays, a more stable daughter nuclide is formed from transformation of an unstable parent nuclide through different decay modes. This process continues until a daughter nuclide with the lowest mass in the series is reached [19]. Stable daughter nuclides and stable naturally occurring nuclides have a neutron to proton ratio that generally increases with increasing atomic number, however, an unstable nuclide is radioactive, therefore, it undergoes α or β decay and/or γ ray emission.

Decay of an atom is purely unpredictable (statistical in nature), therefore, it is impossible to predict when a certain atom will decay. Certain radionuclides decay at various rates, thus, each radionuclide has its own decay constant. The universal law of radioactive decay details the statistical behaviour of large number of nuclides as opposed to individual ones [20]. This is described by [21];

$$A = -\frac{dN}{dt} = \lambda N \quad (2.1)$$

where A is the activity of the radioactive nuclei, N is the number of radioactive nuclei, dN/dt is the disintegration/decay rate and λ is the decay constant. The negative sign shows that N is decreasing with time t .

Rearranging and integrating equation 2.1 results in;

$$\int_{N_0}^{N_t} \frac{dN}{N} = - \int_0^t \lambda dt, \quad (2.2)$$

then,

$$\ln N \Big|_{N_0}^{N_t} = -\lambda t \Big|_0^t,$$

and,

$$\ln \frac{N_t}{N_0} = -\lambda t,$$

which simplifies to the exponential decay law;

$$\frac{N_t}{N_0} = e^{-\lambda t}, \quad (2.3)$$

where N_0 is the number of radioactive nuclei existing at time $t = 0$. This number decreases exponentially with time. N_t is the number of radioactive nuclei at time t and λ is the decay constant.

Due to proportionality between number of atoms present in a sample, N and its activity, A , which is the number of disintegrations per second, equation 2.3 can be expressed as;

$$\frac{A}{A_0} = e^{-\lambda t}, \quad (2.4)$$

where A is the activity at time t and A_0 is the activity at time $t = 0$.

The activity of a radionuclide decreases by a factor of one-half during time $t_{\frac{1}{2}}$. This is referred to as the half life of the radionuclide [22]. Calculating $t_{\frac{1}{2}}$ in terms of λ at time t , equation 2.4 becomes;

$$\frac{1}{2} = e^{-\lambda t_{\frac{1}{2}}}, \quad (2.5)$$

using natural logarithm on both sides yields;

$$-\lambda t_{\frac{1}{2}} = \ln \frac{1}{2} = -\ln 2, \quad (2.6)$$

thus,

$$t_{\frac{1}{2}} = \frac{\ln 2}{\lambda} \quad (2.7)$$

The main nuclear decay processes are α or β decay and/or γ ray emission and are described as follows;

2.2.1 Alpha decay

In alpha decay, an α particle is released if a nuclide has too large neutron to proton ratio. This mostly occurs for massive nuclei. The release of a ${}^4\text{He}$ atom (alpha particle) decreases the numbers of neutrons and protons in the parent nuclide thus making it closer to a more stable configuration. When an α particle is emitted, mass number of the parent nuclide lessens by 4 units and the proton number by 2 units [20, 23]. This is shown in Figure 2.1.

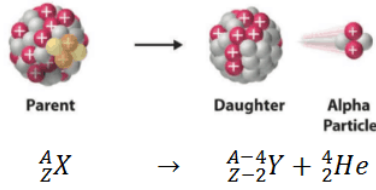


Figure 2.1: Alpha decay reaction [24].

2.2.2 Beta decay

Beta decay process is dependent on the number of protons and neutrons in a nucleus. If a nucleus has more protons than neutrons, extra protons are transformed to neutrons and vice versa. During this process, beta particles (electrons or positrons) are emitted. In beta plus decay, a proton breaks up to produce a neutron, positron and a neutrino as shown in equation 2.8;

$$p \rightarrow n + \beta^+ + \nu \quad (2.8)$$

where p , n , β^+ and ν represent proton, neutron, positron and a neutrino, respectively.

Equation 2.9 shows beta minus decay, where a neutron decays into a proton, electron and an antineutrino. When a β^- particle is emitted, proton number of the parent nuclide increases by 1 unit while the mass number does not change [25].

$$n \rightarrow p + \beta^- + \bar{\nu} \quad (2.9)$$

where $\bar{\nu}$, β^- , p and n represents antineutrino, an electron, a proton and a neutron, respectively. Figure 2.2 also illustrates both beta decay modes.

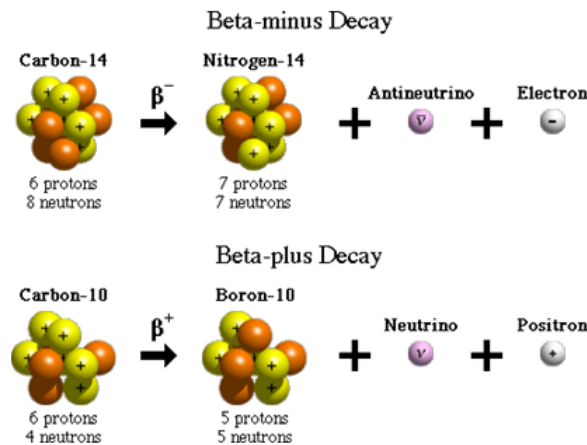


Figure 2.2: Beta decay reaction [26].

2.2.3 Gamma emission

Figure 2.3 shows gamma ray emission which occurs when a nucleus transforms from a higher energy state to a lower energy state.

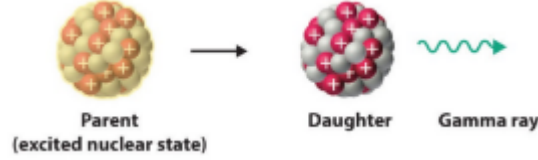


Figure 2.3: Gamma decay reaction [24].

Photons (electromagnetic radiation) are emitted during this process. Unlike in alpha and beta decay modes, the number of protons and neutrons in the parent nuclide does not change in gamma ray emission [27].

2.2.4 Decay series for uranium and thorium

Natural decay series of radionuclides can be divided in 3 groups which are ^{238}U , ^{235}U (normally called actinium series) and ^{232}Th decay series. ^{238}U , ^{235}U and ^{232}Th are unstable parent nuclides which undergo radioactive nuclear decay. Their immediate daughter nuclides are radioactive, therefore, they also decay, leading to a decay chain of nuclides ending at the most stable and non-radioactive isotope [28]. In a decay series, only beta and alpha decays are shown as they change the number of neutrons and protons in a nucleus. This is described in subsections 2.2.1 and 2.2.2. Half lives of the radionuclides are also presented in a decay series. Decay series headed by ^{238}U , ^{235}U and ^{232}Th end with ^{206}Pb , ^{207}Pb and ^{208}Pb , respectively and are shown in Figures 2.4, 2.5 and 2.6 in detail.

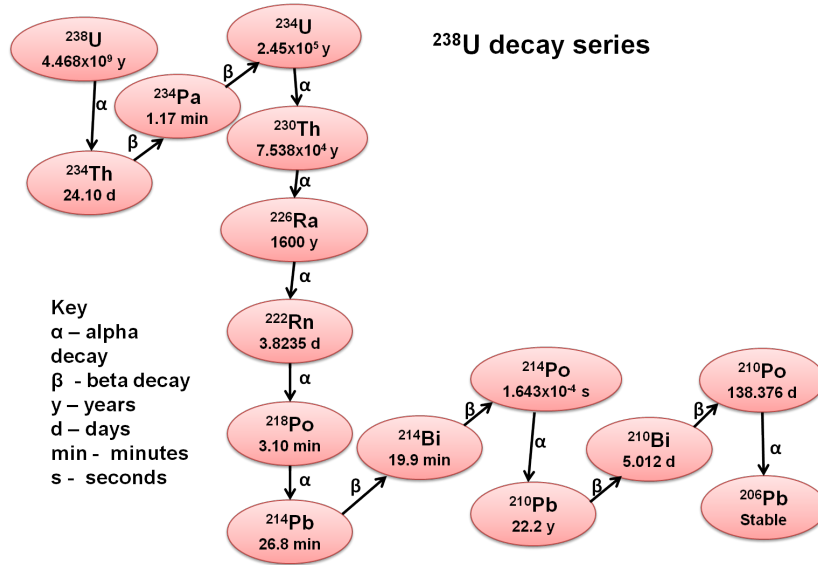


Figure 2.4: Decay series of ^{238}U with half lives of its daughter nuclides [29].

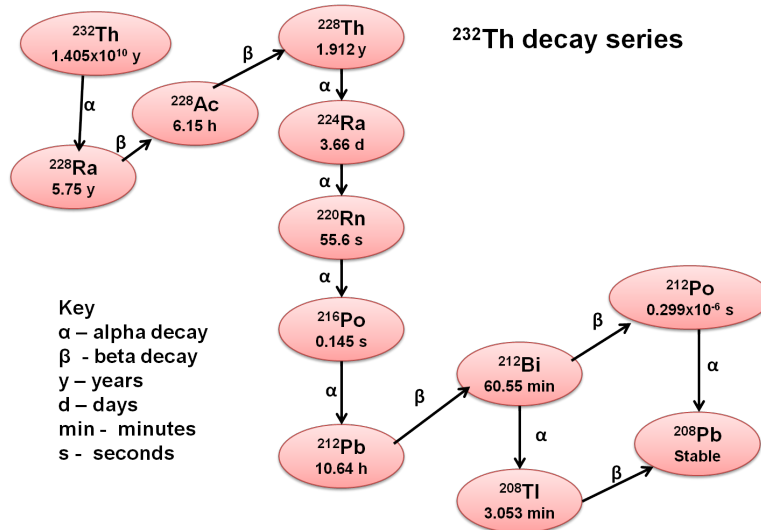


Figure 2.5: Decay series of ^{232}Th with half lives of its daughter nuclides [29].

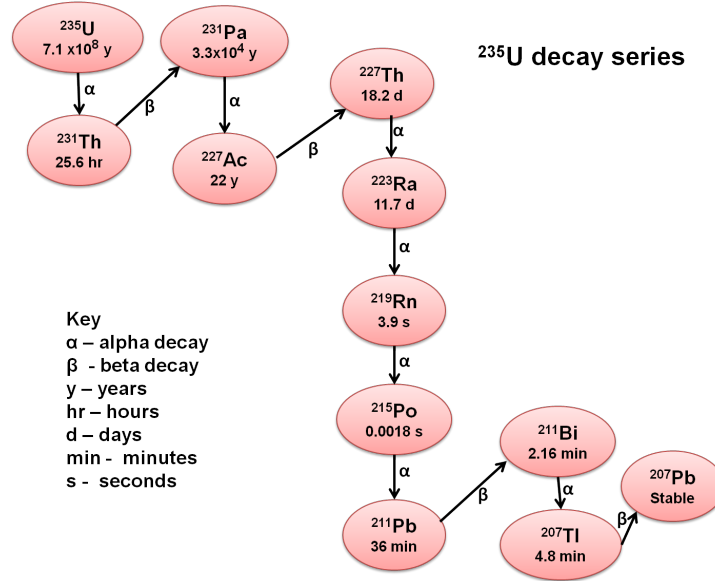


Figure 2.6: Decay series of ²³⁵U with half lives of its daughter nuclides [30].

2.3 Radioactive equilibrium

In a radioactive decay scheme, a parent nuclide (A) with a certain decay constant (λ_A) decays into a daughter nuclide (B) with a different decay constant (λ_B). This means that the parent and daughter nuclide decay at different rates. A point where the production rate of a daughter nuclide is equal to the decay rate of the parent nuclide is called radioactive equilibrium [31]. It has 3 main scenarios, namely; secular equilibrium, transient equilibrium and a state of no equilibrium.

2.3.1 Secular equilibrium

Secular equilibrium occurs when the decay constant of the parent nuclide is very much lower than the decay rate of the daughter nuclide, $\lambda_A \ll \lambda_B$. Parent nuclide has a half life significantly greater than the half life of its immediate daughter nuclide, therefore, $\lambda_A \approx 0$ after a sufficiently long time. The amount of the daughter nuclide produced is determined by the amount of parent nuclide and half lives of both the parent and daughter nuclides [32]. This is illustrated by [31];

$$\frac{dN_B}{dt} = \lambda_A N_A - \lambda_B N_B, \quad (2.10)$$

where λ_A and λ_B are decay constants for parent and daughter nuclide, respectively, N_A and N_B are number of radioactive nuclei for parent and daughter nuclide at any

given time. At secular equilibrium, $\lambda_A N_A = \lambda_B N_B$.

The decay constants of radionuclides A and B are related to their half lives through equation 2.11;

$$\lambda = \frac{\ln 2}{t_{\frac{1}{2}}}, \quad (2.11)$$

where $t_{\frac{1}{2}}$ is the half life of a radionuclide.

The relationship between the half lives and number of radioactive nuclei of the radionuclides is given by;

$$\frac{N_A}{N_B} = \frac{\lambda_B}{\lambda_A} = \frac{(t_{\frac{1}{2}})_A}{(t_{\frac{1}{2}})_B}, \quad (2.12)$$

where $(t_{\frac{1}{2}})_A$ is the half life of the parent radionuclide and $(t_{\frac{1}{2}})_B$ is the half life of the daughter nuclide.

Since $\lambda_A \ll \lambda_B$ and $\lambda_A \approx 0$ after a sufficiently long time, then $e^{-\lambda_A t} = 1$, therefore, the number of radioactive nuclei of the daughter nuclide can be estimated by [31];

$$N_B = \frac{\lambda_A}{\lambda_B} N_A (1 - e^{-\lambda_B t}), \quad (2.13)$$

where λ_A and λ_B are decay constants for radionuclides A and B, N_A and N_B are number of radioactive nuclei for each radionuclide at a given time.

As illustrated in equation 2.12, the number of radioactive nuclei of different daughter nuclides existing at equilibrium are inversely proportional to their decay constants. An example of the establishment of secular equilibrium is shown in Figure 2.7 with radionuclides from ^{238}U decay chain.

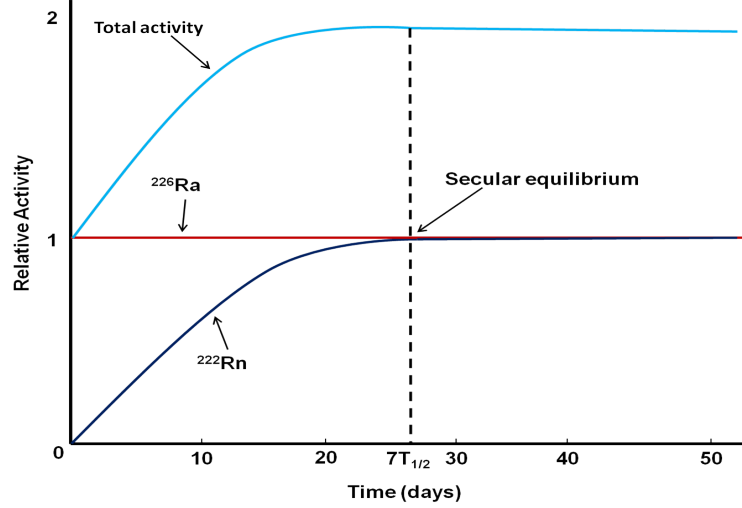


Figure 2.7: Radioactive secular equilibrium of ^{226}Ra and ^{222}Rn [33].

The parent nuclide ^{226}Ra with a half life of 1600 years decays into a daughter nuclide ^{222}Rn with a half life of 3.8235 days. After about 7 half lives of the daughter nuclide, the decay rate of ^{226}Ra equals the production rate of ^{222}Rn [28, 29].

2.3.2 Transient equilibrium

Transient equilibrium occurs when the half life of the parent nuclide is larger than the half life of the daughter nuclide. This means that the decay rate of the parent is smaller than the decay rate of the daughter nuclide, $\lambda_A < \lambda_B$. Unlike in secular equilibrium, λ_A cannot be neglected, thus, the relative activity of the parent nuclide is not constant [31]. Using this and equation 2.3, the number of radioactive nuclei of a daughter nuclide can be calculated as follows;

$$N_B(t) = \frac{\lambda_A}{\lambda_B - \lambda_A} N_A(0) (e^{-\lambda_A t} - e^{-\lambda_B t}), \quad (2.14)$$

Since $e^{-\lambda_B t}$ decreases with time, it becomes negligible compared to $e^{-\lambda_A t}$, therefore, equation 2.14 reduces to;

$$N_B(t) = \frac{\lambda_A}{\lambda_B - \lambda_A} N_A(0) e^{-\lambda_A t}. \quad (2.15)$$

When a transient equilibrium is reached, the ratio of N_B to N_A approaches a constant value. This is verified by using equation 2.3 as;

$$N_A(t) = N_A(0) e^{-\lambda_A t}, \quad (2.16)$$

Then, equation 2.15 is simplified to;

$$N_B(t) = \frac{\lambda_A}{\lambda_B - \lambda_A} N_A(t). \quad (2.17)$$

The time of when transient equilibrium is reached is dependent on the half lives of both the parent and daughter nuclide. The shorter the half life of the daughter nuclide in comparison to the parent nuclide, the faster the time it takes to reach equilibrium [34]. Figure 2.8 shows ^{212}Pb decaying into ^{212}Bi as an example of transient equilibrium. This is observed from a ^{232}Th headed decay series shown in Figure 2.5 with ^{212}Bi having a half life of 60.55 minutes compared to its parent nuclide ^{212}Pb with a half life of 10.64 hours [29].

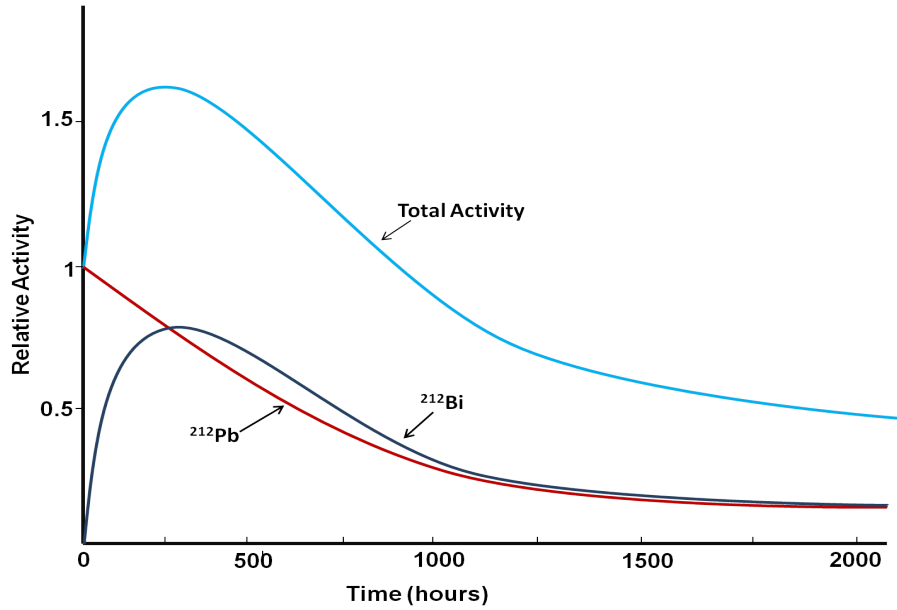


Figure 2.8: Radioactive transient equilibrium [33].

2.3.3 No equilibrium state

The state of no radioactive equilibrium occurs when the half life of the daughter nuclide is longer than the half life of the parent nuclide. An example of this state is observed in the decay series headed by ^{238}U shown in Figure 2.4 where ^{218}Po with a half life of 3.05 minutes decays into ^{214}Pb with a half life of 26.8 minutes [29]. This state is illustrated in Figure 2.9.

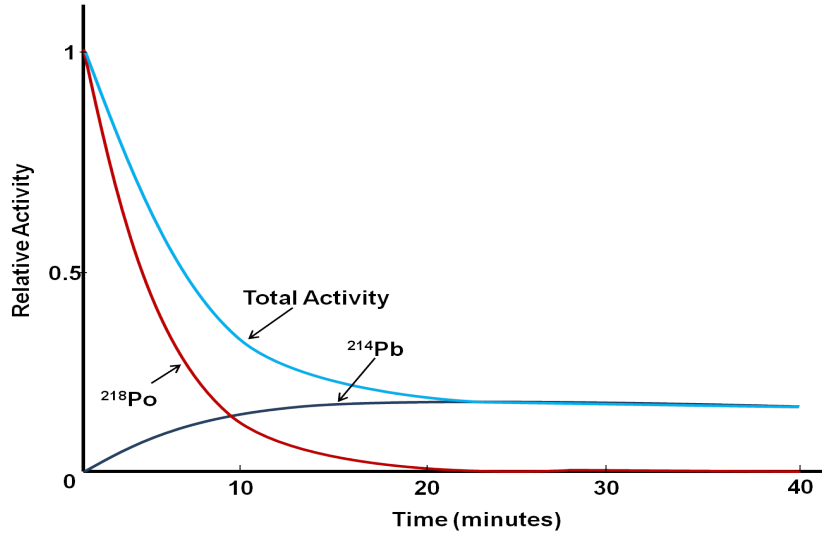


Figure 2.9: No radioactive equilibrium state [33].

As the parent nuclide decays, the number of radioactive nuclei of the daughter nuclide will increase to maximum and then ultimately decrease once the parent nuclide is all decayed away [31]. For long duration, the number of radioactive nuclei in the daughter nuclide can be calculated by [33];

$$N_B(t) = \frac{\lambda_A}{\lambda_B - \lambda_A} N_A(0) e^{-\lambda_B t} \quad (2.18)$$

where $N_B(t)$ is the number of radioactive daughter nuclei at time t , λ_A and λ_B are decay constants for radionuclides A (parent nuclide) and B (daughter nuclide) and N_A is the number of radioactive parent nuclei at time $t = 0$.

2.4 Radiation-Matter interactions

Detector operation is dependent on the way in which radiation interacts with a given detector material. Radiation interactions with matter therefore affects the response of the detector [35]. Radiation can be detected either as alpha (α), beta (β), gamma (γ), X or neutron rays [36]. These radiations interact differently with matter and some are illustrated in subsections 2.4.1 to 2.4.2.

2.4.1 Interaction of α particles with matter

Alpha particles have a heavy nucleus with mass number 4 and a proton number 2. They are usually referred to as helium nuclei. Since an alpha particle has no electrons,

it has a positive charge of $+2$ which causes it to remove electrons from orbital atoms close by. It loses its energy with every reaction and eventually gain 2 electrons, thus, becoming a helium atom. It deposits or loses a large amount of energy within a short distance of travel which slows it down. This restricts its penetrating ability. As a result, alpha particles can only pass through a small thickness of a material. It can be stopped by a thin sheet of paper [37, 38].

2.4.2 Interaction of photons (γ) with matter

Since photons are not visible to the detector, their measurement depends on the interaction with electrons of a medium. When incident photons interact with a medium, fast electrons are produced and these electrons are studied in order to infer the behaviour of the photon itself. There are three ways in which a photon interacts with a medium, namely, photoelectric effect, Compton scattering and pair production [11]. These different interactions dominance and occurrence depends on the atomic number of the material and the energy of the gamma ray. Figure 2.10 illustrates the three principal interactions. The left line where $\sigma_f = \sigma_c$ symbolises the energy where photoelectric effect is equally probable to Compton scattering for atomic number Z . Similarly, the right line where $\sigma_c = \sigma_p$ represents gamma energy where Compton scattering and pair production are equally probable for atomic number Z [39].

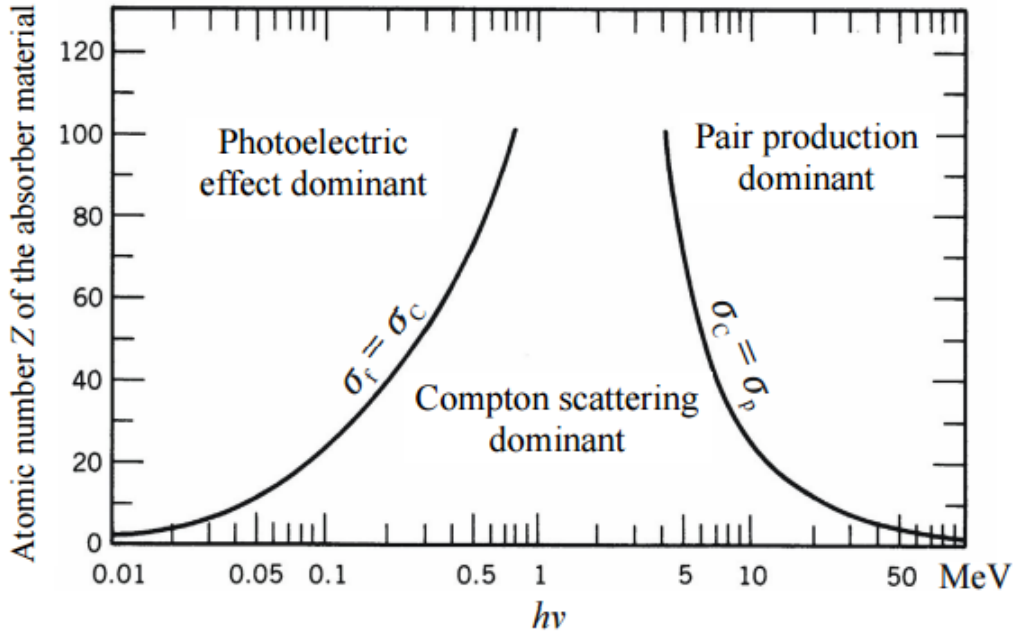


Figure 2.10: Different regions where gamma interactions are dominant[39].

• **Photoelectric effect**

Photoelectric effect is a process that verifies that light comes as discrete wave packets of energy (photons). An atomic electron absorbs energy from an incident photon, if energy absorbed by the electron is equal or greater than its binding energy, then the electron will be emitted and the photon will disappear as it gives up all of its energy to the electron otherwise no electrons will be emitted [40]. During this process, free electrons from other shells will be captured by the valency shell which may lead to production of characteristic x-ray. This is shown in Figure 2.11.

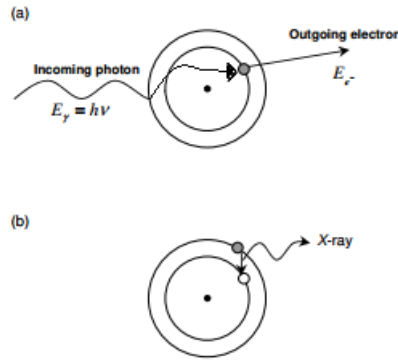


Figure 2.11: Process of photoelectric effect[33].

Energy needed to release a photoelectron is called work function (ϕ) and it differs depending on the metal. The Einstein's general equation for photoelectron energy is given by [41];

$$E_{pe} = h\nu - \phi, \quad (2.19)$$

where;

E_{pe} : is the kinetic energy of photoelectron,

$h\nu$: is energy of photon, where ν is its frequency and h is the Plank's constant ($h = 6.62 \times 10^{-34} \text{ m}^2\text{kg/s}$)

ϕ : is the binding energy of the electron, and is given by;

$$\phi = h\nu_0, \quad (2.20)$$

where ν_0 is the cut off frequency.

As a result, Equation 2.19 can be expressed into;

$$E_{pe} = h\nu - h\nu_0, \quad (2.21)$$

which can be simplified to;

$$E_{pe} = h(v - v_0), \quad (2.22)$$

In the photoelectric process, energy of a photoelectron is divided in the absorbing material through excitation or ionisation. Photoelectric effect mainly depends on low energy photons and absorbers with high atomic number [41].

- **Compton scattering**

Compton scattering describes an interaction between an incident photon and a weakly bound electron. After interaction, the photon loses only a portion of its energy to the electron and is deflected from its initial direction while a recoil electron is formed [27]. The schematic process of Compton scattering is illustrated by Figure 2.12.

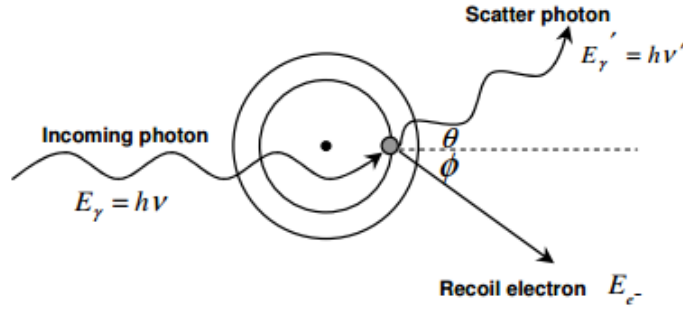


Figure 2.12: Compton scattering interaction of a photon[33].

Due to conservation of total energy and linear momentum, the angle at which the scattered photon and recoil electron are emitted affects their energies. The energy of the scattered photon can be expressed by equation [38];

$$h\nu' = \frac{h\nu}{1 + (h\nu/m_e c^2)(1 - \cos\theta)} \quad (2.23)$$

where; $m_e c^2 = 511 \text{ keV}$ is the rest mass energy of the electron, θ is the scattering angle, $h\nu'$ is energy of scattered photon and $h\nu$ is energy of incident photon.

Kinetic energy of recoil electron is given by the difference between energies of incident and scattered photons, which ranges from zero (when $\theta = 0$) and $2h\nu/(2 + m_e c^2/h\nu)$ (when $\theta = 180^\circ$). It is expressed generally by equation [42],

$$E_{e-} = hv - hv' = hv \frac{(hv/m_e c^2)(1 - \cos\theta)}{1 + hv/m_e c^2(1 - \cos\theta)} \quad (2.24)$$

where E_{e-} is the kinetic energy of recoil electron.

Compton scattering is most probable for gamma-ray energies varying from 0.1 MeV to 10 MeV as illustrated by Figure 2.10.

- **Pair production**

Pair production is most probable at high gamma-ray energies. It occurs when an incident photon energy is considerably higher than the rest mass of the electron. This interaction results in absorption of a photon by Coulomb field of a nucleus which forms an electron positron pair [40]. Since the threshold energy of a photon is $2m_e c^2 = 1022 \text{ keV}$ (rest mass of electron), extra energy carried by the photon is equally distributed as kinetic energy between the positron and electron. This is expressed by equation [27];

$$E_{e-} + E_{e+} = hv - 2m_e c^2, \quad (2.25)$$

where E_{e+} is the kinetic energy of a positron.

As the positron interacts with absorbing material, it slows down and annihilate with an atomic electron of the detector and produces 2 gamma-rays that each has energy of 511 keV. These gamma rays are emitted in different and opposite directions to conserve linear momentum [43]. The process of pair production is schematically shown in Figure 2.13.

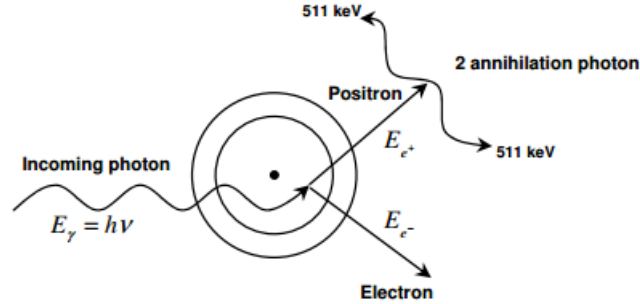


Figure 2.13: Pair production interaction of an incident photon and annihilation[33].

2.5 Biological effects of Ionising Radiation

When a human body is subjected to any kind of radiation, it can result in ionization and excitation of atoms and molecules. Subsequently, the interaction between radiation and biological organisms can lead to impairment and death of living cell or genetic mutation [33]. The radiation type and the radiation energy carried to irradiated tissues and organs during exposure time affects the biological effects of radiation. The amount of ionisation that took place and the energy absorbed by the cells in relation to biological effects can be reviewed in terms of radiation dosimetry which is discussed in detail in Section 2.7.

2.5.1 Sources of Radiation Exposure

Humans are exposed to ionising radiation either internally or externally. Internal exposure takes place when radiation is inhaled or ingested or enters the bloodstream through injections/wounds whereas external exposure comes from radioactive sources that irradiate outside of the body e.g cosmic radiation [44, 45]. In most cases, both internal and external radiation exposure to humans arise from natural sources. However, humans can also be exposed to ionising radiation through artificial sources that mainly result from the use of radioactive materials in human activities. The annual average dose from both natural and artificial sources is analysed in Table 2.1.

Table 2.1: Worldwide annual average dose from natural and artificial sources of radiation [46]

Source	Annual average dose (Worldwide)	Typical range of individual doses	Comments
Natural sources of exposure			
Inhalation (Radon gas)	1.26	0.2 - 10	The dose is much higher in certain dwellings
External terrestrial	0.48	0.3 - 1	The dose is higher in some geographical locations
Ingestion	0.29	0.2 - 1	
Cosmic radiation	0.39	0.3 - 1	The dose increases with altitude
Total of Natural resources	2.4	1 - 13	
Artificial sources of exposure			
Medical diagnosis (not therapy)	0.6	0 - several tens	Individual doses depend on specific examinations
Atmospheric nuclear testing	0.005	Some higher doses around test sites still occur.	The average has fallen to a peak of 0.11 mSv in 1963
Occupational exposure	0.005	0 - 20	The average dose to all workers is 0.7 mSv. Most high exposures are due to natural radiation specifically radon in mines
Chernobyl accident	0.002 ^a	In 1986, average dose to more than 300 000 recovery workers was nearly 150 mSv; and more than 350 000 other individuals received doses greater than 10 mSv.	The average in the northern hemisphere has decreased from a maximum 0.04 mSv in 1986.
Nuclear fuel cycle (public exposure)	0.0002 ^a	Doses are up to 0.02 mSv for critical groups at 1 km from some nuclear reactor sites.	
Total of artificial sources	0.6	From essentially zero to several tens	Individual doses depend primarily on medical treatment

^aGlobally dispersed radionuclides. The value of nuclear fuel cycle represents the maximum per capita annual dose to the public in the future, assuming the practice continued for 100 years, and derives mainly from globally dispersed, long lived radionuclides released during reprocessing of nuclear fuel and nuclear power plant operation.

2.5.2 Radiation protection and dose limits

Ionising radiation causes damage and impairment to biological organs in the human body, as a result, a series of studies have been conducted on biological effects of radiation. The main purpose of these studies were to lay a foundation of the dose limits with the aim of protecting radiation workers and members of the public from exposure to radiation. People who survived Hiroshima and Nagasaki, routine workers exposed to radiation and individuals who were exposed to radiation through accidents were used to gather much knowledge of radiation effects to humans [47]. The Biological Effect of Ionising Radiation (BEIR) in agreement with United Nations Scientific Committee on the Effect of Atomic Radiation (UNSCEAR) and International Commission on

Radiological Protection (ICRP) studied the correlation between biological effects and radiation exposure and their hypotheses is shown in Figure 2.14.

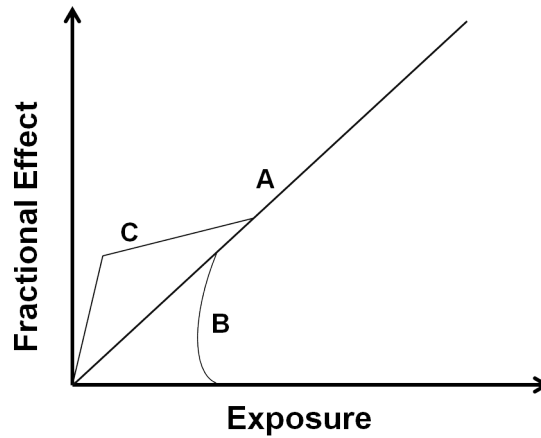


Figure 2.14: The relationship between biological effects of radiation and radiation exposure [47]

From Figure 2.14 above, each curve represents different hypotheses on different occasions. Curve A shows a "no threshold" hypothesis used in initial reports which indicates a linear relationship between the amount of radiation exposure and the radiation effect. Curve B shows a different trend obtained from further studies. The possible hypothesis of this curve was that radiation at extremely low levels could not cause harmful effects to humans, this was termed "threshold effect". Curve C shows a hypothesis where at low levels, the absorbed doses of ionising radiation are more harmful.

The biological effects of radiation can be classified into two types, that is, deterministic and stochastic. Deterministic effects depend on the radiation type, exposure time and the radiation dose. These effects are observed at a certain threshold which differs from one person to another. At doses lower than this threshold, no detrimental effects are observed [33, 47]. However, the severity of the effects increases with the dose. This is similar to Curve B in Figure 2.14.

On the other hand, stochastic effects, also termed probabilistic effects occur randomly and their probability of occurrence increases with an increase in dose. The relationship similar to Curve A in Figure 2.14. Stochastic effects has two types, namely, somatic and genetic. Somatic stochastic effects of radiation are restricted to the exposed individuals who then suffer from these effects for life e.g cataract, skin necrosis and sterility. In genetic stochastic effects, the ionising radiation impairs the genetic ma-

terial in the reproductive cell, therefore, the effects transmit from one generation to another e.g cancer and hereditary defects like down syndrome [46, 48].

In order to reduce human exposure to radiation, all doses must be kept as low as reasonably achievable (ALARA) with the recommended limits from ICRP. The ICRP recommendations for radiation protection standards are based on the following principles;

1. Justification - Any procedure that does not benefit exposed individuals should not be implemented.
2. Optimisation - During a practice, all exposures should be kept as low as reasonably achievable (ALARA) with social and economic factors.
3. Dose limitation - The exposure doses received by individuals should be within the recommended limits.

Table 2.2 below shows the recommended dose limits set and estimated by ICRP publication 60.

Table 2.2: Effective dose limits recommended by ICRP 60 [33, 49]

Application	Dose limits	
	Occupational	Public
Whole body	20 mSv ^a per year, average over a defined period of 5 years ^a	1 mSv ^a in a year
Annual equivalent dose in		
Lens of the eye	150 mSv	15 mSv
Skin	500 mSv	50 mSv
Hand and feet		-

^a To find the recommended limit in rem, 1 mSv = 0.1 rem

^b Maximum dose in any single year do not exceed 50 mSv

2.6 Radiation detectors

Gamma radiation have to undergo the three principal gamma-ray interactions in order to be detected. The primary necessity of radiation detection materials is that, amount of radiation detected is determined by the extent of material's response, i.e

the efficiency of the detector. Through ionisation, gamma-rays react with atoms of the detector to create electrons. An output pulse is produced due to collection of these electrons [41]. The ion pairs created have to be freely movable in order to be detected, therefore, metals and insulated materials are not useful in making radiation detectors. Different radiation detectors, e.g., gas filled, scintillation and semiconductor detectors are used to measure ionising radiation in samples. The intensity, energy and radiation type measured can be provided by these detectors [33]. All radiation detectors are evaluated based on detector sensitivity, energy resolution of the detector, pulse-response time and detector efficiency.

2.6.1 Scintillation detectors

A scintillator is defined as a substance or material that make pulses of light from energy lost during ionisation. It can also be defined as a material that luminescent when exposed to ionising radiation. Scintillating materials have luminescent centres that are used to convert the absorbed ionising radiation into a form that can be detected, therefore, not all materials that absorb ionising radiation can scintillate. When a scintillating material is exposed to ionising radiation, electrons become excited and move from the valence band to the conduction band, leaving a hole behind it. An electron-hole pair will continue to move around until it is trapped by a deliberately-introduced dopant or a defect within the crystal. The trapped electrons will decay and emit a photon resulting in luminescence [50].

Ionising radiation appears as γ -rays, x-rays and α or β particles in most scintillation applications with energies ranging from keV to MeV. Scintillation detectors are used in many fields including, environmental studies, high energy physics, nuclear physics and nuclear medicine. They have a high ability of detecting nuclear radiation which includes both x- and γ -rays [51]. Organic and inorganic scintillators are the two main types of scintillators. Organic scintillators have three types, that is, solid, liquid and gas which are categorised by short lifetime of visible light. These type of scintillators have low atomic number, thus fundamentally used to detect heavy charged particles or electrons. On the other hand, inorganic scintillators are made from for high atomic number particles which makes fast timing a necessity. An example of an inorganic scintillator is Thallium activated sodium iodide(NaI(Tl)) [41].

When a scintillator absorbs the nuclear particle/radiation, it emits a blaze of light called a scintillation. Information about the incident radiation is given when scintillations are transformed into electrical pulses which are then analysed. A light detector,

usually photomultiplier tube (PMT) identifies a flash of light from a scintillation material, which is transformed into photoelectrons by photo-cathode of PMT. These photoelectrons are then escalated to dynodes of PMT by an electric field where they undergo a multiplication process. Every scintillation outputs a charge pulse on the anode of PMT which can be identified and analysed by electronic equipment [51].

2.6.2 Solid-state/Semiconductor detectors

A semiconductor is defined as a substance that is intermediate of a conductor and an insulator in terms of electrical conductivity. The process of radiation detection in semiconductor detectors is determined by energy band structures of semiconducting materials. These bands are called valence and conductor bands. The gap between valence and conductor bands determines whether the substance is a conductor or an insulator. In the conduction band, electrons move freely through a crystal whereas a valence band has bound electrons in specific lattice sites. Materials with no band gap are classified as conductors while insulators have a large band gap (>5 eV) [43]. Band gap of a semiconductor is small, thus, a little quantity of energy is needed for excitation of electron into the conduction band whilst a valence hole is formed in the valence band. Exposure to radiation changes electrical conductivity of a semiconductor. Silicon and germanium are common semiconducting materials used in radiation detectors. In comparison to scintillation detectors, semiconductor detectors have a high resolution which enables precise results in low level radioactivity samples [51].

Electrical properties of semiconductors can be affected by impurities. When a semiconducting material is contaminated by group V elements, a donor state is created by excess electrons below the conduction band. This type of semiconductors are called the n-type. Consequently, when group III elements are added to a semiconductor material, excess holes that create acceptor states in the band gap are formed, these are called p-type semiconductors [51]. Charge carriers move throughout the junction created between p and n-type semiconducting materials. A p-n junction is formed when a p-type and n-type semiconductors are connected to each other. When this happens, the holes in the p-type region are filled by some of the electrons in the n-type region. Subsequently, the p-type region captures electrons from the n-type region. This creates a depletion region in which an electric field is generated. This is illustrated by Figure 2.15.

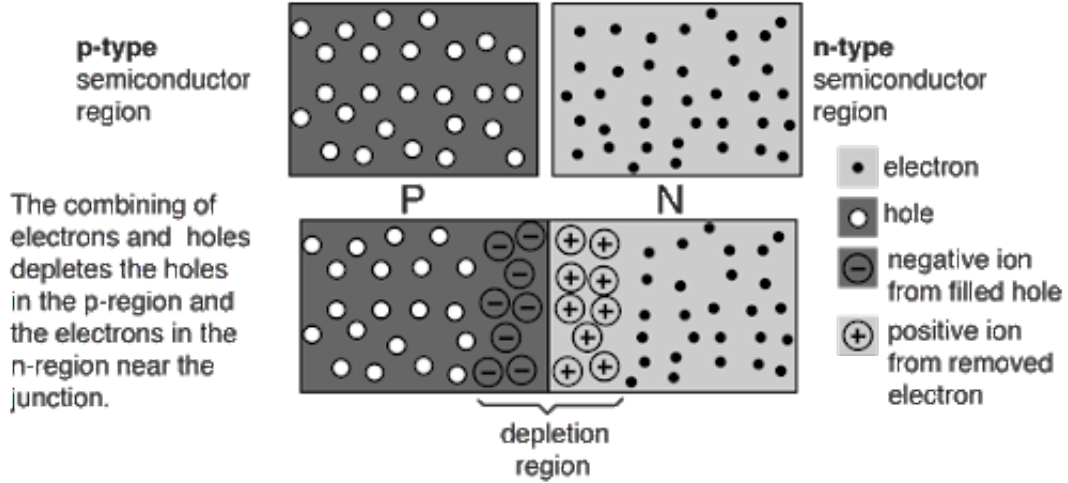


Figure 2.15: A schematic diagram of the p-n junction/ depletion region [52].

The generated electric field generates a flow of electrons and holes in the opposite direction, creating equilibrium between the two processes. The depletion region stays at dynamic equilibrium until an external voltage is applied. When a charged particle deposits energy in the region/junction, more electron-hole pairs are created and become detectable as pulse of current from the detector. A p-n junction semiconductor can be used to detect high energy charged particles, X and gamma rays if the energy deposited within the charge-sensitive region is increased. This energy could be increased by increasing the depth of charge sensitive region or the atomic number of the semiconductor [53], [54].

In this study, a semiconductor detector (High Purity Germanium (HPGe)) is used for detection of gamma radiation in samples. Due to its property of high resolution, it can distinguish two gamma rays of close energy given that the peaks are extremely narrow. Gamma ray spectroscopy permits the naming and quantification of the gamma emitting isotopes in the sample. It gives a spectrum of lines in a single measurement after detecting gamma emitting radionuclides. The height of lines in the spectrum is relative to activity of radionuclides and its energy is estimated by position of the line on horizontal axis [17].

2.7 Radiation dosimetry

Radiation dosimetry is a branch of physical science which is used to quantify the energies from different sources of radiation absorbed by humans or a given material. Calculations on the amount of dose that describes the amount of energy absorbed by a material and the rate of deposition are determined by dosimetry. Dosimetric units that are usually used to quantify radiation include exposure, absorbed dose, dose equivalent and effective dose [55, 56].

2.7.1 Exposure

The quantity of ionization that results from exposure to X and gamma rays is used to define exposure [57]. Exposure is measured in roentgens (R) which was originally defined as the quantity of X and gamma radiation that produces 1 *esu* of charge (either + or -) in every 0.001293 g of air. Since 1 *esu* = $3.34 \times 10^{-10}C$, and;

$$\frac{\Delta Q}{\Delta m}, \quad (2.26)$$

where ΔQ is the summation of all charges of one sign made in air when all electrons released by photons have totally come to a stop and Δm is the mass of air [58]. The definition of roentgen can be expressed as follows;

$$1R = \frac{3.34 \times 10^{-10}C}{0.001293g \times 10^{-3}\frac{kg}{g}} = 2.58 \times 10^{-4}C/kg \quad (2.27)$$

2.7.2 Absorbed dose

The main physical quantity used in radiation dosimetry is the Absorbed Dose. It is defined as the amount of energy absorbed from exposure to ionising radiation per unit mass. It is measured in Gray (Gy), where 1 Gy is the same as 1 joule of absorbed energy per one kilogram of mass of target [57]. The other unit for absorbed dose is *rad* (radiation absorbed dose) and is described as the absorbed energy 100 *erg* per gram which relates to Gray through equation [41];

$$1Gy = 1\frac{J}{kg} = \frac{10^7 erg}{10^3 g} = 10^4 \frac{erg}{g} = 100rad \quad (2.28)$$

Absorbed energy, type of radiation and radiation energy are taken into consideration in determining the biological radiation damage. Generally, due to high intensity levels of high energy ionising radiation, it is more severe than ionising radiation with low

energy, thus, it has more biological effect per unit absorbed dose. As a result, radiation weighting factor (W_R) is introduced. Certain ionising radiation types differ from one energy level to another [47]. These energies as well as their weighting factors are listed in Table 2.3.

Table 2.3: Weighting factors for different radiation types and their energy range [47].

Radiation type	Energy range	weighting factor(W_R)
Photons,electrons, positrons and muons	All energies	1
Neutrons	<10 keV	5
	>10 keV to 100 keV	10
	>2 to 20 MeV	20
	>20 MeV	5
Protons, other than recoil proton	>2 MeV	2
Alpha particles, fission fragments, non-relativistic heavy nuclei		20

2.7.3 Equivalent and effective dose

Equivalent dose (H_T) is defined as the amount of radiation dose absorbed by a tissue or organ. It is used to find out the impact of radiation by the weighting factor listed in Table 2.3 and is calculated using equation 2.29 [59];

$$H_T = \sum_R W_R D_{T,R}, \quad (2.29)$$

where H_T is the equivalent dose, W_R is the radiation weighting factor and $D_{T,R}$ is the absorbed dose.

When absorbed dose is expressed in gray (Gy), then equivalent dose is expressed in sieverts (Sv), hence, $1 Sv = 1 J/kg$. On the contrary, equivalent dose is expressed in *rem* (radiation equivalent man) when the units used for absorbed dose is *rad*, thus, $1 Sv = 100 rem$ [43]. For every tissue, the summation of equivalent doses as well as their corresponding tissue weighting factors is called the effective dose. It is represented mathematically by equation 2.30 [59];

$$E = \sum_{\text{T}} W_{\text{T}} H_{\text{T}}, \quad (2.30)$$

where E is the effective dose, W_{T} is the tissue weighting factor and H_{T} is the equivalent dose. The tissue weighting factor is a measure of the risk of stochastic effects that may arise from irradiation of a specific tissue. It takes into account varying sensitivity to ionising radiation of different organs and tissues in the human body [60]. The tissue weighting factors are listed in Table 2.4.

Table 2.4: Tissue weighting factors [47].

Tissue or Organ	Tissue weighting factor(W_{T})
Gonads	0.20
Colon	0.12
Lung	0.12
Red bone marrow	0.12
Stomach	0.12
Bladder	0.05
Breast	0.05
Oesophagus	0.05
Liver	0.05
Thyroid	0.05
Skin	0.01
Bone surfaces	0.01
Remainder	0.05

Using equations 2.29 and 2.30, the effective dose can be simplified to;

$$E = \sum_{\text{T}} W_{\text{T}} \sum_{\text{R}} W_{\text{R}} D_{\text{T,R}}, \quad (2.31)$$

where W_{T} is the tissue weighting factor, W_{R} is the radiation weighting factor and $D_{\text{T,R}}$ is the absorbed dose.

2.8 Assessing radiological risk to residents

^{226}Ra , ^{232}Th and ^{40}K contents are usually used to determine natural radioactivity of samples due to their natural abundance in soil [61]. Radiological parameters which include, absorbed gamma dose rate ($\dot{D}$), indoor and outdoor annual effective dose equivalent ($AEDE_{\text{indoor}}$, $AEDE_{\text{outdoor}}$), radium equivalent (Ra_{eq}), external hazard index (H_{ex}) and the excess lifetime cancer risk (ELCR) indicate the biological hazard levels presented by the natural radiation [62].

2.8.1 Absorbed dose rate in air

Measured activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K are converted into doses by using conversion factors 0.462, 0.604 and 0.042 adapted from UNSCEAR(2000), respectively [44]. The absorbed gamma dose rate in air above the ground is then calculated by;

$$\dot{D} = 0.042A_{40\text{K}} + 0.462A_{226\text{Ra}} + 0.604A_{232\text{Th}}, \quad (2.32)$$

where $A_{40\text{K}}$, $A_{232\text{Th}}$ and $A_{226\text{Ra}}$ are activity concentrations of ^{40}K , ^{232}Th and ^{226}Ra , respectively.

Weighted mean values for the world population give an absorbed gamma dose rate value of 57 nGy/h in air [63].

2.8.2 Annual effective dose equivalent

Annual effective dose equivalent (AEDE) is estimated using indoor and outdoor occupancy fractions adapted from UNSCEAR (2000). Indoor AEDE is given by [61];

$$AEDE_{\text{indoor}}(\mu\text{Svy}^{-1}) = \dot{D} \times 8760\text{hy}^{-1} \times 0.8 \times 0.7\text{SvGy}^{-1} \times 10^{-3}, \quad (2.33)$$

where, $AEDE_{\text{indoor}}$ is indoor annual effective dose equivalent, $\dot{D}$ is the absorbed dose rate, 0.7 Sv Gy^{-1} is the conversion coefficient from absorbed dose in air to effective dose and 0.8 is the occupancy factor for indoor.

On the other hand, outdoor AEDE is given by [61];

$$AEDE_{\text{outdoor}}(\mu\text{Svy}^{-1}) = \dot{D} \times 8760\text{hy}^{-1} \times 0.2 \times 0.7\text{SvGy}^{-1} \times 10^{-3}, \quad (2.34)$$

where $AEDE_{\text{outdoor}}$ is outdoor annual effective dose equivalent and 0.2 is the occupancy factor for outdoor. The external annual effective dose equivalent is given by [44];

$$AEDE_{\text{External}} = AEDE_{\text{indoor}} + AEDE_{\text{outdoor}}, \quad (2.35)$$

where $AEDE_{\text{External}}$ is external annual effective dose equivalent and $AEDE_{\text{indoor}}$ and $AEDE_{\text{outdoor}}$ are indoor and outdoor annual effective dose equivalent, respectively.

2.8.3 Radium equivalent

Radiation hazards related to ^{226}Ra , ^{232}Th and ^{40}K are assessed using radium equivalent. Its activity usually defines gamma radiation and is based on the assumption that 370 Bq/kg of ^{226}Ra , 259 Bq/kg of ^{232}Th and 4810 Bq/kg of ^{40}K make the same gamma radiation dose rates [64]. It is given by mathematical equation [65];

$$Ra_{\text{eq}} = 0.077A_{40\text{K}} + 1.43A_{232\text{Th}} + A_{226\text{Ra}}, \quad (2.36)$$

where; $A_{226\text{Ra}}$, $A_{232\text{Th}}$, $A_{40\text{K}}$ are activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K in Bq/kg, respectively. The highest acceptable value of radium equivalent activity taken from UNSCEAR(1988) recommendations is 370 Bq/kg which matches the dose limit of 1.0 mSv/y for the general population [64].

2.8.4 External hazard index

Beretka and Mathew (1985) proposed a model which is now used to calculate the external hazard index [66]. This model restricts radiation dose to acceptable dose equivalent limit of 1 mSv/y. In order to maintain an insignificant radiation hazard, the value of this index has to be less than unity as shown in equation [67];

$$H_{\text{ex}} = \frac{A_{226\text{Ra}}}{370} + \frac{A_{232\text{Th}}}{259} + \frac{A_{40\text{K}}}{4810} \leq 1, \quad (2.37)$$

where $A_{40\text{K}}$, $A_{232\text{Th}}$ and $A_{226\text{Ra}}$ are activity concentrations of ^{40}K , ^{232}Th and ^{226}Ra , respectively.

The value of unity in external hazard index corresponds to the upper limit of radium equivalent, thus, if an area has a radium equivalent of less than 370 Bq/kg, its highly probable that its hazard index is also less than unity. All the values that are above these limits show a significant radiation hazard to residents [68].

2.8.5 Excess lifetime cancer risk (ELCR)

Excess lifetime cancer risk is calculated to estimate cancer risk due to exposure to external gamma radiation. It is a probability that a stochastic effect will take place in an individual over a given period of time. Where 0.05 is the fatal cancer risk for

general public, $AEDE_{\text{outdoor}}$ is outdoor annual effective dose equivalent and 70 years is the life expectancy of a person, ELCR is estimated by equation [69];

$$ELCR = 0.05 \times AEDE_{\text{outdoor}} \times 70\text{years} \quad (2.38)$$

The world mean value of excess lifetime cancer risk is quoted as 0.29×10^{-3} [70].

2.9 Exposure scenarios

To estimate exposure scenarios, the public was classified by body weight and age. The exposure scenarios were chosen to deduce an understanding of the levels of radiation exposures that could have reached the public due to habitation in the selected study area. They describe different elements for exposure pathways to humans which can be external or internal. Effective dose equivalent and absorbed dose rate are mainly used to describe these scenarios [71]. Different possible scenarios for residents and visitors of Serule are explained in detail.

2.9.1 Farmer:

Domestic animals in the study area use free range grazing. They wander around looking for grass and water, therefore, farmers have to herd them on a regular basis. Farmers also have to inspect their crops regularly. Usually, they eat food grown from their fields or locally produced and get milk and meat from their domestic animals. They mostly do manual work and spend most of their time outdoors. These people can be exposed to radiation through inhalation, ingestion through food chain and external exposure from the ground.

2.9.2 Visitor:

This type of scenario focuses on occasional visitors. People who visit the study area from time to time are mainly exposed to radiation through direct exposure from the ground and inhalation of soil particle.

2.9.3 Commercial food diet by urban resident:

An individual who buys processed milk, meat and food from grocery stores represents commercial food diet by urban resident. The milk they use is taken from different cows from different areas, mixed, processed and packaged. This scenario estimates the

dose based on the usage of food grown locally since it is probable for an urban resident to grow their own vegetables.

2.9.4 Migrant farm worker:

This scenario focuses on nomadic farm workers. They move from one place to another looking for farm work jobs. It also affects their children as they migrate with them. They spend most of their time outdoors doing manual work and are at the site for a limited time of the year. Their dose mainly comes from inhalation of dust and ingestion of soil particles. They obtain food and milk from local sources.

2.9.5 Radiation pathways from soil to humans

Human radiation doses can be increased by release of radionuclides into the environment. This goes through different pathways that are categorized into external or internal irradiation. External irradiation is when there is direct radiation that reaches humans through dermal contact whereas internal irradiation means the intake of radiation through ingestion or inhalation [72]. Figure 2.16 shows how radiation from soil reaches humans through different environmental and exposure pathways.

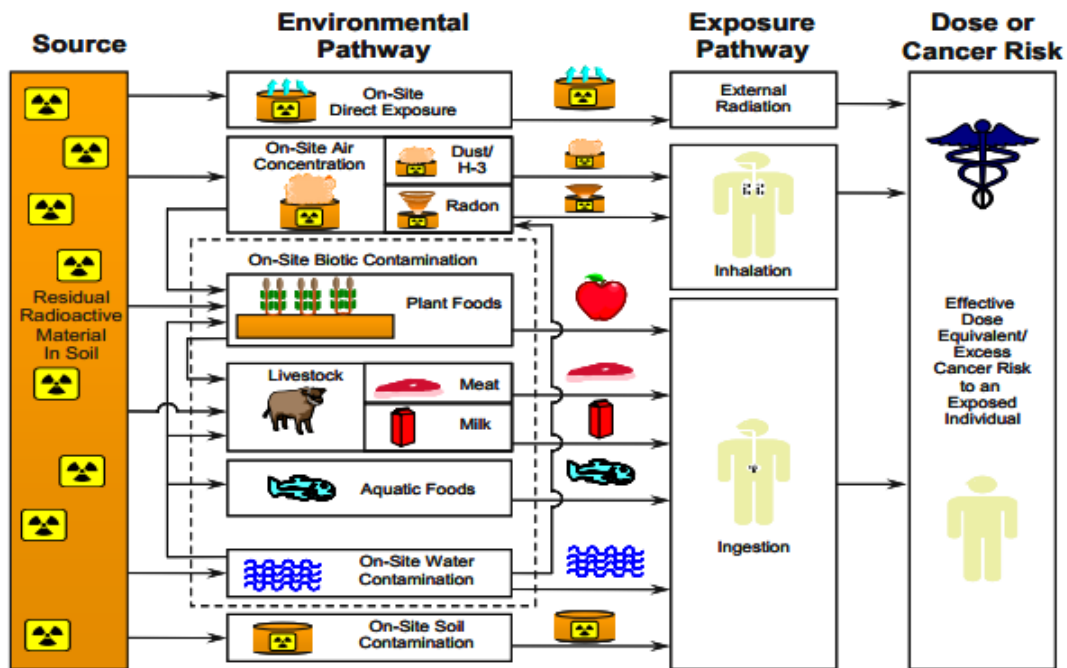


Figure 2.16: Transport of radiation from soil to humans through different exposure pathways [73].

Radiation from soil can reach humans through direct ingestion or ingestion of materials that got their way into animal and plant life through food chain. Radioactive materials in soil can be released into air and water. When released in air, they are affected by factors such as velocity of the wind and height of release and can reach a human through various pathways. The released radiation can fall back and be deposited into the ground and find way into the food chain of both plant and animal life. Moreover, humans can inhale the airborne products directly. In the same way, direct deposition of radioactive materials into water can pass on to humans through food chain or drinking (direct ingestion) [74]. Contamination in soil can be carried into streams and rivers by rain water thereby contaminating water. In addition, radioactive materials in soils can reach ground water through leaching.

2.10 Assessment of human health risk due to toxic heavy metals

Human health risk assessment process is made up of identification of hazard, exposure assessment, toxicity assessment and risk characterization which are used to quantify carcinogenic and non-carcinogenic risks to humans through different exposure pathways [75].

2.10.1 Hazard identification

Hazard identification process investigates concentrations of chemicals or toxic heavy metals that are present in the study area. Toxic heavy metals are regarded as a potential hazard to residents, therefore, their exposure assessment to humans have to be evaluated in order to determine the potential health risk they pose to humans [75]. In this study, these concentrations are determined by ICP-MS (Agilent 7500 series). The ICP-MS can measure low concentrations of elements in liquid samples. It uses inductively coupled plasma to ionize samples which are then classified according to their mass and detected. It can also detect various isotopes of the same element, which enables isotope labelling [76].

2.10.2 Exposure assessment

Exposure assessment is required to estimate the length, intensity and frequency of human exposure to a contaminant. This is accomplished by calculating average daily intake (ADI) of toxic heavy metals due to different exposure pathways to humans.

Due to physiological and behavioural deviations, ADI's of adults and children are calculated separately [77]. Exposure parameters used are shown in Table 2.5.

Table 2.5: Different exposure parameters used for assessment of health risk in soil [78].

Parameter	Child	Adult	Unit
Body weight (BW)	15	70	kg
Exposure frequency (EF)	350	350	days/year
Exposure duration (ED)	6	30	years
Ingestion rate (IR)	200	100	mg/day
Inhalation rate (INR)	10	20	m ³ /day
Skin surface area (SA)	2100	5800	cm ²
Soil adherence factor (AF)	0.2	0.07	mg/cm ²
Dermal absorption factor (ABS)	0.1	0.1	-
Dermal exposure ratio (FE)	0.61	0.61	-
Particulate emission factor (PEF)	1.3×10^9	1.3×10^9	m ³ /kg
Conversion factor (CF)	10^{-6}	10^{-6}	kg/mg
Average time (AT)			
For carcinogens	365×70	365×70	days
For non-carcinogens	$365 \times ED$	$365 \times ED$	

The ADI's of toxic heavy metals in humans are calculated differently for each exposure pathway. Using exposure parameters in Table 2.5, ADI's due to ingestion, inhalation and dermal contact are calculated as explained in sub-subsections 2.10.2.1, 2.10.2.2 and 2.10.2.3.

2.10.2.1 Toxic heavy metals ingestion through soil

A mathematical representation of ADI due to ingestion of toxic heavy metals through soil is given by equation [79];

$$ADI_{\text{ing}} = \frac{C \times IR \times EF \times ED \times CF}{AT \times BW}, \quad (2.39)$$

where ADI_{ing} is the average daily intake of toxic heavy metals through ingestion of soil in mg/kg/day, C is the concentration of a toxic heavy metal in soil in mg/kg, IR is the ingestion rate in mg/day, EF is the exposure frequency in days/year, ED is the exposure duration in years, CF is the conversion factor in kg/mg, AT is the average exposure time period in days and BW is the body weight of an individual exposed in kg.

2.10.2.2 Toxic heavy metal inhalation of soil particles

Equation 2.40 shows how the ADI due to inhalation of toxic heavy metals from soil particles is calculated [79].

$$ADI_{inh} = \frac{C \times INR \times EF \times ED}{AT \times BW \times PEF}, \quad (2.40)$$

where ADI_{inh} is the average daily intake of toxic heavy metals through inhalation of soil in mg/kg/day, C is the concentration of a toxic heavy metal in soil in mg/kg, INR is the inhalation rate in m³/day, EF is the exposure frequency in days/year, ED is the exposure duration in years, AT is the average exposure time period in days, BW is the body weight of an individual exposed in kg and PEF is the particulate emission factor in m³/day.

2.10.2.3 Dermal contact with soil

ADI of skin contact with a toxic heavy metal from soil is calculated by equation [79];

$$ADI_{dem} = \frac{C \times SA \times FE \times AF \times ABS \times EF \times ED \times CF}{AT \times BW}, \quad (2.41)$$

where ADI_{dem} is the exposure dose of toxic heavy metals through dermal contact in mg/kg/day, C is the concentration of a toxic heavy metal in soil in mg/kg, SA is the skin surface area exposed in cm², FE is the dermal exposure ratio to soil, AF is the adherence factor in soil in mg/cm², ABS is the dermal absorption factor, EF is the exposure frequency in days/year, ED is the exposure duration in years, CF is the conversion factor in kg/mg, AT is the average exposure time period in days and BW is the body weight of an individual exposed in kg.

2.10.3 Assessment of toxicity/Dose response assessment

Toxicity assessment is estimated using exposure levels of toxic heavy metals. The two essential indices for this estimation are CSF (cancer slope factor) and RfD (reference dose) shown in Table 2.6 [80]. These values were obtained from USEPA and Department of Environmental Affairs (South Africa) [78].

Table 2.6: Reference doses and cancer slope factors for toxic heavy metals [78].

Toxic heavy metal	Reference dose (RfD)			Cancer slope factor (CSF)		
	Ingestion	Inhalation	Dermal	Ingestion	Inhalation	Dermal
As	3.00×10^{-4}	3.00×10^{-4}	3.00×10^{-4}	1.50×10^0	1.50×10^1	1.50×10^0
Pb	3.60×10^{-3}	-	-	8.50×10^{-3}	4.20×10^{-2}	-
Hg	3.00×10^{-4}	8.60×10^{-5}	3.00×10^{-4}	-	-	-
Cd	5.00×10^{-4}	5.70×10^{-5}	5.00×10^{-4}	-	6.30×10^0	-
Cr	3.00×10^{-3}	3.00×10^{-5}	-	5.00×10^{-1}	4.10×10^1	-

2.10.4 Characterization of risk

Risk characterization estimates the potential health risk due to exposure to carcinogenic and non-carcinogenic hazards for both adults and children. Non-carcinogenic risk is estimated through a hazard quotient which is calculated using doses/ADI's of different exposure pathways divided by reference doses [81]. Individual cancer risk of different exposure pathways are added up to calculate the carcinogenic risk.

2.10.4.1 Assessment of non-carcinogenic risk

Equation 2.42 shows the mathematical representation of hazard quotient calculated in order to estimate the non-carcinogenic risk [82].

$$HQ = \frac{ADI}{RfD}, \quad (2.42)$$

where HQ is the hazard quotient, ADI is the average daily intake or exposure dose, RfD is the reference dose value or toxicity threshold value of a particular toxic heavy metal in mg/kg/day.

To calculate overall potential of non-carcinogenic risk due to all exposure pathways, hazard index is applied as depicted in equation [82];

$$HI = \sum_{i=1}^n HQ_i = \sum_{i=1}^n \frac{ADI_i}{RfD_i}, \quad (2.43)$$

where HI is the hazard index, n is the number of toxic heavy metals considered and HQ_i , ADI_i , RfD_i are values for a specific toxic heavy metal i .

2.10.4.2 Assessment of carcinogenic risk

Carcinogenic risk is calculated as the probability of an exposed individual to carcinogens to develop cancer in a lifetime. The lifetime cancer risk to an individual is obtained by equation [82];

$$Risk_{\text{pathway}} = \sum_{i=1}^n ADI_i CSF_i, \quad (2.44)$$

where $Risk$ is an individual's probability to develop cancer in a lifetime, CSF_i is cancer slope factor for a specific toxic heavy metal i shown in Table 2.6 and ADI_i is the average daily intake or exposure dose for a particular toxic heavy metal i .

Contributions from different exposure pathways result in an individual's excess lifetime cancer risk. This is illustrated by equation [82];

$$Risk_{\text{tot}} = Risk_{\text{ing}} + Risk_{\text{inh}} + Risk_{\text{dem}}, \quad (2.45)$$

where $Risk_{\text{ing}}$, $Risk_{\text{inh}}$, $Risk_{\text{dem}}$ are cancer risks due to ingestion, inhalation and dermal contact of carcinogens.

2.10.5 Heavy metals considered

Metals play a crucial role in all living organisms but toxic at higher concentrations. However, there are some metals that are of no use to living organisms and in the human physiology. Examples of these metals include arsenic, mercury and lead which are toxic at low concentrations [83]. Heavy metals can be classified into toxic and radiotoxic. These can reach a person through different exposure pathways, that is, ingestion, inhalation and through dermal contact.

2.10.5.1 Toxic heavy metals;

- **Arsenic**

Exposure to extremely low levels of arsenic can cause carcinogenic risk to humans. Once absorbed through inhalation or ingestion, arsenic is distributed to the internal organs e.g. spleen, aorta, lungs, liver and kidneys [84]. However, it is distributed to skin through dermal contact. Symptoms differ from one type of exposure to another. Diabetes, peripheral nerve damage and strange patterns of skin pigmentation are a result of chronic exposure of lower levels of this metal [85]. Acute exposure to arsenic and its compounds can result in abdominal pain,

burning sensation of mouth and throat, nausea, vomiting and diarrhoea.

- **Mercury**

Mercury exists as organic or non-organic. The inorganic mercury is very toxic at low levels and inhalation of mercury vapour can cause chest pains, headache, nausea, cough, renal and liver failure in severe cases [86]. Chronic exposure results in serious disruption of the central nervous system together with the skin, kidneys, liver and gastronomical tract. Human toxicity is affected by exposure rate, dose and form of mercury [87].

- **Cadmium**

Cadmium is also a toxic heavy metal than can cause carcinogenic risk to humans. It accumulates in human body with time and exposure [88]. In the long run, exposure to low levels of cadmium localises it primarily in the kidney and liver. It also accumulates in organs like lungs, spleen, testes, pancreas and other endocrine organs. Occupational exposure to this metal results in lung, kidney and prostate cancers [89]. Low doses of this metal can result in testicular necrosis where as high doses may lead to placental and sensory ganglia necrosis.

- **Chromium**

Chromium exists in different oxidation states with trivalent and hexavalent as the most stable forms of chromium [90]. Trivalent chromium is a beneficial element to animals where as hexavalent chromium is toxic, has poor absorption and is associated with human carcinogenesis [91]. The health hazards that result from chromium exposure are skin allergies, lung and nasal cancers, ulcers, reproductive problems and death in severe exposure cases [90].

- **Lead**

Lead is considered as one of the most toxic heavy metals which do not have any biological function to the body [91]. As its levels increase in the body, it affects renal, cardiovascular, nervous, skeletal, digestive and reproductive systems. Acute exposure to lead may result in nausea, anaemia, fatigue and abdominal pain [92].

2.10.5.2 Radiotoxic heavy metals;

- **Uranium**

Uranium has a density of 19.1 g/cm^3 which makes it the heaviest naturally occurring metal. Due to all of its isotopes being radioactive, it is primarily regarded as radiotoxic. Mechanisms of uranium toxicity may lead to protein modifications

and changes in enzyme activity. Their interaction with the Deoxyribonucleic acid (DNA) may cause mutagenesis or carcinogenesis. Kidneys are the primary target organs for uranium [93].

- **Thorium**

Thorium has 12 known radioactive isotopes, thus making it a toxic radioactive element that has been a threat to public health throughout the years. Its ions often contaminate ground and surface water sources which causes a threat to the environment [94]. Once thorium ions enter living organisms, it gathers in lungs, liver, marrow and renal system. Toxicity of thorium is low in comparison to toxicity of uranium. This is as a result of its stability at room temperature and pressure [95].

2.11 Calculations of correlation between radionuclides and toxic heavy metals

A Pearson's correlation coefficient (r) is used to calculate all the correlations in this study. It explains a linear level of relationship between 2 variables, x and y , which represents radionuclides and heavy metals considered in this study. Negative correlation shows that the 2 variables, that is, x and y are inversely proportional to each other and a positive correlation means the variables are directly proportional. A zero correlation means there is no linear relationship between variables. It is represented mathematically by equation [96];

$$r = \frac{n \sum xy - \sum x \sum y}{\sqrt{(n \sum x^2 - (\sum x)^2)(n \sum y^2 - (\sum y)^2)}}, \quad (2.46)$$

where r is the Pearson's correlation coefficient and x and y are variables. Table 2.7 shows what (r) represents in different cases.

A Pearson's correlation has a maximum of + 1.00 and a minimum of -1.00, therefore, any value that does not fall within this range is invalid. A correlation of +1.00 or -1.00 means a perfect linear relationship between 2 variables and a correlation value that is closer to zero shows no association or different behaviour between variables [97]. However, significance levels of correlation were calculated using Pearson's P value (R) calculator. Confidence level of 0.01 verifies that correlation is 99% significant, 0.05 confirms that correlation is 95% significant and 0.10 means that correlation is 90% significant.

Table 2.7: Different cases which are a possible result of Pearson's correlation coefficient [96].

Case	Relation between variables	Practical meaning in this study
$0.60 \leq r \leq 1.00$	strong positive correlation	60 - 100 % chance that the variables have similar transport behaviour or are from the same origin
$0.00 \leq r \leq 0.40$	weak positive correlation	0 - 40 % chance that the variables have similar transport behaviour or are from the same origin
$0.40 < r < 0.60$	moderate positive correlation	Between 40 and 60 % chance that the variables have similar transport behaviour or are from the same origin
$r = 0$	zero/no correlation	No linear relationship between variables
$-0.60 \leq r \leq -1.00$	strong negative correlation	60 -100 % chance that the variables have different transport behaviour or are not from the same origin
$-0.00 \leq r \leq -0.40$	weak negative correlation	0 - 40 % chance that the variables have different transport behaviour or are not from the same origin
$-0.40 < r < -0.60$	moderate negative correlation	Between 40 and 60 % chance that the variables have different transport behaviour or are not from the same origin

Experimental Methods and Techniques

This study was conducted in a bid to evaluate NORMs and heavy metal concentrations in the surface soil around Serule prospective mining area in Botswana. To achieve this, sample collection, preparation and analysis for natural radiation and heavy metal concentrations were carried out and are discussed in detail in this chapter. A series of experiments carried out, experimental setups as well as equipment used and its parameters are also described.

3.1 Study area

Serule is a village located in the north-eastern part of Botswana with coordinates 21°50'S and 27°25'E and has an average altitude of 937 m. It is adjacent to the country's main road (A1) and the railway line that cuts across Botswana from South Africa to Zimbabwe [98]. The village is located 350 km north of the country's capital city (Gaborone) and 90 km south of Francistown (the second biggest city) [99]. According to the latest population census (2011), the total number of people living in Serule is 3639 [100]. Large uranium deposits were discovered by an Australian company named A-cap Energy Ltd in the underlying rocks of Serule. It was licensed to start a shallow open pit uranium mining in 2016 with a lease of about 144 km². As a result, evaluating concentrations of NORMs and toxic heavy metals in the area before mining starts is a necessity as it serves as baseline data. About $\frac{2}{3}$ of the leased area was covered during sample collection. The study area consists of different types of soils which include but are not limited to, leptosols, lixosols, eutric arenosols, chromic livosols and regosols [101]. The study area with reference to Botswana is shown in Figure 3.1.



Figure 3.1: Location of study area with reference to Botswana map.

3.2 Sample collection

Different sampling methods can be used in environmental analyses of radionuclides and toxic heavy metals. An area of chosen square metres can be demarcated at every sampling point. Samples from a few positions of the selected area can be mixed together to represent a position. This method is generally ideal for small sampling areas which are mostly even. For large sampling areas, which are mostly forests with an uneven geographical representation, random sampling method is adopted. The study area was not easily accessible for demarcation, therefore, the random sampling method was adopted. The sampling points were limited by accessibility of the sampling area, therefore, more samples were collected from areas that were accessible, as a result, sampling points appear clustered in the central region in Figure 3.2.

A shovel was used to clear the ground and remove vegetation, then an auger was twisted about 15 cm deep into the ground to lift out a soil sample. It was then emptied into a ziplock polyethylene bag which was sealed and labelled. GPS coordinates of the location where a sample was collected was recorded. The rest of the samples were collected in a similar manner. Samples were randomly collected from 29 different locations in Serule area. A control sample was collected on the outside of study area following the same procedure and it was labelled the control. Different locations of sample collection included the prospective uranium mining licensed area, areas

near boreholes, people's residences, cattle posts and areas outside the licensed area. Specific GPS coordinates of each sample collection location are presented in Table A.1 of Appendix A and shown in Figure 3.2.

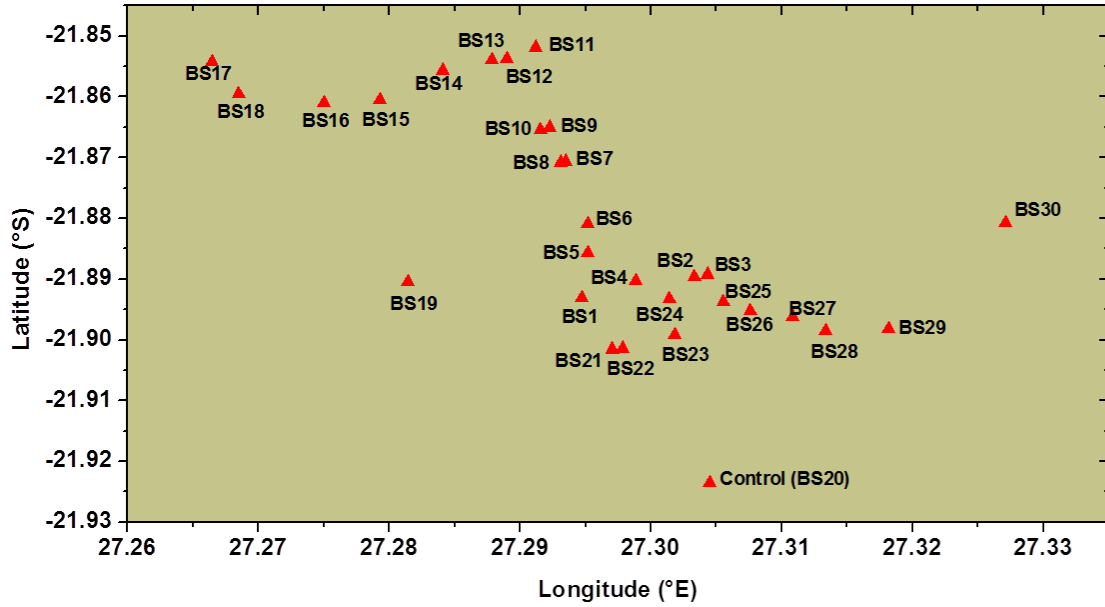


Figure 3.2: GPS coordinates of locations where samples were collected in the study area.

To avoid cross contamination between samples, a brush was used to clean the auger before collecting the next sample. Samples were labelled according to sequence of collection and date. For example, a sample collected on the third location was labelled BS3 (Botswana Serule sample 3) and the date of collection was stated. Figure 3.3 shows some of the equipment used during soil sampling.



Figure 3.3: Equipment used in soil sampling a) a shovel used for ground clearing b) an auger for collecting soil from 15 cm deep c) brush for cleaning the auger and d) a polyethylene plastic bag to contain soil samples.

Samples were then transported to BIUST radiation materials store laboratory in the Physics and Astronomy department where they were stored prior to sample preparation.

3.3 Sample preparation for gamma-ray spectroscopy

Gamma-ray spectroscopy was used to analyse samples for existing radionuclides and their activity concentrations. Samples were prepared following the Environmental Measurements Laboratory standard procedures [102]. Sample preparation for this technique was carried out in a Mining and Geotechnical engineering laboratory in BIUST and protective clothing was worn throughout the process. Organic matter was removed from samples and disposed accordingly. Samples were then placed in moisture cans and were heated in an oven for 24 hours at a temperature of 60°C to ensure that they were completely dry. After the samples cooled, they were sieved with a 1.18 mm sieve to remove larger grains and grass roots. Larger soil particles were ground with a mortar and pestle before sieving them. Sieving samples was to ensure that they have similar particle size. An empty 550 ml beaker was weighed and the mass was recorded. Each sample was then filled in a separate beaker to the brim in order to match the

volume of the standard used for detector calibration. Samples were then weighed and sealed with a PVC tape and stored in a BIUST radiation materials store laboratory for a month in order to allow radioactive secular equilibrium. This type of equilibrium is explained in detail in subsection 2.3.1. Masses of the various samples are shown in Table A.1 (Appendix A). Figure 3.4 shows the equipment that was used for sample preparation.

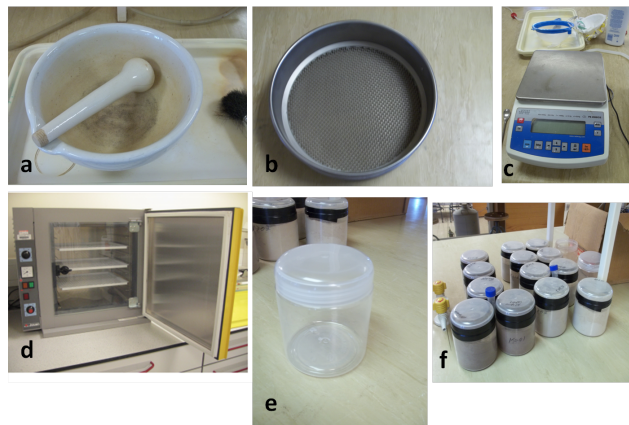


Figure 3.4: Apparatus used during sample preparation for gamma ray spectrometry a)Mortar and pestle for crushing large soil particles b) 1.18 mm standard sieve c) Top pan balance for weighing samples d) Oven for drying samples d) 550 ml plastic beaker for containing samples f) PVC tape sealed samples ready for storage.

The High Purity Germanium detector (HPGe) of North-West University (NWU) in Mafikeng, South Africa was used to carry out the gamma ray spectroscopy analysis of the soil samples. This equipment is shown in Figure 3.5. The HPGe detector is placed inside a 10 cm low level thick lead shielding to prevent background radiation.



Figure 3.5: The gamma-ray spectroscopy of North-West University, Mafikeng, South Africa.

3.4 Sample preparation for ICP-MS analysis

ICP-MS was used to measure concentrations of heavy metals in samples. After removing organic matter from samples as explained in section 3.3, a small amount of each sample was pocketed separately in smaller polyethylene bags and transported to an Eco-analytica laboratory for soil, plant and water analysis in Potchefstroom, North West University in South Africa, where sample preparation for ICP-MS analysis took place.

About 20 mg of each sample was weighed into Teflon tubes before 9 ml of 65% concentrated nitric acid (HNO_3) and 3 ml of 32% hydrochloric acid (HCl) were slowly added. The mixtures were gently swirled and left for 10 minutes before the tubes were tightly capped and weighed again. The tubes were then properly placed inside a high performance Milestone, Ethos UP, Maxi 44 microwave digestion system for closed vessel acid digestion. The system reached a power of 1800 MW and a temperature of 200°C in 20 minutes which were maintained for 15 minutes. A temperature feedback control was used to monitor the reaction. This was to ensure that there was no leakage in vessels.

After the digestion period elapsed, tubes were allowed to cool before removing them from the system. Each tube was then weighed and if the mass of tube before and after digestion had a difference of more than 1%, then the sample was considered compromised. The tubes were uncapped and aired out in a fume exhausted enclosure then transferred into a 50 ml acid cleaned volumetric flask and diluted with distilled water such that the solution reached the maximum volume of the flask. This was left overnight to allow sediments to settle. Solutions that had particulate matter were then filtered using acid cleaned apparatus. Sample solutions were transferred into 15 ml centrifuge tubes then analysed for concentration of heavy metals using ICP-MS (Agilent 7500 series).

From the results obtained from both techniques, a correlation between concentrations of radionuclides and heavy metals was established. Also, radiological and toxicological risks to residents were estimated and discussed in Chapter 4.

3.5 Experimental setups

3.5.1 HPGe detection system

A HPGe detector was used to perform gamma ray spectroscopy analysis in this study. A broad energy germanium detector (BE6530) was used to identify and quantify gamma emitting isotopes from soil samples. It is a product of Canberra industries and for energy 1332 keV in gamma ray emission of ^{60}Co , it has relative efficiency of 60% and a 2.0 keV resolution [103]. It can detect various gamma emitting radionuclides in samples. Activities and specific energies of detected radionuclides can be obtained from spectral lines [39, 104]. In this study, the HPGe detector of North West University in Mafikeng, South Africa was used for gamma ray spectroscopy. A schematic layout of the HPGe counting system is shown in Figure 3.6.

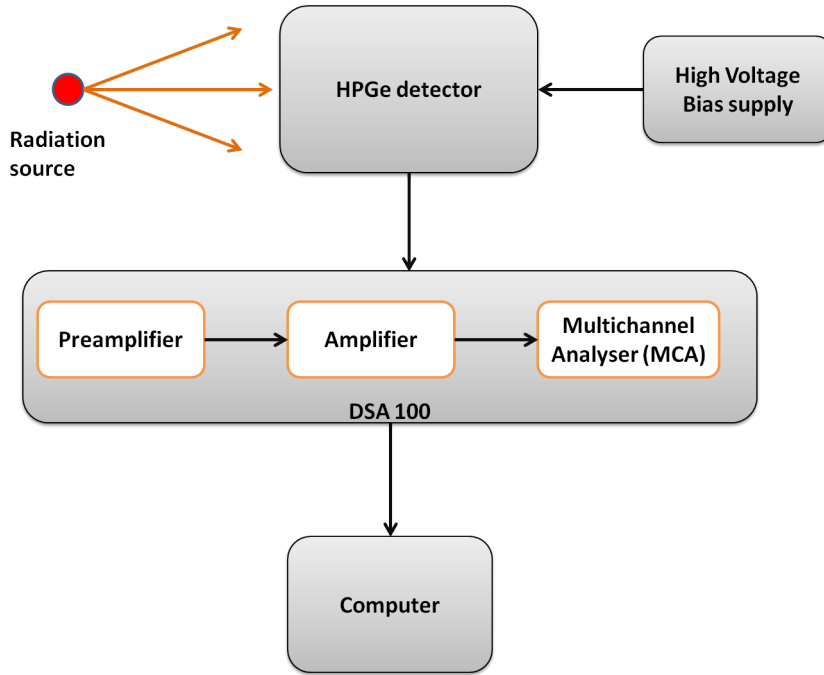


Figure 3.6: Layout of gamma-ray spectrometric analysis system.

The HPGe counting system consists of a detector, high voltage bias supply, DSA 100 and a computer. Uses of these components are described as follows;

Detector: gamma rays emitted by samples interact with the detector through three principal interaction processes, that is, photoelectric effect, Compton scattering and pair production [105]. Electronic charges relative to the gamma-ray energy reaching the detector are then produced. To prevent background radiation, the detector is

placed in a low level lead shield with a thickness of 10 cm [106].

High voltage bias supply: produces electric field that collects electronic charges produced by the interaction of gamma rays and the detector [39]. This is needed to keep the system running. The high voltage bias power supply was set to 4500 V which was cooled beforehand by liquid nitrogen to reduce leakage current noise [104, 107].

DSA 100: contains the electronic counting system, namely, a preamplifier, amplifier and a Multi-Channel Analyser (MCA). The system gathers and stores electric charge from the detector and outputs a gamma-ray spectrum [39].

- **Pre-amplifier:** collects all charge carriers and converts them to a voltage pulse. The pulse is then modified in terms of shape and size in order to be suitable for the amplifier [39].
- **Amplifier:** shapes pulses and enlarges them. These pulses are then classified by their height to wipe out the noise and baseline shifts [39].
- **Multi Channel Analyser (MCA):** from the amplifier, pulses are converted to a digital number by an analogue to digital convertor (ADC) in the multichannel analyser. This digital number is referred to as a channel. According to the pulse height range, the number of pulses are determined and stored in each channel number which adds to the gamma-ray spectrum [105]. The HPGe detector in this study uses an 8192 channel MCA.

Computer: visualises obtained gamma ray spectrum from samples. Basic spectrum analysis is controlled by the Genie 2000 software (a spectrum analysis software) through the computer [39].

Background radiation of the HPGe detector was measured before and after analysing all samples measurements and it was subtracted from each sample measurement. To obtain a gamma ray spectrum of high signal-to-noise ratio, counting was carried out for 43200 s for each sample, background measurement and standard sources.

3.5.1.1 Energy calibration

Energy calibration of the detector is necessary for identification of radionuclides available in the background and low activity environmental samples. It shows the relationship between channel numbers and energy [107]. A reference material used for energy calibration of the detector in this study was a uranium ore prepared by International

Atomic Energy Agency (IAEA) and coded as IAEA-RGU-1. Its spectrum was collected for 43200 s and energy peaks were recorded against associated channel numbers.

The plot is a linear curve which is represented mathematically by the equation;

$$E = 0.2205keV/Ch + 0.04368keV, \quad (3.1)$$

where E is energy in keV and Ch is the channel number.

For spectra collected with the same detector, energies of any other peaks that do not belong to IAEA-RGU-1 standard source were calculated using equation 3.1. The energy calibration curve shown in Figure 3.7 was obtained from this relation. However, calibration was done regularly under the same conditions in order to avoid spectra shift.

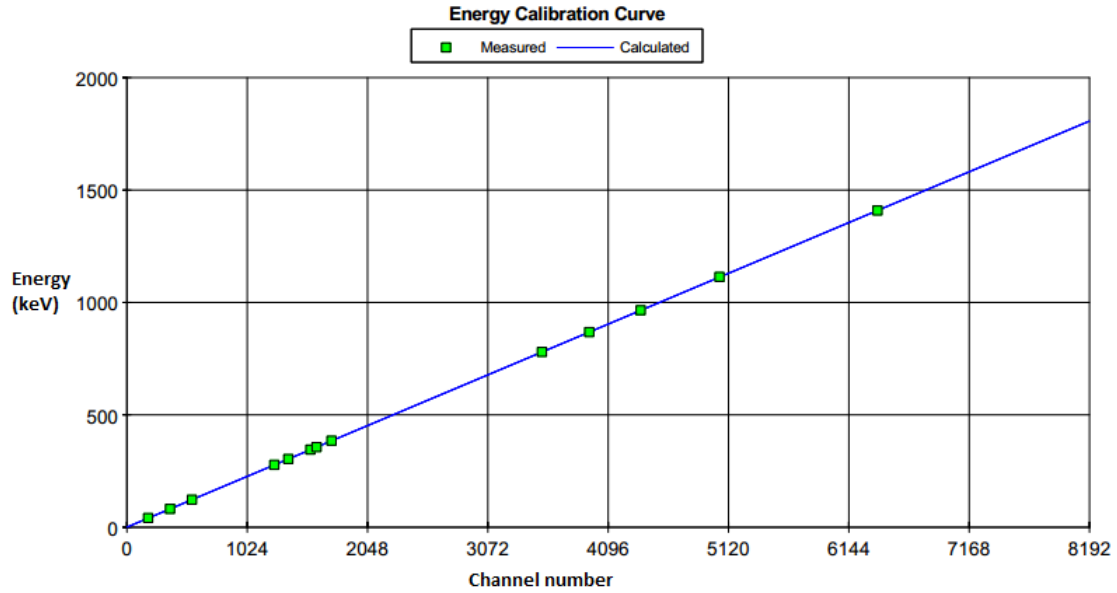


Figure 3.7: Energy calibration curve from the IAEA-RGU-1 standard source.

The reference sample spectrum used for energy calibration obtained from the gamma ray spectroscopy system is shown in Figure 3.8.

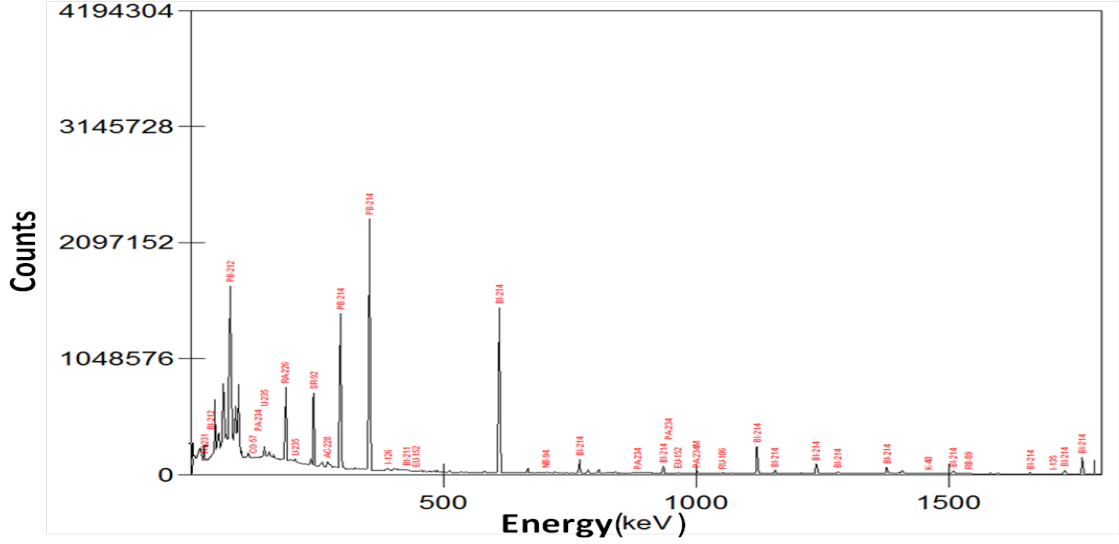


Figure 3.8: The reference sample spectrum used for energy calibration.

3.5.1.2 Efficiency calibration

For a detection to be possible, gamma radiation must interact with a material. It can travel relatively large distances before an interaction takes place, therefore, radiation detectors are usually less than 100% efficient. For this reason, it is essential to calculate the precise figure of efficiency of the detector [40]. Absolute full energy peak efficiency is defined as [107];

$$Eff = \frac{C_t}{N_\gamma} \times 100\%, \quad (3.2)$$

where C_t is total number of counts detected per unit time and N_γ is number of gamma rays emitted by the source per unit time. N_γ is given by equation;

$$N_\gamma = D_s I_\gamma(E_\gamma), \quad (3.3)$$

where D_s is activity of source, $I_\gamma(E_\gamma)$ is the emission probability.

IAEA-RGU-1 standard source used for calibration of the detector had the same geometry as samples. It was analysed for 43200 s to obtain a gamma ray spectrum. An efficiency calibration curve obtained from IAEA-RGU-1 standard source is shown in Figure 3.9 and is defined by equation 3.4.

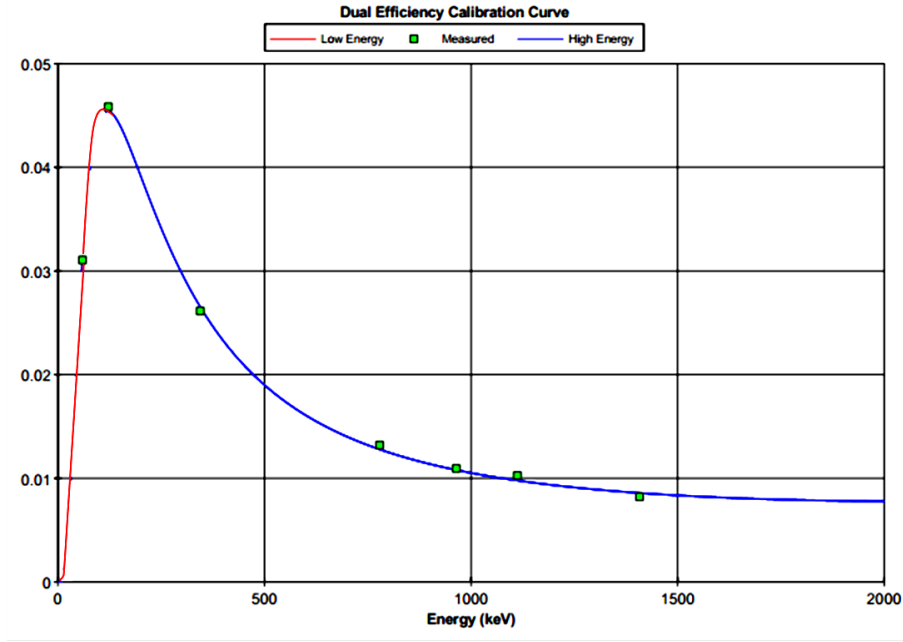


Figure 3.9: Efficiency calibration curve of the HPGe detector.

Equation 3.4 calculates efficiencies for all measured data and can be used for all environmental samples analysed with the same detector. However, a regular efficiency calibration is necessary.

$$\ln(Eff) = -9.207 + 4.414 \ln E - 2.755 \ln E^2 + 0.543 \ln E^3, \quad (3.4)$$

where Eff is the efficiency of the detector at a certain energy peak and E is the full energy peak.

3.5.1.3 Minimum Detectable Activity (MDA)

Minimum detectable activity is defined as the least amount of a radionuclide that can be detected in a given spectrum measurement. It is affected by the efficiency of the detector, detector environment and spectrum counting time. Radiation counts of background radiation and its spectrum were obtained by recording counts of an empty 550 ml polyethylene beaker in the HPGe detection system for 43200 s. For lowest MDA, it is essential to reduce background counts, increase efficiency of the detector and counting time of spectrum. The detector was placed in a 10 cm thick lead shielding to minimize background counts [108]. MDA's of different radionuclides were calculated using Genie software 2000 and equation;

$$MDA = \frac{\phi \sqrt{N_B}}{I_\gamma \epsilon m T}, \quad (3.5)$$

where ϕ is the statistical coverage factor of 1.645 with 95% confidence interval, N_B is the background under a specific photo peak, I_γ is the probability of a specific photo peak energy to be emitted, ϵ is absolute efficiency of the detector, m is mass of sample and T is time taken for collection of spectrum.

3.5.1.4 Gamma lines considered

Gamma emitting radionuclides were analysed in the spectra adapted from gamma-ray spectroscopy system. Activity concentrations of these gamma emitting radionuclides in units Bq/kg were obtained by dividing established activities by the mass of a given sample. It was then obtained equation [67], [109];

$$A_{Bq/kg} = \frac{N}{I_\gamma \epsilon(E_\gamma) m}, \quad (3.6)$$

where; N = corrected net peak area for a specified energy peak (peak area in the background spectrum subtracted from peak area of sample spectrum), I_γ = probability of gamma emission corresponding to the energy peak, $\epsilon(E_\gamma)$ = efficiency of the detector at photo peak energy and m = mass of sample in kg listed in Table A.1 in Appendix A.

Radionuclides ^{238}U , ^{232}Th , their daughter nuclides and non-series ^{40}K make a large contribution to natural radioactivity in soil, therefore, they are usually used in determination of soil radioactivity [110]. However, activity concentrations of ^{238}U and ^{232}Th were obtained by calculating weighted mean activities of their gamma emitting daughter radionuclides using equation B.1 in Appendix B. Activity concentration of ^{40}K was obtained straight from its peak. Daughter nuclides starting from ^{226}Ra in the ^{238}U series (shown in Figure 2.4) are radiologically dominant thus leading to reference being made to radium rather than uranium [61]. Also, ^{210}Pb was observed since it is a ^{238}U decay series daughter nuclide that has the longest half-life. These selected radionuclides were used for gamma-ray analysis and are described as follows;

- ^{238}U

^{238}U is a naturally occurring radionuclide that migrates and redistributes through surface and ground water sources [111]. It makes more than 99% of natural uranium, thus making it a great health concern. Uranium ore consists of all decay products of isotopes of ^{238}U [112]. Activity concentration of ^{238}U was calculated using weighted mean concentration of ^{234}Th at peak energies 63.29 keV and 92.59 keV and ^{234m}Pa at peak energy 1001.03 keV.

- **^{226}Ra**

^{226}Ra is a particular concern in the decay series of ^{238}U due to its high potential of large dietary exposure via agricultural products. Its moderate level of decay aids soil accumulation and its soil to plant transfer is larger than of thorium, uranium and lead. It has high dose coefficients due its long term staying power in the body and moderate absorption rate in the gastrointestinal system [113]. Weighted mean concentrations of ^{214}Bi (at energies 609.32 keV, 1120.29 keV and 1764.54 keV) and ^{214}Pb (at peak energies 351.95 keV and 295.22 keV) were used to establish activity concentrations of ^{226}Ra [106].

- **^{210}Pb**

During ^{238}U decay process, diffusion of ^{222}Rn from ground into the atmosphere results in formation of ^{210}Pb . This makes most of ^{210}Pb found in the environment [114]. It is one of the final radionuclides that are long lived in ^{238}U decay series. ^{210}Pb isotope mainly reaches humans through ingestion or inhalation. Due to its chemical properties, it cannot be eliminated, therefore, it accumulates in the body causing radiological impacts once it reaches a threshold level [115]. Its activity concentration was calculated directly from its peak energy of 46.54 keV.

- **^{40}K**

Naturally occurring potassium has three isotopes; ^{39}K , ^{40}K and ^{41}K . Only ^{40}K is radioactive [61]. Although ^{40}K is essential for the body, it can also cause both internal and external radiation hazard. This hazard is linked to cell damage that poses a possibility of cancer induction [116]. Peak energy of ^{40}K at 1460.82 keV was used to calculate its activity concentration.

- **^{232}Th**

Naturally occurring thorium is mainly present as ^{232}Th . Its decay products have different physical and chemical properties whose concentrations vary with respect to geological conditions. Environmental exposure to this radionuclide is mainly associated with bone cancer and its main exposure concern is through ingestion (food chain and drinking water) and inhalation [117, 116]. Activity concentration of ^{232}Th was computed from mean peak energies of ^{228}Ac (338.32 keV and 911.20 keV) and ^{212}Pb (238.63 keV) [106].

3.5.1.5 Main limitations and sources of error in the HPGe measurements

In gamma ray spectrometry, indirect measurements are used to quantify natural radionuclides. The interferences resulting from the analysis should be taken into consideration since they affect accuracy of results. Assuming that secular equilibrium is reached in the uranium and thorium decay series, the quantitative analysis of ^{238}U and ^{232}Th can be drawn from their gamma-emitting daughter nuclides. ^{238}U is mainly quantified by ^{234}Th or ^{234m}Pa which have some imperfections when analysed. In general, ^{234}Th can be analysed from gamma-rays with peak energies 63.3 keV and 92.6 keV. However, these peak energies have interferences with other gamma lines of ^{234}Th at 62.88 keV and 92.80 keV, respectively. As a result, ^{234}Th doublets are formed. Other gamma-ray peaks mainly from thorium decay series also interfere with gamma lines from ^{234}Th . For thorium rich samples, the interferences should be corrected in order to get accurate results from analysis of ^{234}Th [118].

On the other hand, although gamma lines from ^{234m}Pa have no interference with other gamma-ray peaks in natural radionuclides, using ^{234m}Pa as an indicator of ^{238}U is impractical, particularly in low activity levels of uranium decay series. This is due to its high minimum detectable activity and uncertainty resulting from very low intensity of gamma-rays it emits. The interferences should be taken into consideration for more accurate results during analysis.

3.5.2 ICP-MS analysis system

3.5.2.1 Description of ICP-MS and its components

Trace metal analysis of elements that have naturally occurring isotopes can be performed by ICP-MS, therefore, most of the elements in the periodic table can be measured by ICP-MS. It is recommended over other techniques since it has low detection limits (below or at single parts per trillion for most of the periodic table elements), analysis of isotopes can be achieved readily and the magnitude of its analytical working range is nine orders [119]. Figure 3.10 shows a setup of the ICP-MS system.

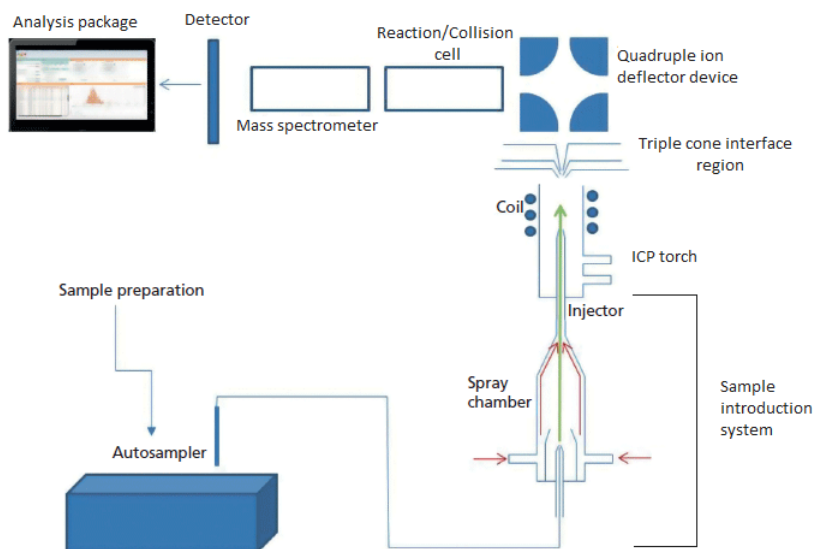


Figure 3.10: A schematic setup of ICP-MS system [120].

Sample introduction : A peristaltic pump introduces a digested liquid sample from the autosampler into the system by pumping it into a nebuliser which forms an aerosol of fine droplets [121].

ICP torch : Plasma is produced through coupling of argon (passing through ICP torch) and energy from radio frequency generator. It makes a very hot zone (approximately 6000°C) that dries up liquid droplets and heats them into a gas. Gas atoms absorb more energy as they go through the plasma, as such, they lose one electron and become positively charged ions which enters into an interface region [119].

Interface region : It consists of a sample cone, skimmer cone and hyper-skimmer cone which filters non-ionised material and shapes the ion beam before it enters a quadrupole ion deflector.

The vacuum system : Removes almost all of the gas molecules between interface region and the detector (about 1 m distance).

Ion deflection device : Deflects and focuses ions of specified mass at 90°, separating them from photons and neutrals.

Collision/Reaction cell : One type of interference removal should be chosen depending on the nature of samples being analysed. Collision cell mode removes interferences that are minor while reaction mode removes large interferences [119].

Mass spectrometer : It separates ions from one another using a mass-charge ratio and eject unstable ones. For different mass-charge ratios to pass through, conditions of a quadrupole mass spectrometer are rapidly changed by the electronics. This is to cover for a full range of mass-charge ratios [121].

The detector : Consists of an active surface (dynode) that loses an electron each time an ion strikes it. As the ions hit the dynode, an amplification process begins. Ions that hit the first dynode are diverted to the next one where more electrons are produced. The system then measures pulses that are produced during this process and analyses them through a computer software [119].

An Agilent ICP-MS 7500 series of Eco-analytica laboratory for soil, plant and water analysis in Potchefstroom, North West University in South Africa was used to carry out heavy metal analysis of all samples in this study. Description of its general design is discussed in subsection 3.5.2.1. Samples for this technique were prepared using EPA 3051A method of acid digestion described in section 3.4.

The ICP-MS has a micro-mist nebulizer and standard quart spray chamber. For standard low interference levels ($\leq 1.5\%$), a solution consisting of Ce, Li, Tl and Y (1 ppb) was used to optimise the instrument while a high sensitivity was maintained across the mass range. Table 3.1 gives instrumental parameters set before running the samples.

Table 3.1: Parameters used when operating ICP-MS.

Parameter	Value
Sampling depth	8 mm
Spray chamber temperature	2°C
Forward power	1550 W
Plasma gas flow	15 L/min
Nebulizer gas flow	1.2 L/min

An Agilent ICP-MS 7500 series of North West University was used for sample analysis of heavy metals. A typical Agilent 7500 series ICP-MS is shown in Figure 3.11.

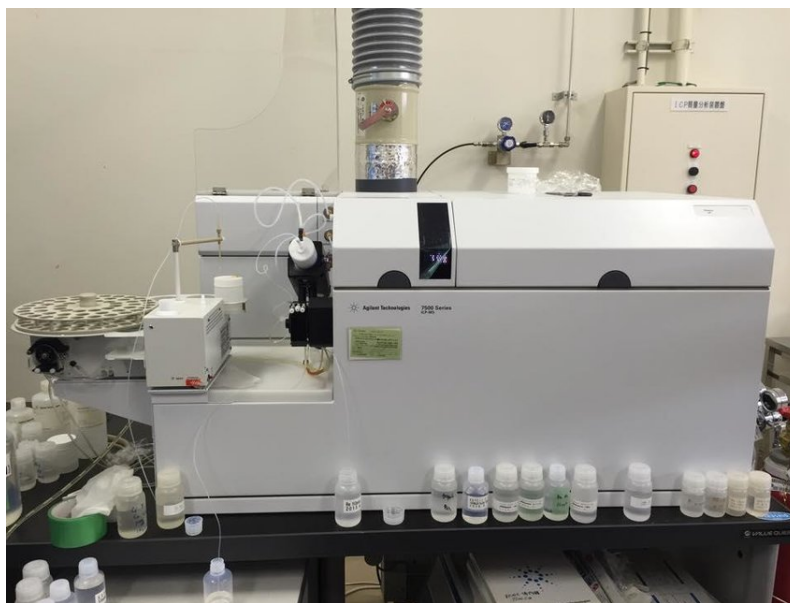


Figure 3.11: An Agilent 7500 series ICP-MS system [122].

3.5.2.2 Calibration of ICP-MS

ICP-MS system was calibrated with a multi-element standard solution that has a valid certificate. One straight calibration line was obtained from analysis of each element. Each calibration line had at least four concentrations. In each case, measurement of one reagent solution was made and the unit automatically measured and averaged at least three measurements. From the calibration curve, correlation coefficient should be greater than 0.995, if not, a higher measurement uncertainty should be expected. An aqueous certified reference sample was used to verify the quality and correctness of calibration. It was analysed after every 20 samples and the system was recalibrated if the deviations were greater than 20% [123].

3.5.2.3 Preparation of the system

The system was started at least 30 minutes before operation to make sure that it was stable enough for measurement. An optimising solution was used to check the system in terms of mass calibration of the spectrometer, sensitivity and stability of the signal and resolution. It kept minimal formation of double charged ions and oxides, as such, it was made of elements of different masses that form double charged ions and oxides at different rates. In cases of any interferences, they were minimized as much as possible by varying the settings [123].

3.5.2.4 ICP-MS detection limit

Detection limits obtained from the Agilent 7500 series ICP-MS used in this study are shown in Table 3.2. All concentrations that were less than the detection limits stated for various elements were regarded as BDL (below detection limit). However, specific concentrations were recorded for values above the detection limit.

Table 3.2: Detection limit of elements detected in mg/kg obtained from the Agilent 7500 series ICP-MS used.

Element	Detection limit (<i>mg/kg</i>)
⁹ Be	4.31x10 ⁻⁶
¹¹ B	2.46x10 ⁻³
²³ Na	1.48x10 ⁻⁴
²⁵ Mg	2.99x10 ⁻⁵
²⁷ Al	1.77x10 ⁻³
³¹ P	9.44x10 ⁻⁴
³⁹ K	3.38x10 ⁻³
⁴³ Ca	1.65x10 ⁻³
⁴⁷ Ti	4.14x10 ⁻⁵
⁵¹ V	2.94x10 ⁻⁵
⁵³ Cr	8.86x10 ⁻⁴
⁵⁵ Mn	1.63x10 ⁻⁵
⁵⁷ Fe	1.10x10 ⁻³
⁵⁹ Co	8.04x10 ⁻⁶
⁶⁰ Ni	6.70x10 ⁻⁵
⁶³ Cu	1.22x10 ⁻⁵
⁶⁶ Zn	7.65x10 ⁻⁵
⁷⁵ As	1.22x10 ⁻⁵
⁸² Se	1.08x10 ⁻⁴
⁸⁵ Rb	2.28x10 ⁻⁶
⁸⁸ Sr	5.56x10 ⁻⁶
⁹⁸ Mo	2.26x10 ⁻⁶
¹⁰⁵ Pd	8.91x10 ⁻⁷
¹⁰⁷ Ag	9.84x10 ⁻⁶
¹¹¹ Cd	3.28x10 ⁻⁵
¹²¹ Sb	4.00x10 ⁻⁶
¹³⁷ Ba	2.14x10 ⁻⁵
¹⁹⁵ Pt	6.23x10 ⁻⁶
¹⁹⁷ Au	1.04x10 ⁻⁵
²⁰² Hg	8.49x10 ⁻⁶
²⁰⁵ Tl	9.34x10 ⁻⁶
²⁰⁸ Pb	1.33x10 ⁻⁶
²⁰⁹ Bi	2.41x10 ⁻⁶
²³² Th	2.33 x10 ⁻⁶
²³⁸ U	1.11 x10 ⁻⁶

3.5.2.5 Limitations and sources of errors of ICP-MS Measurement

The main source of error in ICP-MS measurement is contamination, as a result, analysts have to play an active role in error reduction in their ICP-MS analyses in order to overcome this limitation. Small amounts of Laboratory contamination can dramatically alter analytical results. Common sources of contamination in standards and samples are lab-ware, acids, water, sample preparation and storage [124].

- **Lab-ware:** Glassware like pipettes and beakers increases the potential of contamination when re-used. It can also contaminate samples with elements like sodium, silicon and boron even when cleaned.
- **Acids:** In sample preparation, high purity acids are recommended to be used to dilute and prepare standards and samples in order to lower all the possible contamination from the source of acid. To find out the elemental contamination levels in the acid, it is necessary to check the acid's certificate of analysis.
- **Water:** It is an essential component in the lab. Commercially produced water can differ in pH, soluble silica and solutes. The water that comprises the least amount of impurities possible is regarded as high quality. The standard of high quality can be contaminated by poor water quality used for dilution.
- **Sample preparation:** Different sample preparation techniques (e.g open vessel digestion and microwave digestion) and apparatus used can also contaminate the samples. Contaminants from previous samples or containers can be leached by microwave vessels. The potential of contamination with the number of steps a sample goes through during preparation.
- **Storage:** After testing and analysis standards and samples are usually stored until needed again. The quality and accuracy of a standard is affected if not stored properly according to the manufacturer's storage conditions.

Results and Discussion

Results obtained in the present study are presented and discussed thoroughly in this chapter. Activity concentrations of different radionuclides, their radiological risk, toxicological risk of toxic heavy metals as well as the correlation between existence of toxic heavy metals and radionuclides were discussed in detail. Values obtained were compared to the world average or the maximum allowable limits recommended.

4.1 Minimum detectable activity (MDA)

Minimum detectable activities of radionuclides were calculated from a Genie 2000 software and equation 3.5 as explained in Chapter 3 sub-subsection 3.5.1.3. As illustrated in Table A.2 and by equations 3.2 and 3.5, number of counts of a radionuclide in a spectrum at a particular energy determines absolute efficiency of the detector at that energy. This affects MDA of the radionuclide. The MDA's of radionuclides found in the background were tabulated in Table A.2 in Appendix A.

4.2 Activity concentrations

Results presented in Figure 4.1 show activity concentrations of selected radionuclides in all samples and the control sample. Activity concentrations of ^{226}Ra , ^{238}U and ^{232}Th were obtained by calculating weighted mean activity concentrations of their gamma emitting daughter nuclides. However, activity concentrations of ^{40}K and ^{210}Pb were calculated from their peak energies. This was explained in detail in Chapter 3 sub-subsection 3.5.1.4.

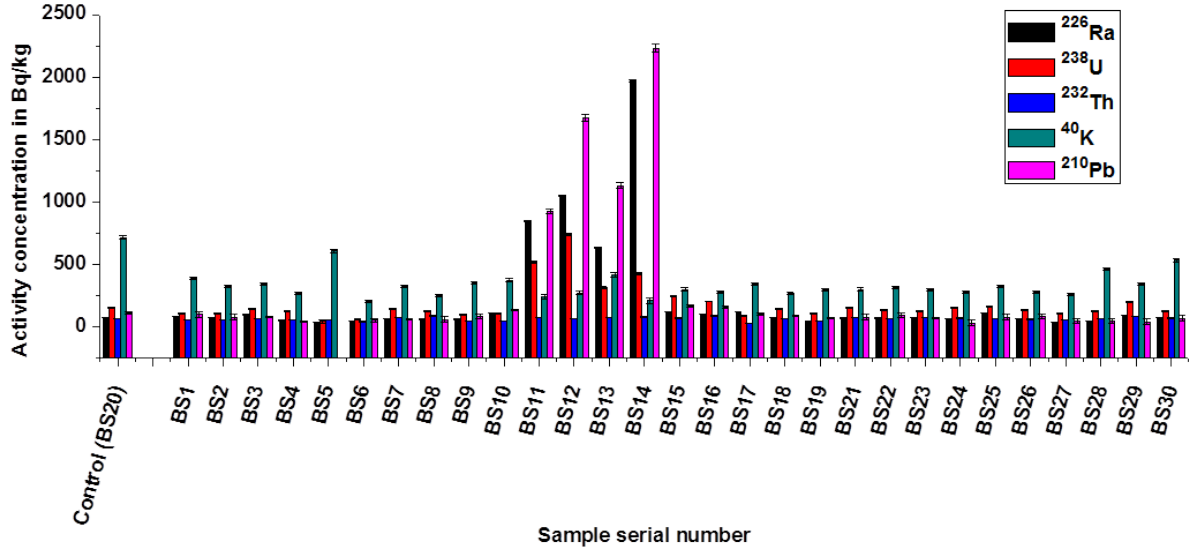


Figure 4.1: Activity concentrations of ^{226}Ra , ^{238}U , ^{232}Th , ^{40}K and ^{210}Pb obtained from soil samples in Serule area of Botswana.

In Figure 4.1, activity concentrations of selected radionuclides were plotted against corresponding samples from the study area. Samples BS11, BS12, BS13 and BS14 showed significantly high activity concentrations of ^{226}Ra and ^{210}Pb compared to other samples and the control sample. The segment that begins with ^{226}Ra in the ^{238}U decay series is radiologically dominant, therefore, assuming a radioactive secular equilibrium between ^{238}U and ^{226}Ra , elevated concentrations of ^{226}Ra in these samples showed that they were collected from areas with high content of ^{238}U . Moreover, this was verified by high concentrations of ^{210}Pb since it has the longest half-life in the segment that begins with ^{226}Ra in ^{238}U decay series. It was concluded that areas with samples that showed elevated concentrations of ^{226}Ra and ^{210}Pb had high activity of ^{238}U . Moreover, the activity concentration of ^{238}U in these samples was high compared to the rest of the samples, together with the control. This could be where the future uranium mining pit will be located once the mining commences. Other areas were found to have low activity of ^{238}U .

Of all the 30 samples analysed for gamma ray spectroscopy, 4 were found to have high activity of ^{238}U , 25 with low activity of ^{238}U and 1 was a control sample. It was also shown that ^{40}K was the most abundant radionuclide in most samples including the control. This was as a result of its natural abundance in soil due to decomposition of organic matter. Activity concentrations of ^{40}K do not change significantly between samples collected in areas with high activity of ^{238}U and areas with low activity of ^{238}U , therefore, ^{40}K was not considered a contaminant in these areas. This shows that

there are no commercial agricultural activities taking place in the study area. Since most commercial farmers use commercial fertilisers which are rich in ^{40}K , for example N:P:K (Nitrogen, Phosphorus, Potassium), areas where commercial fertilisers are normally used would show elevated concentrations of ^{40}K compared to others. Activity concentration levels of ^{232}Th were within a narrow range of $(29.50 \pm 0.5) \text{ Bq/kg}$ - $(87.58 \pm 1) \text{ Bq/kg}$ for all samples, thus making ^{232}Th a non-contaminant in the area. The control was also within the narrow range of $(29.50 \pm 0.5) \text{ Bq/kg}$ - $(87.58 \pm 1) \text{ Bq/kg}$ created by all samples from the study area with a value of $(65.66 \pm 0.8) \text{ Bq/kg}$.

Table 4.1 shows average activity concentrations of radionuclides in the study area and their ranges in comparison to the world average values.

Table 4.1: Average activity concentrations of radionuclides in Bq/kg in comparison to the world average.

Radionuclide		Area			Control (*)	World average
		All areas excluding the control (*)	Areas with high activity of ^{238}U (*)	Areas with low activity of ^{238}U (*)		
^{226}Ra	Mean	218.24 ± 7	1126.26 ± 6	72.96 ± 2	72.76 ± 0.9	33 [44]
	Range	$(34.85 \pm 0.7) - (1967.82 \pm 8)$	$(633.93 \pm 5) - (1967.82 \pm 8)$	$(34.85 \pm 0.6) - (120.04 \pm 1)$	-	-
^{238}U	Mean	179.61 ± 16	498.21 ± 10	128.63 ± 12	150.15 ± 3	33 [44]
	Range	$(41.29 \pm 12) - (739.53 \pm 10)$	$(312.97 \pm 7) - (739.53 \pm 10)$	$(41.29 \pm 12) - (243.57 \pm 5)$		-
^{232}Th	Mean	62.10 ± 3	71.39 ± 1	60.62 ± 3	65.66 ± 0.7	45 [44]
	Range	$(29.50 \pm 0.5) - (87.58 \pm 1)$	$(64.88 \pm 1) - (78.13 \pm 1)$	$(29.50 \pm 0.5) - (87.58 \pm 1)$		-
^{40}K	Mean	324.48 ± 54	248.18 ± 22	331.10 ± 28	712 ± 14	420 [44]
	Range	$(202.10 \pm 7) - (605.60 \pm 13)$	$(209.80 \pm 22) - (416.50 \pm 17)$	$(202.10 \pm 7) - (605.60 \pm 13)$		-
^{210}Pb	Mean	279.48 ± 54	1490.20 ± 29	77.69 ± 45	107.90 ± 6	-
	Range	$(30.37 \pm 19) - (2234.00 \pm 33)$	$(922.80 \pm 18) - (2234.00 \pm 33)$	$(30.37 \pm 19) - (163.20 \pm 7)$		-

(*): present study

Table 4.1 shows that all areas excluding the control had average activity concentrations of ^{226}Ra ranging from (72.76 ± 2) Bq/kg - (1126.26 ± 6) Bq/kg. The lower limit of this range was contributed by areas with low activity of ^{238}U which ranged from (34.85 ± 0.7) Bq/kg - (120.04 ± 1) Bq/kg. The control was within this range with a value of (72.76 ± 0.9) Bq/kg. On the other hand, the upper limit was contributed by areas with high activity of ^{238}U with activity concentrations that ranged from (633.93 ± 5) Bq/kg - (1967.82 ± 8) Bq/kg. All these values exceeded the world average value of 33 Bq/kg. This could be a result of large uranium deposits in the bed rock of the study area. However, average activity concentration of ^{226}Ra in areas with high activity of ^{238}U was significantly higher than the world average and other areas. This verified that areas with high activity of ^{238}U have a high content of ^{238}U .

According to UNSCEAR (2000), the world average activity concentration of ^{238}U in soil is 33 Bq/kg [44]. The activity concentrations of ^{238}U were from (128.63 ± 12) Bq/kg - (498.21 ± 10) Bq/kg for all the locations in the study area excluding the control. Areas with high activity of ^{238}U had average activity concentration of (498.21 ± 10) Bq/kg of ^{238}U with range (312.97 ± 7) Bq/kg - (739.53 ± 10) Bq/kg. These concentrations were much higher than the world average value which shows that the study area have elevated concentrations of ^{238}U than recommended. Areas with low activity of ^{238}U showed an average activity concentration of (128.63 ± 12) Bq/kg for ^{238}U with activity concentrations ranging from (41.29 ± 12) Bq/kg - (243.57 ± 5) Bq/kg. The average activity concentration of the control sample was within this range with a value of (150.15 ± 3) Bq/kg.

Activity concentrations of ^{232}Th in areas with high activity of ^{238}U had ^{232}Th activity concentrations ranging from (64.88 ± 1) Bq/kg - (78.13 ± 1) Bq/kg while areas with low activity of ^{238}U ranged from (29.50 ± 0.5) Bq/kg - (87.58 ± 1) . The control had an average of 65.66 ± 0.8 of ^{232}Th activity concentration which was within a narrow range of (60.62 ± 3) Bq/kg - (71.39 ± 1) Bq/kg of average activity concentrations of ^{232}Th in all areas. Table 4.1 shows that all average activity concentrations of ^{232}Th were higher than the world average value of 45 Bq/kg. However, the narrow range between these activities makes ^{232}Th a non-contaminant in the area.

Table 4.1 shows that the control had the highest average activity concentration of ^{40}K with a value of (712 ± 14) Bq/kg compared to other areas which had averages ranging from (248.18 ± 22) - (331.10 ± 28) Bq/kg. It was also higher than the world average value of 420 Bq/kg. Since there are no commercial agricultural activities in the area

where the control sample was collected, this could be a result of high decomposition level of organic residues. Areas with high activity of ^{238}U and areas with low activity of ^{238}U had average activity concentrations of ^{40}K of (248.18 ± 22) Bq/kg and (331.10 ± 28) Bq/kg, respectively. These concentrations were lower than the world average value of 420 Bq/kg.

Documented values for the world average activity concentration of ^{210}Pb could not be accessed. In reference to the control (107.90 ± 6) Bq/kg, recorded values of ^{210}Pb in areas with high activity of ^{238}U showed a far greater value of (1490.20 ± 29) Bq/kg. In areas with low activity of ^{238}U , average activity concentration of ^{210}Pb (77.69 ± 45) Bq/kg was lower than of the control and average activity concentration of all areas (279.48 ± 53) Bq/kg was 2.59 times higher. This showed that areas with high activity of ^{238}U had significantly high concentrations of ^{210}Pb which confirmed that they have a high ^{238}U content since ^{210}Pb is the daughter nuclide of ^{238}U that has the longest half life.

4.3 Toxic heavy metal concentrations

A 7500 series Agilent ICP-MS was used to measure the mass concentrations of all elements found in soil samples in this study. Out of 35 elements found in the soil samples, 5 were analysed as toxic heavy metals and 2 were analysed as radiotoxic heavy metals. Mass concentrations of various other elements that were obtained in ICP-MS analysis were listed in Appendix A.

The results shown in Table 4.2 illustrate mass elemental concentrations of toxic heavy metals found in areas with high activity of ^{238}U , that is, BS11, BS12, BS13 and BS14 shown in Figure 4.1. Average concentrations showed that toxic heavy metals in areas with high activity of ^{238}U increased from Hg to Cr in the order $\text{Hg} < \text{Cd} < \text{As} < \text{Pb} < \text{Cr}$ with values, 0.0475, 0.133, 9.56, 26.4 and 101 in mg/kg, respectively. The respective ranges of Hg, Cd, As, Pb and Cr were found to be as follows; (0.0422 - 0.0506) mg/kg, (0.127 - 0.145) mg/kg, (7.43 - 10.5) mg/kg, (22.1 - 31.2) mg/kg and (88.3 - 112) mg/kg, respectively.

Table 4.2: Mass elemental concentrations of toxic heavy metals (*mg/kg*) in areas with high activity of ^{238}U .

Sample serial number	Hg	Cd	As	Pb	Cr
BS11	0.0498	0.129	10.5	22.1	102
BS12	0.0506	0.127	7.43	31.2	103
BS13	0.0475	0.145	10.4	27.8	112
BS14	0.0422	0.129	9.94	24.3	88.3
Average	0.0475	0.133	9.56	26.4	101
Minimum	0.0422	0.127	7.43	22.1	88.3
Maximum	0.0506	0.145	10.5	31.2	112
Standard Deviation	0.00377	0.00836	1.45	3.96	9.90

Mass elemental concentrations of toxic heavy metals found in areas with low activity of ^{238}U are shown in Table 4.3. The results showed that average mass concentrations of toxic heavy metals varied greatly in these areas and had a similar trend as in areas with high activity of ^{238}U . Hg had the lowest average concentration of 0.0588 mg/kg and Cr had the highest average concentration of 83.1 mg/kg among others. Other toxic heavy metals (Cd, As and Pb) had average concentrations of 0.114, 4.92 and 22.8 mg/kg, respectively. It was also shown that the ranges of mass concentrations of Hg, Cd, As, Pb and Cr were (0.0282 - 0.257) mg/kg, (0.0842 - 0.164) mg/kg, (2.50 - 11.9) mg/kg, (9.99 - 36.3) mg/kg and (51.3 - 127) mg/kg in that order.

Table 4.3: Mass elemental concentrations of toxic heavy metals (*mg/kg*) in areas with low activity of ^{238}U .

Sample serial number	Hg	Cd	As	Pb	Cr
BS1	0.130	0.164	7.84	21.3	127
BS2	0.0455	0.118	6.36	21.8	81.0
BS3	0.0426	0.138	11.9	36.3	109
BS4	0.0399	0.103	3.87	22.3	89.3
BS5	0.0383	0.102	2.94	23.9	61.3
BS6	0.0427	0.102	4.26	24.8	60.6
BS7	0.0412	0.117	5.32	21.1	82.3
BS8	0.0454	0.104	5.03	20.7	71.3
BS9	0.0461	0.105	2.79	16.7	83.5
BS10	0.0509	0.109	3.16	17.5	84.8
BS15	0.0408	0.138	5.60	18.1	87.6
BS16	0.0390	0.134	7.57	30.4	88.5
BS17	0.257	0.129	7.40	16.9	72.0
BS18	0.112	0.138	6.97	25.9	51.3
BS19	0.0644	0.0881	2.97	15.1	57.1
BS21	0.0488	0.110	3.79	22.7	98.9
BS22	0.0490	0.107	3.43	31.0	97.6
BS23	0.0492	0.115	3.83	27.0	116
BS24	0.0447	0.0951	3.72	23.1	89.9
BS25	0.0454	0.115	3.61	29.6	98.1
BS26	0.0404	0.127	2.88	16.0	97.2
BS27	0.0371	0.0908	2.50	18.5	74.5
BS28	0.0546	0.0842	3.31	29.6	57.1
BS29	0.0361	0.118	6.73	29.0	77.9
BS30	0.0282	0.0900	5.13	9.99	63.1
Average	0.0588	0.114	4.92	22.8	83.1
Minimum	0.0282	0.0842	2.50	9.99	51.3
Maximum	0.257	0.164	11.9	36.3	127
Standard Deviation	0.0471	0.0193	2.22	6.09	19.1

All mass concentrations of toxic heavy metals from areas with high activity of ^{238}U and areas with low activity of ^{238}U were averaged using weighted mean average (shown in Equation B.1, Appendix B) and values were recorded in Table 4.4. These average values also followed an ascending order from Hg to Cr, with $\text{Hg} < \text{Cd} < \text{As} < \text{Pb} < \text{Cr}$ and values 0.0573 mg/kg, 0.116 mg/kg, 5.56 mg/kg, 23.3 mg/kg and 85.6 mg/kg, respectively. The ranges of mass concentrations of toxic heavy metals Hg, Cd, As, Pb and Cr were (0.0282 - 0.257) mg/kg, (0.0842 - 0.164) mg/kg, (2.50 - 11.9) mg/kg, (9.99 - 36.3) mg/kg and (51.3 - 127) mg/kg, in that order. These ranges were the same as ranges from areas with low activity of ^{238}U shown in Table 4.3. This meant that for

all areas excluding the control, the highest and lowest mass concentrations for each toxic heavy metal was from areas with low activity of ^{238}U .

Table 4.4: Mass elemental concentrations of toxic heavy metals (mg/kg) in all areas excluding the control.

	Pb	Cr	Cd	As	Hg
Average	23.3	85.6	0.116	5.56	0.0573
Minimum	9.90	51.3	0.0842	2.50	0.0282
Maximum	36.3	127	0.164	11.9	0.257
Standard Deviation	5.92	19.1	0.0193	2.67	0.0438

Elemental mass concentrations of toxic heavy metals in the control sample are shown in Table 4.5.

Table 4.5: Mass elemental concentrations of toxic heavy metals (mg/kg) in the control sample.

	Hg	Cd	As	Pb	Cr
Control	0.0537	0.12	2.88	21.4	109

The average mass concentrations of the control also followed a similar trend of areas with high activity of ^{238}U and areas with low activity of ^{238}U with mass concentrations of toxic heavy metals as follows; 0.0537 mg/kg for Hg, 0.12 mg/kg for Cd, 2.88 mg/kg for As, 21.4 mg/kg for Pb and 109 mg/kg for Cr. The mass concentration of Cr in the control was much higher than the averages in Table 4.4. This could be as a result of the type rock composition of the area.

Table 4.6 shows maximum permissible limits of toxic heavy metals of the WHO, EU and different countries in comparison with the weighted mean averages in the current study. Maximum allowable limits for Hg are currently not available in the WHO and EU standards, but, all the average values for Hg in all the areas in the study area excluding the control were much less than of other countries. Cd allowable limit for both WHO and EU is 3 mg/kg. Mass concentration of Cd in the control area, areas with high activity of ^{238}U , areas with low activity of ^{238}U and the average of all areas excluding the control were 0.12, 0.133, 0.114 and 0.116 in mg/kg, respectively. All these values were much less than the WHO and EU maximum permissible limits as well as other countries. It showed that average mass concentration of As of all areas excluding the control and of the control area were slightly higher than the maximum

allowable limit value of the WHO of 20 mg/kg but it was comparable with other countries.

Table 4.6: Maximum permissible limits of mass concentrations of toxic heavy metals in soil (*mg/kg*) for different countries in comparison to the present study.

Area	Hg	Cd	As	Pb	Cr	Ref
All areas excluding the control	0.0573	0.116	5.56	23.3	85.6	(*)
Areas with high activity of ^{238}U	0.0475	0.133	9.56	26.4	101	(*)
Areas with low activity of ^{238}U	0.0588	0.114	4.92	22.8	83.1	(*)
Control	0.0537	0.120	2.88	21.4	109	(*)
FAO/WHO Guidelines	-	3.00	20.0	100	10.0	[125]
EU Standards	-	3.00	-	300	150	[126]
South Africa	0.93	7.50	5.80	20.0	6.50	[127]
China	0.70	0.50	30.0	80.0	200	[128]
Tanzania	2.00	1.00	1.00	200	100	[129]
United Kingdom	10.0	10.0	32.0	450	130	[128]
Canada	0.80	3.00	20.0	200	250	[129]
Australia	1.00	3.00	20.0	300	50.0	[130]
Germany	0.50	1.00	50.0	70.0	60.0	[128]
Poland	-	3.00	-	100	100	[83]
United States of America	1.00	0.480	0.110	200	11.0	[129]

(*) : present study
 - : not available

Mass concentration of Pb in the control, areas with high activity of ^{238}U , areas with low activity of ^{238}U and all areas excluding the control were 21.4, 26.4, 22.8 and 23.3 in mg/kg, respectively. These concentrations were much lower than the WHO recommended limit of 100 mg/kg. The concentrations were much closer to the allowable limit of South Africa (20 mg/kg) and far much lower than of other countries. Areas with low activity of ^{238}U and areas with high activity of ^{238}U had Cr mass concentrations of 83.1 mg/kg and 101 mg/kg, respectively. The control had a mass concentration of 109 mg/kg for Cr which was higher than all areas in present study. These concentrations were much higher than the WHO limit but comparable to other countries. This could be a result of different type of rock composition.

Figure 4.2 shows mass concentrations of radiotoxic heavy metals found in samples. Mass concentrations of thorium were comparable throughout the samples including the control. Thorium concentrations in areas with high activity of ^{238}U varied from (15.08 - 17.42) mg/kg with a mean value of 16.13 mg/kg whereas areas with low activity of ^{238}U varied from (5.58 - 17.83) mg/kg with a mean value of 11.01 mg/kg. The

control had thorium concentration level of 11.67 mg/kg.

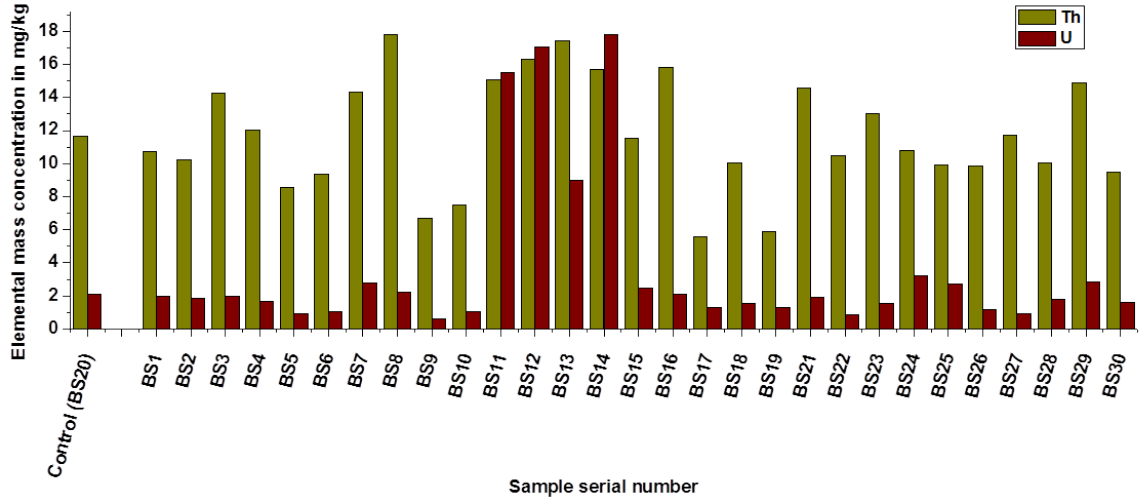


Figure 4.2: Mass elemental concentrations of radiotoxic heavy metals in mg/kg.

On the other hand, areas with high activity of ^{238}U showed elevated concentrations of uranium heavy metal ranging from (9.00 - 17.78) mg/kg with an average value of 14.84 mg/kg. Concentration of uranium heavy metal in areas with high activity of ^{238}U was within a range of (0.64 - 3.20) mg/kg and had an average value of 1.74 mg/kg. A mass concentration of 2.09 mg/kg of uranium was observed in the control. These verified that indeed there was high uranium content in areas with high activity of ^{238}U as concluded with activity concentrations of uranium and its daughter nuclides in section 4.2. The allowable limits of radiotoxic heavy metals could not be accessed, therefore, the values obtained were not compared to any limit.

4.4 Relationship between toxic heavy metals and radionuclides

Pearson's correlation coefficients were calculated between selected radionuclides and toxic heavy metals of different locations in the study area using equation 2.46 given in Chapter 2 section 2.11. Table 4.7 shows a correlation matrix between toxic heavy metals and radionuclides in areas with high activity of ^{238}U . It shows that for significance a level of 0.10, there was a strong positive correlation between ^{226}Ra and ^{210}Pb , ^{40}K and Cd and ^{40}K and Th. A strong negative correlation was also observed between ^{226}Ra and Cr and ^{232}Th and Hg. At 0.05 significance level, a strong negative correlation between heavy metal U with ^{40}K and Cd was observed. Also, Th and As showed

a strong positive correlation at the same significance level. From these correlations, it means that there was a 90% confidence and a 60 - 100% chance that the pairs ^{226}Ra and ^{210}Pb , ^{40}K and Cd and ^{40}K and Th were from the same origin or had similar transport behaviour. However, there was also a 90% confidence that the pairs ^{232}Th and Hg and ^{226}Ra and Cr have a 60 -100% chance that they were from different origins or had different transport behaviours. For a significance level of 0.05, there was a 95% certainty that a relation of U with ^{40}K and Cd had a 60 - 100% chance that they do not share the same origin.

Table 4.7: Pearsons correlation coefficient between toxic heavy metals and radionuclides in areas with high activity of ^{238}U .

	^{226}Ra	^{232}Th	^{40}K	^{238}U	^{210}Pb	Pb	Cr	Cd	As	Hg	Th	U
^{226}Ra	1	0.576	-0.708	0.0207	0.914***	-0.231	-0.950***	-0.533	-0.074	-0.800	-0.419	0.709
^{232}Th		1	-0.0288	-0.805	0.437	-0.480	-0.468	0.319	0.647	-0.945***	0.0362	-0.118
^{40}K			1	-0.460	-0.491	0.433	0.876	0.925***	0.162	0.241	0.903***	-0.954**
^{238}U				1	0.142	0.449	-0.106	-0.763	-0.864	0.572	-0.319	0.649
^{210}Pb					1	0.177	-0.764	-0.430	-0.368	-0.704	-0.09214	0.607
Pb						1	0.439	0.115	-0.805	0.352	0.690	-0.142
Cr							1	0.687	-0.00508	0.675	0.681	-0.821
Cd								1	0.494	-0.0614	0.787	-0.974**
As									1	-0.389	0.988**	-0.445
Hg										1	0.0533	-0.159
Th											1	-0.757
U												1

*significant at 0.01 level, ** significant at 0.05 level, ***significant at 0.10 level

Table 4.8 shows the Pearson's correlation coefficient matrix between radionuclides and toxic heavy metals in areas with low activity of ^{238}U . Strong positive correlations at 0.01 significance level were observed between U with ^{232}Th , ^{238}U and Th , ^{226}Ra with Cd , ^{238}U with ^{232}Th , Th with ^{232}Th and As with Cd . These observations conclude that there was a 99% confidence that these pairs had a 60 - 100% chance that they had similar transport behaviour or same origin. ^{226}Ra with ^{238}U and As , ^{238}U with Th and Cd with Cr showed a moderate positive correlation at the same significance level. A positive moderate correlation was observed between Pb with ^{232}Th and Th , ^{238}U with ^{210}Pb and Hg with Cd at 0.05 significance level while between Hg with ^{232}Th and Th there was a negative moderate correlation. However, all correlations at significance level 0.10 were weak positive correlations. All positive moderate correlations means that there was a 40 - 60% chance that the variables had the same origin whereas weak positive correlations represent that there was a less than 40% chance. On the other hand, negative moderate correlations concluded that the pairs had a 40 - 60% chance that they do not have the same origin or similar transport behaviour.

Table 4.8: Pearsons correlation coefficient between toxic heavy metals and radionuclides in areas with low activity of ^{238}U .

	^{226}Ra	^{232}Th	^{40}K	^{238}U	^{210}Pb	Pb	Cr	Cd	As	Hg	Th	U
^{226}Ra	1	0.0974	-0.0577	0.552*	0.749	0.0832	0.365	0.603*	0.508*	0.353***	0.0227	0.364***
^{232}Th		1	-0.0874	0.660*	0.0306	0.407**	0.195	0.123	0.249	-0.448**	0.878*	0.624*
^{40}K			1	-0.282	-0.256	-0.114	-0.179	-0.171	-0.0370	-0.0134	-0.286	-0.145
^{238}U				1	0.504**	0.254	0.274	0.341***	0.299	-0.224	0.524*	0.684*
^{210}Pb					1	-0.0831	0.289	0.570*	0.313	0.215	-0.00790	0.0103
Pb						1	0.269	0.231	0.391***	-0.155	0.454**	0.282
Cr							1	0.539*	0.239	-0.0353	0.309	0.230
Cd								1	0.696*	0.407**	0.191	0.220
As									1	0.329	0.340***	0.348***
Hg										1	-0.403**	-0.137
Th											1	0.560*
U												1

*significant at 0.01 level, ** significant at 0.05 level, ***significant at 0.10 level

Pearson's correlation coefficient matrix between average concentrations of toxic heavy metals and radionuclides from areas with high activity of ^{238}U and areas with low activity of ^{238}U is shown in Table 4.9. At significance level 0.01, ^{238}U was positively moderately correlated with toxic heavy metals; As and Th. This means that there was a 99% confidence that these pairs had a 40 - 60% chance of sharing the same origin or having similar transport behaviour. There was also a strong positive correlation between radionuclide ^{238}U with ^{226}Ra , ^{210}Pb and radiotoxic heavy metal U, therefore, a 60 - 100% probability that these pairs were from the same origin exists at the same confidence level. A weak positive correlation was observed at 0.10 significance level between ^{238}U with radionuclide ^{232}Th and toxic heavy metals; Cr and Cd. These pairs had less than 40% chance of having similar transport behaviour or originating from the same source.

Table 4.9: Pearson's correlation coefficient between toxic heavy metals and radionuclides in all areas excluding the control.

	^{226}Ra	^{232}Th	^{40}K	^{238}U	^{210}Pb	Pb	Cr	Cd	As	Hg	Th	U
^{226}Ra	1	0.269	-0.278	0.789*	0.979	0.170	0.243	0.304	0.557	-0.0708	0.453	0.936
^{232}Th		1	-0.127	0.355***	0.263	0.412	0.250	0.205	0.357	-0.453	0.846	0.323
^{40}K			1	-0.295	-0.248	-0.107	-0.165	-0.166	-0.130	0.00677	-0.291	0.283
^{238}U				1	0.845*	0.291	0.355***	0.345***	0.536*	-0.132	0.571*	0.930*
^{210}Pb					1	0.207	0.283	0.334	0.561	-0.0777	0.490	0.947
Pb						1	0.325	0.282	0.386	-0.164	0.492	0.230
Cr							1	0.596	0.376	-0.0598	0.431	0.311
Cd								1	0.722	0.344	0.344	0.320
As									1	0.195	0.543	0.597
Hg										1	-0.386	-0.106
Th											1	0.549
U												1

*significant at 0.01 level, ** significant at 0.05 level, ***significant at 0.10 level

4.5 Radiological risk to residents

As described in Chapter 2 section 2.8, the radiological risk to residents was determined using radiological parameters; annual effective dose equivalent, radium equivalent, external hazard index and excess lifetime cancer risk. To obtain some of these radiological parameters, absorbed dose rate was required.

4.5.1 Absorbed dose rate

Results presented in Figure 4.3 show calculated absorbed dose rate of all soil samples collected from different locations in the study area. It shows that absorbed dose rate in areas with high activity of ^{238}U varied from (206.32 ± 3) nGy/h to (392.17 ± 5) nGy/h with a mean value of 285.14 nGy/h. Areas with low activity of ^{238}U had absorbed dose rate that varied from (60.31 ± 2) nGy/h to (165.69 ± 2) nGy/h with a mean value of 109.84 nGy/h. A value of (138.72 ± 1) nGy/h was recorded for the control. This verified that areas with high activity of ^{238}U had the highest levels of the absorbed dose rate compared to other areas. All areas had average absorbed dose rate that was higher than the world average value of 57 nGy/h [63].

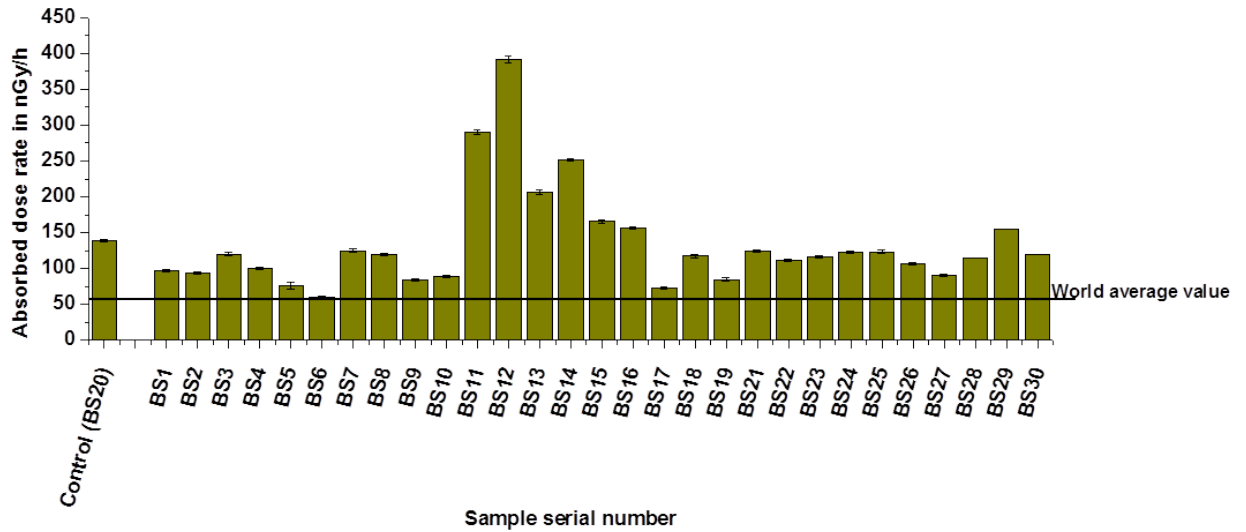


Figure 4.3: A graph showing calculated absorbed dose rate for all the soil samples.

4.5.2 Annual effective dose equivalent (AEDE)

Figure 4.4 shows calculated annual effective dose equivalent from outdoor terrestrial gamma radiation.

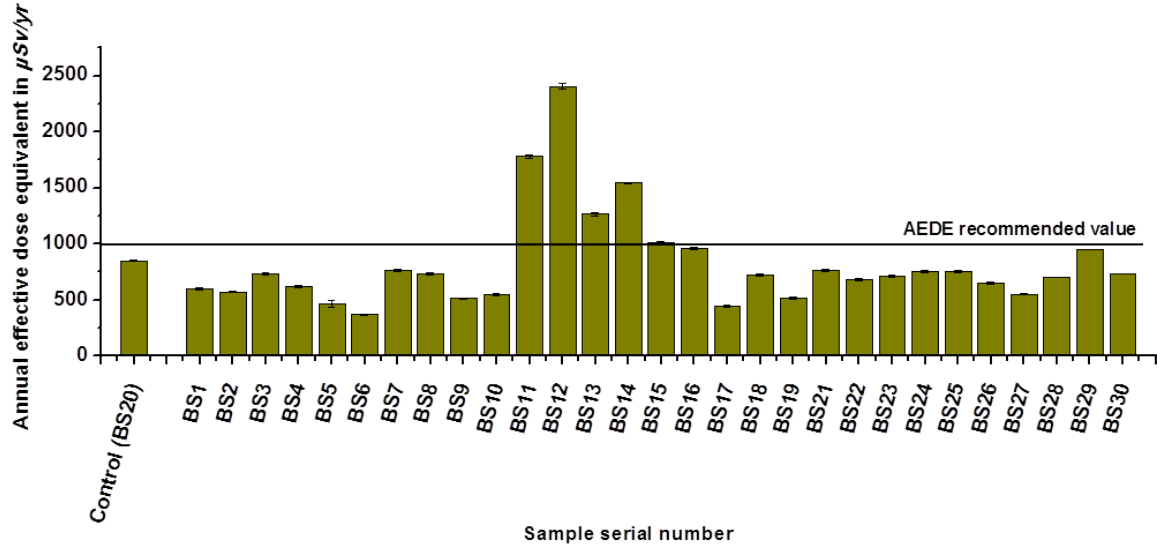


Figure 4.4: The annual effective dose equivalent for all soil samples.

It shows average annual effective dose equivalent of $821.86 \mu\text{Sv/yr}$ of all areas excluding the control ranging from $(369.82 \pm 8) \mu\text{Sv/yr}$ - $(2404.78 \pm 25) \mu\text{Sv/yr}$. Areas with high activity of ^{238}U varied from $(1265.13 \pm 17) \mu\text{Sv/yr}$ - $(2404.78 \pm 25) \mu\text{Sv/yr}$ with an average of $1748.51 \mu\text{Sv/yr}$ while areas with low activity of ^{238}U varied from $(369.82 \pm 8) \mu\text{Sv/yr}$ - $(1016.01 \pm 10) \mu\text{Sv/yr}$ with an average of $673.59 \mu\text{Sv/yr}$. The control showed a value of $(850.62 \pm 5) \mu\text{Sv/yr}$. Average annual effective dose equivalent in areas with high activity of ^{238}U was significantly higher than the recommended value of $1000 \mu\text{Sv/yr}$. The control, areas with low activity of ^{238}U and the average of all areas excluding the control were all lower than the recommended value of annual effective dose equivalent of $1000 \mu\text{Sv/yr}$. The dose of $1000 \mu\text{Sv/yr}$ corresponds to the maximum recommended radium equivalent activity, therefore, areas with high activity of ^{238}U were expected to have a high value of radium equivalent since their dose was above maximum recommended dose.

4.5.3 Radium equivalent

Radium equivalent of different locations was calculated using equation 2.36 in Chapter 2 and the results are shown in Figure 4.5. Average radium equivalent for all areas

excluding the control was calculated to be 332.05 Bq/kg with a minimum value of (116.57 ± 2) Bq/kg and a maximum value of (2095.70 ± 9) Bq/kg. Areas with low activity of ^{238}U showed an average of 185.13 Bq/kg and varied from (116.57 ± 2) Bq/kg - (247.42 ± 2) Bq/kg.

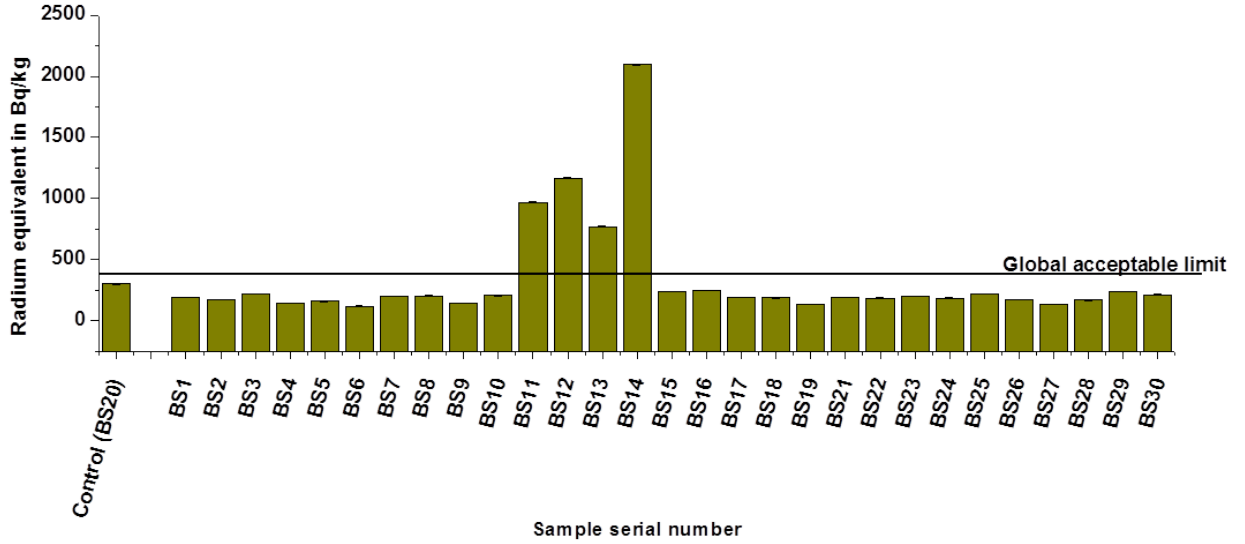


Figure 4.5: Radium equivalent calculated for all samples in comparison to the acceptable limit of 370 Bq/kg.

Areas with high activity of ^{238}U had average radium equivalent of 1250.24 Bq/kg which varied from (771.01 ± 5) Bq/kg - (2095.70 ± 9) Bq/kg. Radium equivalent for areas with high activity of ^{238}U was considerably higher than the global acceptable limit of 370 Bq/kg whereas areas with low activity of ^{238}U was lower than this value. The radium equivalent values for areas with high activity of ^{238}U corresponds to values from annual effective dose equivalent of the same area. This confirmed that areas with high activity of ^{238}U pose a radiological risk to residents. The control showed a radium equivalent of (298.87 ± 2) Bq/kg which was much less than the global acceptable limit of 370 Bq/kg, therefore, the location where it was collected does not pose a radiological threat to residents.

4.5.4 External hazard index

Figure 4.6 shows calculated external hazard index from different locations using equation 2.37. The recommended limit of external hazard index is unity, which corresponds to radium equivalent of 370 Bq/kg [64, 68]. Areas with high activity of ^{238}U had elevated values of external hazard index ranging from (2.08 ± 0.01) Bq/kg - (5.66 ± 0.02) Bq/kg. In comparison to other areas and the recommended limit, areas with

high activity of ^{238}U had much greater index which pose a radiological risk to residents. Areas with low activity of ^{238}U had values ranging from (0.31 ± 0.005) Bq/kg - (0.67 ± 0.005) Bq/kg which were much lesser than unity. The control showed an index value of (0.81 ± 0.01) . These indices were lower than the recommended value of unity which verifies that these areas had an insignificant radiation hazard.

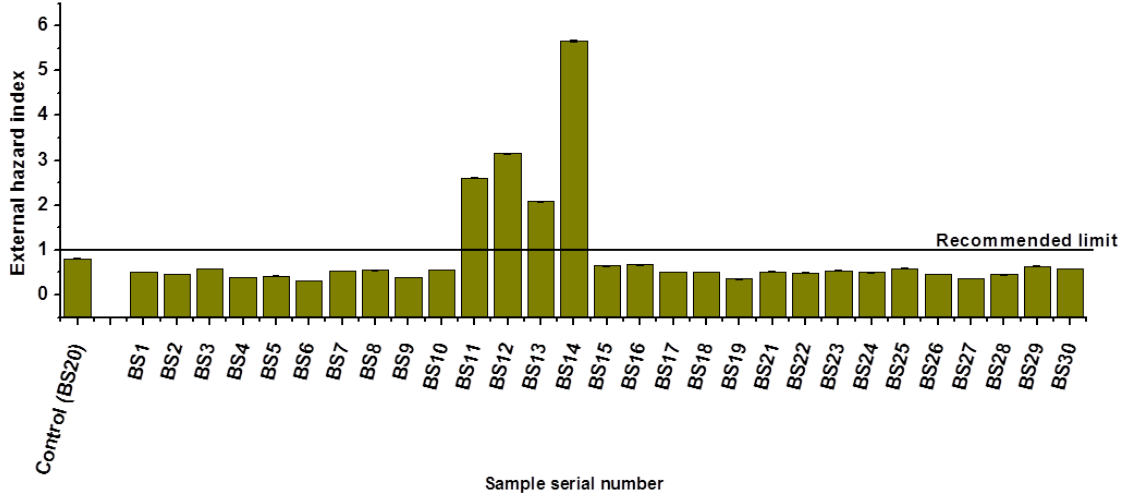


Figure 4.6: The external hazard index for all soil samples.

4.5.5 Excess lifetime cancer risk

Figure 4.7 shows the excess lifetime cancer risk (ELCR) calculated using equation 2.38 for a duration of life of 70 years and a risk factor of 0.05/Sv for public [70]. ELCR in areas with high activity of ^{238}U ranged from 0.89×10^{-3} - 1.68×10^{-3} with a mean value of 1.22×10^{-3} . The mean value and individual values of samples in areas with high activity of ^{238}U were all greatly higher than the recommended limit of 0.29×10^{-3} . On the other hand, ELCR in areas with low activity of ^{238}U varied from 0.26×10^{-3} - 0.71×10^{-3} and had a mean value of 0.47×10^{-3} . Almost all samples from these area had ELCR that was higher than the recommended limit of 0.29×10^{-3} . The control sample had ELCR of 0.60×10^{-3} which was considerably higher than the recommended limit. This means that cancer risks due to radionuclides in areas with high activity of ^{238}U , areas with low activity of ^{238}U and the control are a concern to the public since values were much greater than the recommended limit of 0.29×10^{-3} for ELCR.

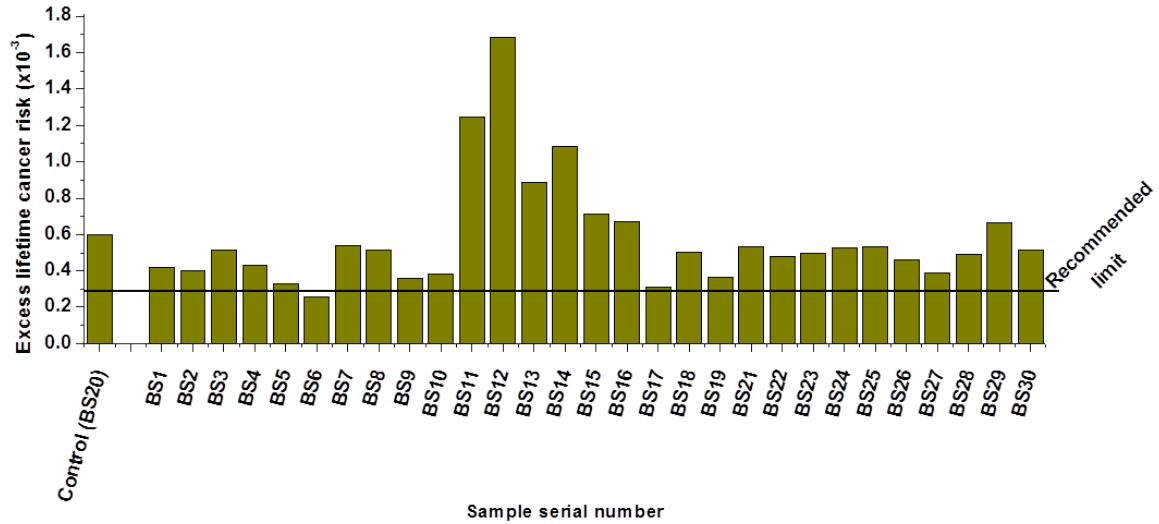


Figure 4.7: The excess lifetime cancer risk to residents.

4.6 Toxicological risk due to toxic heavy metals

4.6.1 Hazard identification

A total of 35 elements were found in soil samples from the study area using the Agilent 7500 series ICP-MS. Hg, Cd, As, Pb, Cr were identified and considered as possible hazardous elements for residents. These elements were evaluated in terms of carcinogenic and non-carcinogenic risk. Th and U were considered as radiotoxic and their concentration levels were shown in Figure 4.2. Concentrations of various other elements were all listed in Table A.3 in Appendix A.

4.6.2 Exposure assessment

Tables 4.10 and 4.11 show the estimated average daily intakes (ADI's) or exposure doses for adults and children which were calculated using equations 2.39, 2.40 and 2.41. Values from these tables were then used to calculate carcinogenic and non-carcinogenic risk using reference doses (RfD) and cancer slope factor (CSF) shown in Table 2.6.

Table 4.10: Average daily intake values of toxic heavy metals for adults and children in *mg/kg/day* for non-carcinogenic risk calculations.

	Receptor	Pathway	Pb	Cr	Cd	As	Hg
Areas with high activity of ^{238}U	adult	ingestion	1.54711E-05	5.95186E-05	7.78327E-08	5.61502E-06	2.79041E-08
		inhalation	2.38017E-09	9.15671E-09	1.19743E-11	8.63849E-10	4.29294E-12
		dermal	3.83158E-06	1.47404E-05	1.9276E-08	1.39062E-06	6.91073E-09
	child	ingestion	2.88795E-05	0.000111101	1.45288E-07	1.04814E-05	5.20877E-08
		inhalation	1.11075E-09	4.27313E-09	5.58799E-12	4.0313E-10	2.00337E-12
		dermal	3.69946E-06	1.42321E-05	1.86114E-08	1.34266E-06	6.67243E-09
Areas with low activity of ^{238}U	adult	ingestion	1.33606E-05	4.87609E-05	6.66552E-08	2.88726E-06	3.45247E-08
		inhalation	2.05548E-09	7.50167E-09	1.02546E-11	4.44193E-10	5.31149E-12
		dermal	3.30889E-06	1.20761E-05	1.65078E-08	7.15058E-07	8.55038E-09
	child	ingestion	2.49398E-05	9.10203E-05	1.24423E-07	5.38955E-06	6.4446E-08
		inhalation	9.59223E-10	3.50078E-09	4.7855E-12	2.0729E-10	2.47869E-12
		dermal	3.19479E-06	1.16597E-05	1.59386E-08	6.90401E-07	8.25554E-09
Control sample	adult	ingestion	2.93151E-05	0.000149315	1.64384E-07	3.94521E-06	7.35616E-08
		inhalation	4.51001E-09	2.29715E-08	2.52898E-11	6.06955E-10	1.13172E-11
		dermal	7.26017E-06	3.69794E-05	4.07112E-08	9.7707E-07	1.82183E-08
	child	ingestion	0.000273607	0.001393607	1.53425E-06	3.68219E-05	6.86575E-07
		inhalation	1.05234E-08	5.36003E-08	5.90095E-11	1.41623E-09	2.64067E-11
		dermal	3.50491E-05	0.000178521	1.96537E-07	4.71689E-06	8.79503E-08

Table 4.11: Average daily intake values of toxic heavy metals for adults and children in *mg/kg/day* for carcinogenic risk calculations.

	Receptor	Pathway	Pb	Cr	Cd	As	Hg
Areas with high activity of ^{238}U	adult	ingestion	3.60993E-05	0.000138877	1.8161E-07	1.31017E-05	6.51096E-08
		inhalation	5.55374E-09	2.13656E-08	2.79399E-11	2.01565E-09	1.00169E-11
		dermal	8.94036E-06	3.43942E-05	4.49774E-08	3.24477E-06	1.6125E-08
	child	ingestion	0.000336927	0.001296183	1.69502E-06	0.000122283	6.07689E-07
		inhalation	1.29587E-08	4.98532E-08	6.51932E-11	4.70318E-09	2.33727E-11
		dermal	4.31603E-05	0.000166041	2.17132E-07	1.56644E-05	7.7845E-08
Areas with low activity of ^{238}U	adult	ingestion	3.11747E-05	0.000113775	1.55529E-07	6.73693E-06	8.05575E-08
		inhalation	4.79611E-09	1.75039E-08	2.39275E-11	1.03645E-09	1.23935E-11
		dermal	7.72074E-06	2.81776E-05	3.85183E-08	1.66847E-06	1.99509E-08
	child	ingestion	0.000290964	0.001061903	1.4516E-06	6.2878E-05	7.5187E-07
		inhalation	1.11909E-08	4.08424E-08	5.58308E-11	2.41839E-09	2.89181E-11
		dermal	3.72725E-05	0.00013603	1.8595E-07	8.05468E-06	9.63146E-08
Control sample	adult	ingestion	1.25636E-05	6.39922E-05	7.04501E-08	1.6908E-06	3.15264E-08
		inhalation	1.93286E-09	9.84495E-09	1.08385E-11	2.60123E-10	4.85022E-12
		dermal	3.1115E-06	1.58483E-05	1.74477E-08	4.18744E-07	7.80783E-09
	child	ingestion	2.34521E-05	0.000119452	1.31507E-07	3.15616E-06	5.88493E-08
		inhalation	9.02002E-10	4.59431E-09	5.05796E-12	1.21391E-10	2.26344E-12
		dermal	3.00421E-06	1.53018E-05	1.6846E-08	4.04305E-07	7.5386E-09

4.6.3 Characterization of risk

Assessing non-carcinogenic risk

Table 4.12 shows hazard quotients (HQ) of different exposure pathways and toxic heavy metals. These were calculated using equation 2.42 in Chapter 2. For areas with high activity of ^{238}U , adults and children showed similar behaviour of HQs throughout different areas and various toxic heavy metals considered. Toxic heavy metals Cr and Pb showed a higher percentage of total effect on both adults and children through ingestion, however, these toxic heavy metals had very insignificant levels in dermal contact. Low levels of Cr, Cd, As and Hg reached both adults and children through inhalation. There is a likelihood of health effects due to exposure if HQ is above 1. Since all values of HQ recorded were < 1 , residents are nearly free of the non-carcinogenic risk due to toxic heavy metals in areas with high activity of ^{238}U .

In areas with low activity of ^{238}U , high levels of Cr due to ingestion were observed in both adults and children whereas there was a noticeable value due to inhalation and an insignificant value as a result of dermal contact with soil. Pb mainly reached both adults and children through ingestion and did not appear in inhalation and dermal contact. Other metals, that is, Cd, As and Hg had HQ that do not vary significantly from one exposure pathway to the other. All hazard quotient values for adults and children were considerably lower than 1, therefore, residents of areas with low activity of ^{238}U have a close to zero non-carcinogenic risk.

In the control, both adults and children showed a similar trend with HQ values in descending order of $\text{Cr} > \text{Pb} > \text{As} > \text{Hg} > \text{Cd}$. Summation of HQ's results in hazard indices (HI's). Table 4.12 also shows values of HI's calculated using equation 2.43 in Chapter 2. The control had high values of hazard index (HI) for both adults and children compared to areas with high activity of ^{238}U and areas with low activity of ^{238}U . The total HI for children from the control was 2.718×10^{-5} which was greater than 2.702×10^{-5} of areas with high activity of ^{238}U and 2.209×10^{-5} of areas with low activity of ^{238}U . HI of adults from the control area was 2.915×10^{-6} which was larger than 2.905×10^{-6} of areas with high activity of ^{238}U and 2.372×10^{-6} of areas with low activity of ^{238}U . Cr had the largest values of HI for both adults and children in both areas compared to other toxic heavy metals studied. HI for ingestion of toxic heavy metals showed a larger value in comparison to other exposure pathways. All values shown in Table 4.12 are less than unity, therefore, the non-carcinogenic threat to humans due to these toxic heavy metals is negligible.

Table 4.12: Hazard index (HI) values of different exposure pathways both areas with high and low activity of ^{238}U .

	Receptor	Pathway	Pb	Cr	Cd	As	Hg	Total(HI)
Areas with high activity of ^{238}U	adult	ingestion	4.99244E-07	2.30475E-06	6.65259E-10	7.99887E-08	3.97508E-10	2.88505E-06
		inhalation	-	4.79869E-11	3.30277E-14	1.2306E-11	7.84803E-15	6.03337E-11
		dermal	-	-	1.64758E-10	1.981E-08	9.84468E-11	2.00732E-08
		Total(HI)	4.99244E-07	2.3048E-06	8.3005E-10	9.98111E-08	4.95963E-10	2.90518E-06
	child	ingestion	4.65961E-06	2.1511E-05	6.20909E-09	7.46562E-07	3.71007E-09	2.69271E-05
		inhalation	-	1.11969E-10	7.70646E-14	2.87139E-11	1.83121E-14	1.40779E-10
		dermal	-	-	7.95384E-10	9.56345E-08	4.7526E-10	9.69052E-08
		Total(HI)	4.65961E-06	2.15112E-05	7.00455E-09	8.42225E-07	4.18535E-09	2.70242E-05
	adult	ingestion	4.31139E-07	1.88818E-06	5.69722E-10	4.11304E-08	4.91821E-10	2.36151E-06
		inhalation	-	3.93134E-11	2.82846E-14	6.32775E-12	9.71006E-15	4.56792E-11
		dermal	-	-	1.41097E-10	1.01864E-08	1.21804E-10	1.04493E-08
		Total(HI)	4.31139E-07	1.88822E-06	7.10847E-10	5.13231E-08	6.13635E-10	2.37201E-06
	child	ingestion	4.02396E-06	1.7623E-05	5.3174E-09	3.83884E-07	4.59033E-09	2.20408E-05
		inhalation	-	9.17314E-11	6.59974E-14	1.47648E-11	2.26568E-14	1.06585E-10
		dermal	-	-	6.81159E-10	4.91755E-08	5.88021E-10	5.04447E-08
		Total(HI)	4.02396E-06	1.76231E-05	5.99863E-09	4.33074E-07	5.17837E-09	2.20913E-05
Control sample	adult	ingestion	4.0542E-07	2.47799E-06	6.02158E-10	2.40863E-08	4.4911E-10	2.90854E-06
		inhalation	-	5.15937E-11	2.98949E-14	3.70559E-12	8.86681E-15	5.5338E-11
		dermal	-	-	1.4913E-10	5.96522E-09	1.11226E-10	6.22557E-09
		Total(HI)	4.0542E-07	2.47804E-06	7.51318E-10	3.00552E-08	5.60345E-10	2.91482E-06
	child	ingestion	3.78392E-06	2.31279E-05	5.62014E-09	2.24806E-07	4.19169E-09	2.71464E-05
		inhalation	-	1.20385E-10	6.97549E-14	8.64637E-12	2.06892E-14	1.29122E-10
		dermal	-	-	7.1994E-10	2.87976E-08	5.36955E-10	3.00545E-08
		Total(HI)	3.78392E-06	2.3128E-05	6.34015E-09	2.53612E-07	4.72866E-09	2.71766E-05

Assessing carcinogenic risk

The carcinogenic risk was calculated based on toxic heavy metals; Pb, Cr, Cd, As and Hg. The regulatory cancer risk limit suggested by the US Environmental Protection Agency (EPA) is 1×10^{-4} . However, there are still no documented values for individual cancer risk in Botswana.

Table 4.13 shows the carcinogenic risk for adults and children calculated separately using equation 2.44 for different exposure pathways and areas. The total carcinogenic risk for adults in areas with high activity of ^{238}U was 4.0×10^{-5} , with ingestion as the leading pathway contributor with 3.83×10^{-5} . Dermal contact contributed 2.08×10^{-6} whereas inhalation was the least distributor contributing 3.80×10^{-7} . Toxic heavy metals contributed to the total risk in descending order of Cr, As, Pb, Cd and Hg with values 3.01×10^{-5} , 1.05×10^{-5} , 1.32×10^{-7} , 7.54×10^{-11} and 0, respectively. In children, a total of 7.37×10^{-5} was observed where ingestion contributed 7.15×10^{-5} , dermal contact contributed 2.01×10^{-6} and inhalation added 1.81×10^{-7} . Toxic heavy metals Cr, As, Pb, Cd and Hg contributed 5.57×10^{-5} , 1.77×10^{-5} , 2.46×10^{-7} , 3.52×10^{-11} and 0, respectively. It was observed that, although all calculated values were less than the allowable carcinogenic risk limit of 1×10^{-4} adapted from EPA, children in areas with high activity of ^{238}U showed a higher carcinogenic risk compared to adults.

In areas with low activity of ^{238}U , the total carcinogenic risk in adults was calculated to be 3.02×10^{-5} . Ingestion was the main contributor to the total risk with a value of 2.88×10^{-5} , followed by dermal contact with 1.07×10^{-6} and inhalation being the least contributor with 3.14×10^{-7} . Cr, As, Pb, Cd and Hg also contributed to the total risk with values 2.47×10^{-5} , 5.41×10^{-6} , 1.14×10^{-7} , 6.46×10^{-11} and 0, respectively. The total carcinogenic risk in children was 5.50×10^{-5} , which was considerably below the recommended value of 1×10^{-4} . The main percentage was contributed by ingestion which added 5.38×10^{-5} to the total risk. Dermal contact added 1.036×10^{-6} to the total risk whereas inhalation contributed 1.47×10^{-7} .

In the control, total carcinogenic risk in adults was 3.57×10^{-5} , contributed mainly by ingestion with 3.46×10^{-5} , followed by dermal contact with 6.28116×10^{-7} and inhalation with 4.08×10^{-7} . In children, the total carcinogenic risk was 6.55×10^{-5} . The leading contributor to this total was through ingestion by 6.47×10^{-5} , then dermal contact by 6.06×10^{-7} and the least contributor was through inhalation by 1.90×10^{-5} . All these values were less than the recommended value of 1×10^{-4} , therefore, the carcinogenic risk due to toxic heavy metals in Serule area is insignificant.

Table 4.13: Carcinogenic risk for different toxic heavy metals and exposure pathways in different areas.

	Receptor	Pathway	Pb	Cr	Cd	As	Hg	Total risk
Areas with high activity of ^{238}U	adult	ingestion	1.31505E-07	2.97593E-05	-	8.42253E-06	-	3.83133E-05
		inhalation	9.99673E-11	3.75425E-07	7.54378E-11	1.29577E-08	-	3.88558E-07
		dermal	-	-	-	2.08592E-06	-	2.08592E-06
		Total risk	1.31605E-07	3.01347E-05	7.54378E-11	1.05214E-05	0	4.07878E-05
	child	ingestion	2.45475E-07	5.55507E-05	-	1.57221E-05	-	7.15182E-05
		inhalation	4.66514E-11	1.75198E-07	3.52043E-11	6.04694E-09	-	1.81327E-07
		dermal	-	-	-	2.014E-06	-	2.014E-06
		Total risk	2.45522E-07	5.57259E-05	3.52043E-11	1.77421E-05	0	7.37135E-05
Areas with low activity of ^{238}U	adult	ingestion	1.13565E-07	2.43804E-05	-	4.33088E-06	-	2.88249E-05
		inhalation	8.633E-11	3.07569E-07	6.46043E-11	6.6629E-09	-	3.14382E-07
		dermal	-	-	-	1.07259E-06	-	1.07259E-06
		Total risk	1.13651E-07	2.4688E-05	6.46043E-11	5.41013E-06	0	3.02118E-05
	child	ingestion	2.11988E-07	4.55101E-05	-	8.08432E-06	-	5.38064E-05
		inhalation	4.02874E-11	1.43532E-07	3.01487E-11	3.10935E-09	-	1.46712E-07
		dermal	-	-	-	1.0356E-06	-	1.0356E-06
		Total risk	2.12029E-07	4.56537E-05	3.01487E-11	9.12303E-06	0	5.49888E-05
Control sample	adult	ingestion	1.06791E-07	3.19961E-05	-	2.5362E-06	-	3.46391E-05
		inhalation	8.11802E-11	4.03643E-07	6.82824E-11	3.90185E-09	-	4.07694E-07
		dermal	-	-	-	6.28116E-07	-	6.28116E-07
		Total risk	1.06872E-07	3.23997E-05	6.82824E-11	3.16822E-06	0	3.56749E-05
	child	ingestion	1.99342E-07	5.9726E-05	-	4.73425E-06	-	6.46596E-05
		inhalation	3.78841E-11	1.88367E-07	3.18651E-11	1.82086E-09	-	1.90257E-07
		dermal	-	-	-	6.06457E-07	-	6.06457E-07
		Total risk	1.9938E-07	5.99144E-05	3.18651E-11	5.34252E-06	0	6.54563E-05

Conclusions and recommendations

In this chapter, answers to the aim and objectives of this research project were stated. Recommendations for future work were also looked into.

The aim of this study was to evaluate Naturally Occurring Radioactive Materials (NORMs) and toxic heavy metals in the surface soil around Serule prospective uranium mining area in Botswana. The study was inspired by limited to no studies in the area to assess the radionuclides and toxic heavy metal levels as well as the human health risk due to the pre-mined soils of Serule. Soil samples were collected randomly from different locations in order to carry out the experiments that fulfil the aim. A High Purity Germanium (HPGe) detector was used to determine activity concentrations of natural radionuclides, whereas Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) was used to measure mass concentrations of toxic heavy metals. These measurements were compared with the world recommended values to determine the harmfulness of Serule soils.

Daughter nuclides of uranium-thorium decay chain headed by ^{238}U and ^{232}Th and a non-series ^{40}K were detected. These were used to determine activity concentrations of considered radionuclides, ^{226}Ra , ^{238}U , ^{232}Th , ^{210}Pb and ^{40}K . The lowest activity concentrations of these radionuclides that could be measured by the detector were determined by the activity concentrations found in the background. These were the minimum detectable activities of radionuclides and were tabulated in Table 3.5 in Appendix A. Since there are no industrial activities that can produce radionuclides in the study area, man-made radionuclides were not detected in samples.

Average activity concentrations of ^{226}Ra , ^{238}U , ^{232}Th , ^{210}Pb and ^{40}K in areas with high activity of ^{238}U were found to be (1126.26 ± 6) Bq/kg, (498.21 ± 10) Bq/kg, (71.39 ± 1) Bq/kg, (1490.20 ± 29) Bq/kg and (284.18 ± 22) Bq/kg, respectively. Areas with low activity of ^{238}U had average activity concentrations of (72.96 ± 2) Bq/kg, (128 ± 12) Bq/kg, (60.62 ± 3) Bq/kg, (77.69 ± 45) Bq/kg and (331.10 ± 28) Bq/kg for ^{226}Ra , ^{238}U , ^{232}Th , ^{210}Pb and ^{40}K , in that order. However, average activity concentrations for ^{226}Ra , ^{238}U , ^{232}Th of areas with high activity of ^{238}U and areas with low activity of ^{238}U exceeded the world average values of 32, 33 and 45 Bq/kg, respectively, adapted from UNSCEAR (2000). On the other hand, average concentrations for ^{40}K for all areas excluding the control showed values that were less than the world average value of 420 Bq/kg, thus, ^{40}K was not considered as a potential harm to residents. There were no published world average values of ^{210}Pb , for this reason, its harmfulness to residents could not be determined.

Heavy metal mass concentrations were also determined. As, Hg, Cd, Cr and Pb were assessed as toxic heavy metals and U and Th were evaluated as radiotoxic heavy metals. Mass concentrations of toxic heavy metals considered were in the descending order $\text{Cr} > \text{Pb} > \text{As} > \text{Cd} > \text{Hg}$ for all areas in the present study with Cr levels being the only concentration levels higher than recommended.

A Pearson's correlation calculator was used to determine correlation between radionuclides and toxic heavy metals. Concentration values from areas with high activity of ^{238}U and areas with low activity of ^{238}U were assessed individually, then averaged and their correlation coefficients were established. The results showed that at confidence intervals of 90%, 95% and 99%, some radionuclides and toxic heavy metals in the study area have a high chance of co-existing or sharing the same transport behaviour while others have a moderate to low chance.

The radiological risk to residents was determined by using radiological parameters; radium equivalent and external hazard index. Areas with high activity of ^{238}U showed a mean value of 1250 Bq/kg of radium equivalent with range (771.01 ± 5) Bq/kg to (2095.70 ± 9) Bq/kg. All these values were higher than the WHO recommended value of 370 Bq/kg adapted from UNSCEAR (1988). Furthermore, a mean external hazard index value of 3.38 was found in these areas with a range of 2.080 ± 0.01 to 5.66 ± 0.02 which were much greater than the permissible limit of unity. For these reasons, it was concluded that areas with high activity of ^{238}U pose a radiological risk to residents. In contrary, areas with low activity of ^{238}U showed a mean value of 185.13 Bq/kg with

range (116.57 ± 2) Bq/kg to (247.42 ± 2) Bq/kg for radium equivalent and a mean of 0.89 and range 0.31 ± 0.005 to 0.67 ± 0.005 for external hazard index. All the values recorded were below the recommended values of radium equivalent and external hazard index respectively, therefore, residents of areas with low activity of ^{238}U are considered nearly free from the radiological risk. The control showed a radium equivalent value of (221.48 ± 2) Bq/kg and 0.81 ± 0.01 for external hazard index, which were both lower than the set recommended values, thus, an area where the control sample was collected is nearly pristine.

Average daily intakes (ADI's) or exposure doses were used to calculate carcinogenic and non-carcinogenic risks due to the toxic heavy metals. Carcinogenic risk was determined for adults and children for different areas. The allowable cancer risk limit was 1×10^{-4} according to EPA. In areas with high activity of ^{238}U , the total carcinogenic risk for adults was 4.00×10^{-5} and 7.37×10^{-5} for children. These values were within the allowable limit but showed that children are more prone to cancer compared to adults in these areas. In areas with low activity of ^{238}U , the total carcinogenic risk for adults was 3.02×10^{-5} and 2.88×10^{-5} for children, which was within the permissible limit. In the control, the total carcinogenic risk for adults was calculated to be 3.57×10^{-5} and 6.55×10^{-5} for children. It was observed that both adults and children from areas with high activity of ^{238}U are more vulnerable to cancer collated with those from areas with low activity of ^{238}U and the control.

For non-carcinogenic risk, hazard quotient (HQ) was calculated from ADI using equation 2.42. Any $\text{HQ} > 1$ is considered to pose health risk to humans. For both adults and children in areas with high activity of ^{238}U , areas with low activity of ^{238}U and the control, all HQ values were considerably lower than 1, therefore, they had a close to zero non-carcinogenic risk. Furthermore, hazard index was also determined in these areas and all results were less than unity. For this reason, the toxicity threat to humans by toxic heavy metals in the study area is nearly zero.

5.1 Recommendations

5.1.1 For radiation protection of workers and the public once the mining operations start

Since ionising radiation damages cells and cell recovery is not efficient enough at high doses, the amount of radiation exposure to humans has to be limited, regulated and

monitored. Workers are exposed to radiation through different pathways e.g external gamma exposure, inhalation of LLAA (long-lived alpha activity) and inhalation of radon-decay products (R-DP). It is required that, for a fruitful uranium mining, workers need to be protected from radiation and compliance to the recommended ICRP (1991) and IAEA (2011) principles like ALARA (as low as reasonably achievable) and dose limits is mandatory [49, 60, 131]. Table 5.1 below shows exposure pathways and the recommended ways to lower doses resulting from the radiation exposure.

Table 5.1: Recommended radiation protection means to workers

Exposure pathway	Recommended ways to lower radiation doses
External gamma exposure	- High grade ore areas should have limited access time per personnel - Regular cleaning times to avoid build up of active material in air - Active monitoring to keep personnel informed of high dose areas - Use of shielding to minimise dose rates
Inhalation of LLAA (Long-lived alpha activity)	- spray water on dry surfaces to avoid dust - Covering up dry material - Provide workers with respiratory protection equipment
Inhalation of R-DP (Radon- Decay Products)	- Ventilation in work area to provide clean air - Use extractive systems to reduce air residency time - Limited access time per personnel in high R-DP areas - Provide workers with respiratory protection equipment

Communities that are nearby the mining site also have to be protected from radiation. The exposure pathways to this category includes, inhalation of radon-decay products resulting from the spread of radon gas in air, inhalation of long-lived alpha activity as a result of generation of dust from the mine and ingestion of long-lived alpha activity. Long-lived alpha activity can be ingested e.g from soil by children, from crops grown on soil containing long-lived alpha activity and the use of surface or underground water [49, 131]. In order to lower the dose rates resulting from radiation exposure to the public, it is recommended that;

- the public is kept at a distance from the mining facilities to ensure that the exposure to radon is below regulatory limits.
- radon emitting facilities are covered (usually with clay layers) to reduce radon emissions into the atmosphere.
- dust generation areas are limited by covering or keeping them damp.
- discharges and dispersal of hazardous material to the aquatic environment and emissions to groundwater should be restricted.

5.1.2 For future work

This research was conducted as a baseline study of Serule area before mining operations commence. Just twenty-nine samples from Serule area and 1 control sample outside the area were taken for analysis. This only gives a representation of a small portion of the area, as a result, it is recommended that more samples (more than 100) could be taken for analysis which would ensure a more reliable representation of Serule area. Soil samples were collected randomly in this study, as a suggestion for future studies, factors such as soil pH, soil type, electric conductivity and temperature of the soil could be taken into consideration. Another suggestion is that the study could be extended to all other possible pathways to humans such as, vegetation, animal blood/meat, water and radon concentrations in air.

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Appendix A

This Appendix lists GPS coordinates of sampling points, minimum detectable activities of radionuclides and mass concentrations of heavy metals in Tables A.1, A.2 and A.3, respectively.

Table A.1: Masses of samples analysed for gamma ray spectroscopy and their GPS coordinates.

Sample serial number	Mass of sample (g)	Latitude (°)	Longitude (°)	Altitude (m)
Control (BS20)	355.7	21.92356	27.30448	941
BS1	355.2	21.89299	27.29470	944
BS2	355.4	21.88964	27.30333	936
BS3	355.7	21.88918	27.30437	938
BS4	355.2	21.89022	27.29883	938
BS5	355.7	21.88561	27.29520	945
BS6	357.3	21.88096	27.29520	945
BS7	355.7	21.87062	27.29351	933
BS8	355.7	21.87076	27.29314	929
BS9	355.5	21.86499	27.29228	919
BS10	355.9	21.86542	27.29156	925
BS11	355.2	21.85182	27.29120	933
BS12	355.4	21.85368	27.28901	932
BS13	355.2	21.85385	27.28784	933
BS14	355.3	21.85563	27.28411	932
BS15	355.5	21.86045	27.27929	933
BS16	355.3	21.86090	27.27502	933
BS17	355.5	21.85420	27.26645	936
BS18	355.4	21.85944	27.26848	934
BS19	355.3	21.89039	27.28143	949
BS21	355.5	21.90153	27.29704	950
BS22	355.4	21.90136	27.29787	943
BS23	355.5	21.89909	27.30184	944
BS24	355.5	21.89324	27.30142	939
BS25	355.6	21.89373	27.30554	942
BS26	355.8	21.89524	27.30760	940
BS27	355.7	21.89625	27.31083	941
BS28	355.6	21.89850	27.31337	944
BS29	355.5	21.89819	27.31816	945
BS30	355.5	21.88073	27.32714	924

Table A.2 shows minimum detectable activities of radionuclides in the background spectrum. The uncertainties for emission probability are stated in the form 0.0375 (8), which means that the value 0.0375 has an uncertainty of 0.0008, which can also be represented as 0.0375 ± 0.0008 .

Table A.2: Minimum detectable activities of the HPGe system calculated using radionuclides found in background spectrum.

Radio-nuclide	Peak Energy (keV)	Emission Probability $\pm \Delta$ (Emission Probability)	Absolute Efficiency	MDA (Bq/kg)
²¹⁰ Pb	46.54	0.04252(40)	0.000775	0.52
²³⁴ Th	63.29	0.0375(8)	0.000913	0.28
²³⁴ Th	92.59	0.02165(19)	0.00112	0.09
²¹² Pb	238.63	0.430(20)	0.00185	0.01
²⁰⁸ Tl	583.19	0.0300(14)	0.00298	0.01
²⁰⁸ Tl	2614.51	0.9990(40)	0.00662	0.01
²²⁸ Ac	911.20	0.262(8)	0.00378	0.02
⁴⁰ K	1460.82	0.1055(13)	0.00486	0.21

Table A.3 shows elemental mass concentrations of other various heavy metals.

Table A.3: Mass concentrations of other heavy metals

Sample serial number	Be 9	B 11	Na 23	Mg 24	Al 27
Control (BS20)	1.094	5.486	142.4	2788	30100
BS1	1.195	8.612	158.2	3052	32950
BS2	0.8525	6.423	98.2	2483	25040
BS3	1.256	11.13	291.5	3965	37010
BS4	0.8033	1.762	73.23	1201	19850
BS5	0.4945	1.102	86.66	727.4	10710
BS6	0.4281	1.859	82.26	887.6	10520
BS7	1.04	8.886	228.6	1807	26700
BS8	0.7231	3.084	112.9	733.6	17820
BS9	0.7624	7.413	989.4	5454	21830
BS10	0.8413	10.92	2707	5680	24270
BS11	1.671	6.656	544.8	4544	42930
BS12	1.58	13.85	2387	5717	40440
BS13	2.099	17.27	420.7	6179	48110
BS14	1.385	5.632	146.5	2894	34580
BS15	0.9696	3.173	118	1262	24890
BS16	0.9244	3.311	137.8	1485	24980
BS17	0.7799	6.917	277.4	4824	19430
BS18	1.065	6.115	138.2	1776	14300
BS19	0.3712	0.1369	66.9	290.1	5191
BS21	1.196	6.72	129.8	1433	34800
BS22	1.298	7.05	157.1	2023	35970
BS23	1.658	12.09	279.9	2366	46150
BS24	0.8745	5.465	765.5	2162	23780
BS25	1.212	7.756	169.3	2783	24830
BS26	1.13	4.994	98.92	2277	27710
BS27	0.5177	1.019	65.03	577.9	9907
BS28	0.4287	0.7061	67.85	499.1	9044
BS29	1.282	5.792	151.3	1746	26470
BS30	0.5833	2.436	103.4	1443	13090
Average	1.01718	6.12553	373.19167	2501.99	25446.73333
Minimum	0.3712	0.1369	65.03	290.1	5191
Maximum	2.099	17.27	2707	6179	48110
Standard Deviation	0.41330	4.08348	628.80171	1712.05839	11379.81508

Table A.3 continued: mass concentrations of other heavy metals.

Sample serial number	P 31	K 39	Ca 23	Ti 47	V 51
Control (BS20)	164.2	3367	1920	512.7	47.14
BS1	166.7	4539	2325	320.8	63.86
BS2	140.2	3857	1777	177.2	55.89
BS3	176.3	4564	3316	399.1	77.81
BS4	114.5	1021	1073	356.5	36.72
BS5	122.8	967.6	1147	251	25.86
BS6	132.4	1042	1087	217.6	38.03
BS7	170.5	2114	4729	294	58.2
BS8	216.8	1122	858.9	285.8	51.94
BS9	112.6	2383	7935	417.7	49.97
BS10	102.2	2501	11150	489.2	50.44
BS11	129.1	2400	2459	593.1	101.5
BS12	155.4	3776	2654	484.2	95.85
BS13	201.9	6783	2270	490.3	77.13
BS14	119.8	1734	3688	387	82.17
BS15	126.9	1336	2349	367.3	78.48
BS16	139.4	1306	3169	341.3	84.29
BS17	124.3	1971	5514	337.1	49.85
BS18	269.1	1750	30480	89.73	77.74
BS19	136.2	503.4	396.1	175.5	27.34
BS21	149.2	2228	1620	422.7	50.04
BS22	116.6	2655	2185	354.6	47.63
BS23	154.8	2976	2884	398.1	57.93
BS24	112.9	2050	1102	382.8	37.89
BS25	125.3	2842	2486	293.5	43.08
BS26	141.5	2148	2987	281.8	56.36
BS27	88.34	832.7	501.7	247.4	25.48
BS28	88.13	924.2	343.6	197.8	23.59
BS29	168.2	2647	2031	283.7	56.24
BS30	111.7	1675	984.2	227.4	63.81
Average	142.599	2333.83	3580.71667	335.89767	56.40867
Minimum	88.13	503.4	343.6	89.73	23.59
Maximum	269.1	6783	30480	593.1	101.5
Standard Deviation	38.45295	1362.26147	5561.96677	114.28470	20.65899

Table A.3 continued: mass concentrations of other heavy metals.

Sample serial number	Mn 55	Fe 57	Co 59	Ni 60	Cu 63	Bi 209
Control (BS20)	325.4	18210	12.12	41.19	36.37	0.1516
BS1	257.7	19240	10.28	127.8	29.62	0.2044
BS2	227.2	14530	8.667	51.09	33.68	0.1377
BS3	310.7	21100	12.1	46.75	40.06	0.1857
BS4	218.1	10990	10.95	32.84	32.82	0.1257
BS5	104.1	9046	4.547	21.14	20.48	0.05988
BS6	167.6	10230	7.143	20.87	28.96	0.06237
BS7	167.8	13180	10.4	34.54	32.72	0.1726
BS8	149.7	9602	9.002	24.74	25.21	0.1752
BS9	189.5	15140	7.841	25.88	32.28	0.1491
BS10	228	15100	9.231	28.89	32.94	0.1634
BS11	195.2	16710	8.139	40.49	44.98	0.4003
BS12	217.5	14450	10.74	44.57	44.15	0.4346
BS13	186.6	17730	8.852	44.4	40.16	0.54
BS14	132.7	12820	7.901	34.79	36.04	0.4254
BS15	216.8	13480	12.56	35.41	33.08	0.2042
BS16	206.1	13970	13.23	35.14	41.6	0.3235
BS17	185.3	11800	7.326	28.08	22.77	0.1527
BS18	170.2	13090	7.089	25.26	26.09	0.4618
BS19	109.7	4477	6.417	20.66	17.17	0.117
BS21	202.5	17360	10.47	39.54	35.22	0.1728
BS22	255.6	17330	13.38	45.76	35.07	0.1664
BS23	260.6	18430	15.24	50.23	33.21	0.1987
BS24	199.1	12770	8.45	32.73	25.55	0.1418
BS25	215.8	13510	11.93	40.21	33.51	0.1388
BS26	326.6	18790	20.23	40.18	43.37	0.1429
BS27	124.2	6847	7.957	21.79	23.3	0.1041
BS28	90.4	7883	4.581	16.88	21.5	0.07957
BS29	253.5	18330	14.41	31.81	26.1	0.1596
BS30	223.6	17290	9.114	25.25	22.78	0.101
Average	203.92667	14114.5	10.0099	36.96367	31.693	0.20176
Minimum	90.4	4477	4.547	16.88	17.17	0.05988
Maximum	326.6	21100	20.23	127.8	44.98	0.54
Standard Deviation	60.30451	4026.43951	3.29474	19.60655	7.45675	0.12562

Table A.3 continued: mass concentrations of other heavy metals.

Sample serial number	Zn 66	Se 82	Rb 85	Sr 88	Mo 95	Pd 105
Control (BS20)	35.69	0.9837	34.95	26.69	1.168	0.3521
BS1	38.05	1.009	39.91	38.9	20.1	0.3579
BS2	29.56	0.8905	32.8	33.85	3.654	0.3391
BS3	66.52	1.238	42.43	65.03	1.198	0.439
BS4	22.72	1.2	17.53	25.57	1.609	0.3803
BS5	13.15	0.7783	17.51	13.07	1.37	0.2123
BS6	15.62	0.8112	13.36	18.99	1.412	0.2336
BS7	24.89	1.281	27.45	72.99	1.553	0.4071
BS8	15.16	1.275	20.07	57.21	1.688	0.3555
BS9	27.76	1.056	29.52	73.52	1.077	0.3205
BS10	28.74	1.228	28.87	103.6	1.201	0.3732
BS11	37.04	1.384	41.66	93.44	1.282	0.4654
BS12	37.93	2.036	44.94	83.98	1.493	0.5624
BS13	44.17	1.485	61.22	91.64	1.434	0.4838
BS14	28.31	1.311	32.28	136.7	1.471	0.4691
BS15	25.02	1.179	27.82	21.94	1.272	0.3493
BS16	27.59	1.176	27.66	37.81	1.41	0.357
BS17	23.12	0.9445	21.51	50.25	1.155	0.318
BS18	31.11	1.027	20.77	82.96	0.9612	0.4317
BS19	10.37	0.7697	6.597	26	1.185	0.2501
BS21	24.55	1.173	37.15	26.38	1.238	0.3526
BS22	31.22	1.087	36.52	33.07	1.225	0.3905
BS23	32.12	1.313	41.4	53.43	1.421	0.4527
BS24	24.54	1.03	30.03	24.25	0.8894	0.3373
BS25	29.52	1.156	31.48	45.19	1.499	0.3747
BS26	31.11	1.169	32.1	54.93	1.212	0.4239
BS27	11.48	1.074	12.47	15.52	0.9172	0.3216
BS28	13.82	0.7501	13.95	11.66	0.958	0.2447
BS29	24.89	1.272	32.44	34.3	1.263	0.4182
BS30	18.45	0.8052	21.41	19.97	1.068	0.2581
Average	27.474	1.12974	29.26023	49.09467	1.97946	0.36772
Minimum	10.37	0.7501	6.597	11.66	0.8894	0.2123
Maximum	66.52	2.036	61.22	136.7	20.1	0.5624
Standard Deviation	11.21601	0.25866	11.58586	31.25115	3.45589	0.08062

Table A.3 continued: mass concentrations of other heavy metals.

Sample serial number	Ag 107	Sb 121	Ba 137	Pt 195	Au 197	Tl 205
Control (BS20)	0.4257	0.05532	98.64	0.01761	0.01164	0.2859
BS1	0.1269	0.1062	159.1	0.01857	0.03469	0.2928
BS2	0.1097	0.03869	109.9	0.01706	0.01093	0.2187
BS3	0.1886	0.1117	154.1	0.02148	0.01344	0.3035
BS4	0.1318	0.05368	162.7	0.01812	0.00754	0.1598
BS5	0.105	0.04522	84.46	0.01701	0.00841	0.09874
BS6	0.09279	0.05013	56.46	0.01556	0.0065	0.1029
BS7	0.1207	0.5084	258.7	0.02187	0.0059	0.2347
BS8	0.09714	0.103	249.3	0.02032	0.00619	0.1484
BS9	0.1391	0.08893	73.97	0.01868	0.01033	0.2673
BS9	0.1117	0.08821	204.8	0.01779	0.01094	0.2853
BS10	0.2274	2.835	158.7	0.02407	0.0118	0.4592
BS11	0.1671	0.1671	258.6	0.02424	0.00723	0.4117
BS13	0.2082	0.1726	152	0.02599	0.00884	0.5419
BS14	0.1343	0.1694	366.8	0.04939	0.00886	0.4357
BS15	0.1056	0.2791	265	0.02924	0.01239	0.2989
BS16	0.1865	0.2272	172.1	0.02107	0.01121	0.3903
BS17	0.5094	0.1174	83.19	0.0183	0.08051	0.2552
BS18	0.1394	0.04418	211.9	0.01448	0.01406	0.3512
BS19	0.236	0.0434	74.26	0.02102	0.00629	0.07534
BS21	0.2931	0.06442	80.95	0.02035	0.00558	0.2828
BS22	0.1892	0.05449	125.1	0.02163	0.0079	0.3048
BS23	0.1539	0.06309	115.4	0.0193	0.00959	0.4417
BS24	0.4302	0.0568	56.86	0.01753	0.00533	0.3438
BS25	0.1838	0.05602	112.8	0.02088	0.00545	0.5431
BS26	0.1229	0.06104	152.3	0.01789	0.00194	0.2965
BS27	0.06145	0.04654	62.23	0.01675	0.00186	0.101
BS28	0.1275	0.04571	60.26	0.01515	0.00802	0.09133
BS29	0.1141	0.0565	147.9	0.01648	0.00359	0.2698
BS30	0.06725	0.07701	95.46	0.01335	0.00558	0.1795
Average	0.17688	0.19622	145.46467	0.02037	0.01142	0.28239
Minimum	0.06145	0.03869	56.46	0.01335	0.00186	0.07534
Maximum	0.5094	2.835	366.8	0.04939	0.08051	0.5431
Standard Deviation	0.10790	0.50756	76.42911	0.00648	0.01427	0.12907

Appendix B

Equations for calculating weighted mean average and its uncertainty, standard deviation and error propagation

Weighted mean average and weighted mean error

Let a, b, c be activities for a certain target nuclide, and Δa , Δb and Δc be the corresponding activity uncertainties. The weighted mean will be given by;

$$Wm = \frac{\frac{a}{(\Delta a)^2} + \frac{b}{(\Delta b)^2} + \frac{c}{(\Delta c)^2}}{\frac{1}{(\Delta a)^2} + \frac{1}{(\Delta b)^2} + \frac{1}{(\Delta c)^2}} \quad (B.1)$$

Weighted mean error is then calculated as follows;

$$\Delta Wm = \frac{1}{\sqrt{\frac{1}{(\Delta a)^2} + \frac{1}{(\Delta b)^2} + \frac{1}{(\Delta c)^2}}} \quad (B.2)$$

Standard deviation

Standard deviation is calculated as a function of the mean value;

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad (B.3)$$

Then, it is given by ;

$$\sigma = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2} \quad (B.4)$$

It is then used to calculate the uncertainty using formula;

$$u(x) = \frac{\sigma}{\sqrt{n}} \quad (\text{B.5})$$

Error propagation

Table B.1: Formulas used in uncertainty calculations

Equation for calculating z	Standard uncertainty
$z = ax \pm by \pm c,$ where a, b and c are coefficients with zero uncertainty	$u(z) = \sqrt{[au(x)]^2 + [bu(y)]^2}$
$z = cx^a y^b,$ where exponents a and b have zero uncertainty	$u(z) = \sqrt{\left[a \frac{u(x)}{x}\right]^2 + \left[b \frac{u(y)}{y}\right]^2}$