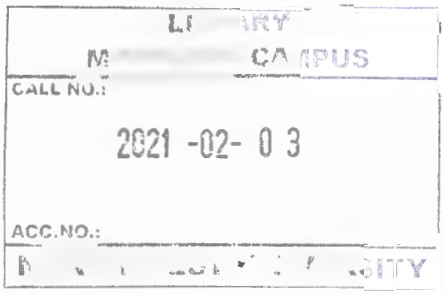
Transfer of radionuclides and toxic elements from the Princess mine dump to water in Roodepoort, South Africa

Sibusiso Goodwill Dlamini

Mini-dissertation submitted in partial fulfilment of the requirements for the degree Master of Science in Applied Radiation Science and Technology at the Mafikeng Campus of the North-West University



Supervisor: Prof M. M. Mathuthu

Co-Supervisor: Prof M. V. Tshivhase

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DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science in Applied Radiation Science and Technology in the North-West University, Mafikeng. It has not been submitted before for any degree or examination in any other University.

Signature:.....

Date:.....

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ABSTRACT

High concentrations of radionuclides and toxic elements in gold mine tailings facilities present a health hazard to the environment and people living near that area. The research was aimed at determining the transfer of radionuclides and toxic elements from the Princess mine dump to water in the Roodepoort area, South Africa. The study focused mainly on the dump and considered it as the main (only) source of pollution to the water. To achieve this, the water samples were taken at sampling points near the dump and along the flowing part of the stream (drainage pipe) before it joined other water sources. Water sampling was done twice; once in the dry season and again during the rainy season. Soil sampling was done on the surface (15 cm) and also 100 cm below the surface. For analysis of the soil samples, a Portable Detection Unit based on HPGe Coaxial Detector (Baltic Scientific Instruments GCD-35190) in the nuclear physics laboratory at CARST was used. The water samples were run using an ICP-MS at the Animal Health Department at the North-West University, Mafikeng Campus. An alpha spectrometer at a SANAS accredited laboratory (Testing Laboratory T0111) was also used to analyze water samples for selected radionuclides. The average activity for uranium and thorium in soil were calculated to be 129±36 Bq/kg and 18.1±4.0 Bq/kg, respectively. In water, sampled during rainy season, thorium and uranium ranged from 1.02E+01 to 1.69E+02µg/ℓ and 1.55E+02 to 5.17E+03 µg/ℓ, respectively. The estimated radiological dose due to direct ingestion of the untreated water was calculated for all the age groups. For children,< 1year, it ranged from 1.27 to 10.20 mSv/a, for 1 to 2 year olds, from 0.26 to 4.29 mSv/a, for 2 to 7 years, from 0.20 to 3.33 mSv/a, for 7 to 12 years, from 0.19 to 3.27 mSv/a, for 12 to 17 years, from 0.29 to 5.53 mSv/a and for adults > 17 years, from 0.27 to 4.52 mSv/a. The dose limit set by Strahlengschutz-Komission of 0.500 mSv/a, the WHO screening value of 0.100 mSv/a and the 0.25 mSv/a set by the South African National Nuclear Regulator were exceeded by the maximum annual levels from the water samples in this research. Radionuclides identified and measured using alpha spectrometry were ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Po, ^{235}U, ^{227}Th, ^{223}Ra, ^{232}Th, ^{228}Th and ^{224}Ra.

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LIST OF ABBREVIATIONS

TSF	Tailings Storage Facility
NORM	Naturally Occurring Radioactive Material
IAEA	International Atomic Energy Agency
HPGe	High Purity Germanium detector
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
XRF	X-Ray Fluorescence
INAA	Instrumental Neutron Activation Analysis
TWQR	Target Water Quality Range
DWA	Department of Water Affairs
GPS	Global Positioning System
AMD	Acid Mine Drainage
NNR	National Nuclear Regulator
CPEP	Contemporary Physics Education Project
US EPA	United States Environmental Protection Agency
SSK	Strahlenschutz-Kommission
WHO	World Health Organization
BTRC	A name given to a sampling point of a place in Mafikeng where people reside
ICRP	International Commission on Radiological Protection
EDTA	Ethylenediaminetetraacetic acid
CARST	Center for Applied Radiation Science and Technology

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CHAPTER 1: INTRODUCTION AND PROBLEM STATEMENT

1.1 Introduction

"The discovery of the Witwatersrand Goldfields in 1886 led to the development of South Africa's world-class gold mining industry, which has dominated the global gold mining industry for 120 years", reported the Virtual Metals Research and Consulting Limited (www.goldinsouthafrica.com). The mining industry is of economic value to the Government of South Africa since it is a source of revenue and it offers quite a large number of job opportunities to the people (Lesikar et al., 2009).

The Witwatersrand basin has been mined for more than 100 years and has produced more than 41000 tonnes of gold. South Africa produced 394 tonnes of gold in 2001 which was the lowest production since 1956 (Mbendi Information Systems, 2003).

During the mining process a lot of waste is produced which is then dumped at selected places near the mine. These places are referred to as mine dumps and/or tailings storage facilities (TSF's).

During the extraction of gold the byproducts (tailings) are discarded and they then present a hazard to humans as well as the environment since these tailings contain toxic elements and radioactive elements which remain active for a very long period of time. These radionuclides are present in soil, rock and can also be found in groundwater and surface water (Lesikar et al., 2009).

Naturally occurring radioactive materials (NORMs) have been there (in existence) since the beginning of times. These NORMs are found almost everywhere, from the earth's crust, walls of buildings, in plants and water (Department of minerals and energy, 2005). Radioactive elements with long half-lives (long-lived) such as uranium, thorium, potassium and any of their decay products such as radium and radon are examples of NORMs. These radionuclides that occur in nature can be broken down into two groups. In the primordial group, the half-life of the nuclide is comparable to the life of the earth, in the order of 10^9 years. The second group is the secondary nuclides, which have gained existence through the decay of the primordial nuclides (they are daughters of the long-lived parents).

The air that humans inhale contains some of the radioactive gases (e.g. radon, thoron). The human body (muscles, bones and tissue) contains some naturally occurring radioactive elements, which do not have any bad effects to the body systems as long as their levels in the body do not exceed a certain amount (Department of minerals and energy, 2005).

Table1 gives a list of examples of radioactivity as it occurs in natural and artificial materials.

Table 1: Examples of radioactivity in natural and artificial materials (DWAF, 2002)

Example of material	*Activity*	*Type of activity*
1 kg of granite	1kBq	NORM
1 kg of coffee	1kBq	NORM
1 kg of coal ash	2kBq	NORM
1 kg superphosphate fertiliser	5kBq	NORM
1 adult human	7kBq	NORM
1 household smoke detector	30 kBq	Artificial
1 kg low level radioactive waste	1 MBq	Artificial
Radioisotope source for medical therapy (Typically Cobalt-60)	100 TBq	Artificial

1.1.1Radioactivity in Water

Naturally occurring radioactivity in drinking water and hot mineral water has been considered by Saqan et al. (2001) and found to constitute a major source of radiation exposure. The most observed gamma emitters are the ^{214}Bi and the ^{214}Pb. Spring water analyzed in Jordan by the Physics Department of the Jordan University of Science and Technology showed that ^{234}Th, ^{226}Ra, ^{214}Pb, ^{214}Bi, ^{228}Ac, ^{228}Th, ^{212}Pb, ^{212}Bi, ^{208}Tl, ^{235}U and ^{40}K radionuclides were present in the spring (Saqan et al., 2001).

1.1.2 Acid Mine Drainage

Wendel (1998) in his study highlighted that water plays a pivotal role in the transportation or transfer of radionuclides through the environment.

Hierro et al. (2012) stated that acid mine drainage (AMD) is one of the major causes of water pollution worldwide. The ore of the Witwatersrand Super group contains significant amounts of sulphide minerals (e.g. the pyrite, FeS_2, which is a significant constituent of gold bearing reefs) (McCarthy, 2011). These sulphide minerals make the gold mine tailings prone to the formation of acid mine drainage. Figure 1 gives a schematic diagram of the generation of Acid mine drainage in the Witwatersrand goldfields tailings.

The exposure of minerals to atmospheric weathering results in oxidation taking place. However, sulphides are stable and very insoluble under reducing conditions but their oxidation as a result of the weathering process releases sulphuric acid which affects the quality of streams and groundwater. Other oxidation products can include partially oxidized oxonians, such as thiosulphate, hydrogen sulphide, iron sulphate in solution and heavy metals associated with uranium mineralization (Fernandes et al., 1998). The above mentioned process can be further explained using equation (1).

$$4FeS_2 + 15O_2 + 14H_2O \xrightarrow{\text{yields}} 4Fe(OH)_3 + 8H_2SO_4, \quad (1)$$

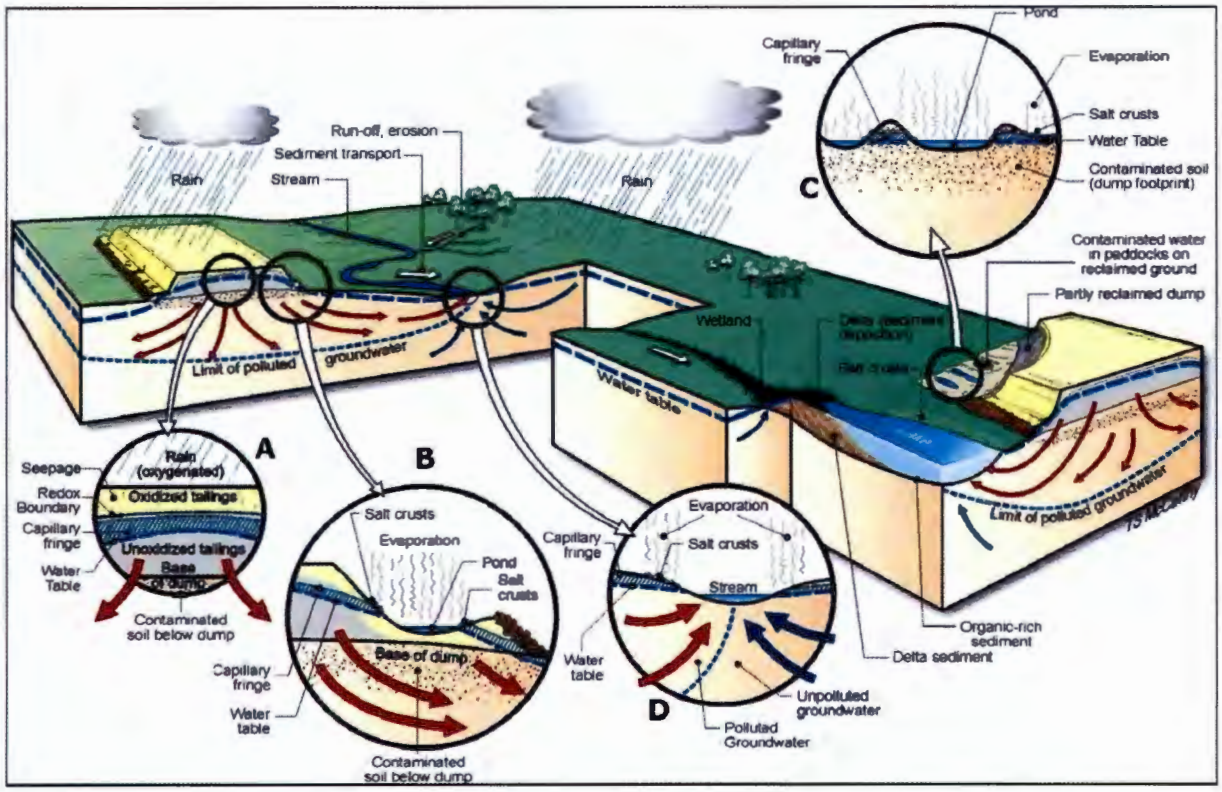

Figure 1: Schematic diagram showing various aspects of the generation and dispersal of acid mine drainage in and around tailings dumps in the Witwatersrand goldfields. Insets show important features and processes in dumps (A), feet of dumps (B), paddocks (C) and streams (D) (Tutu et al., 2008)

1.1.3 Toxic Elements

All metals have the potential of being toxic. They can be regarded toxic once they exceed the required limit in the human body. Figure 2 shows the relationship between essential element at required concentrations and the toxicity once the concentration is in excess (Squibb, 2002).

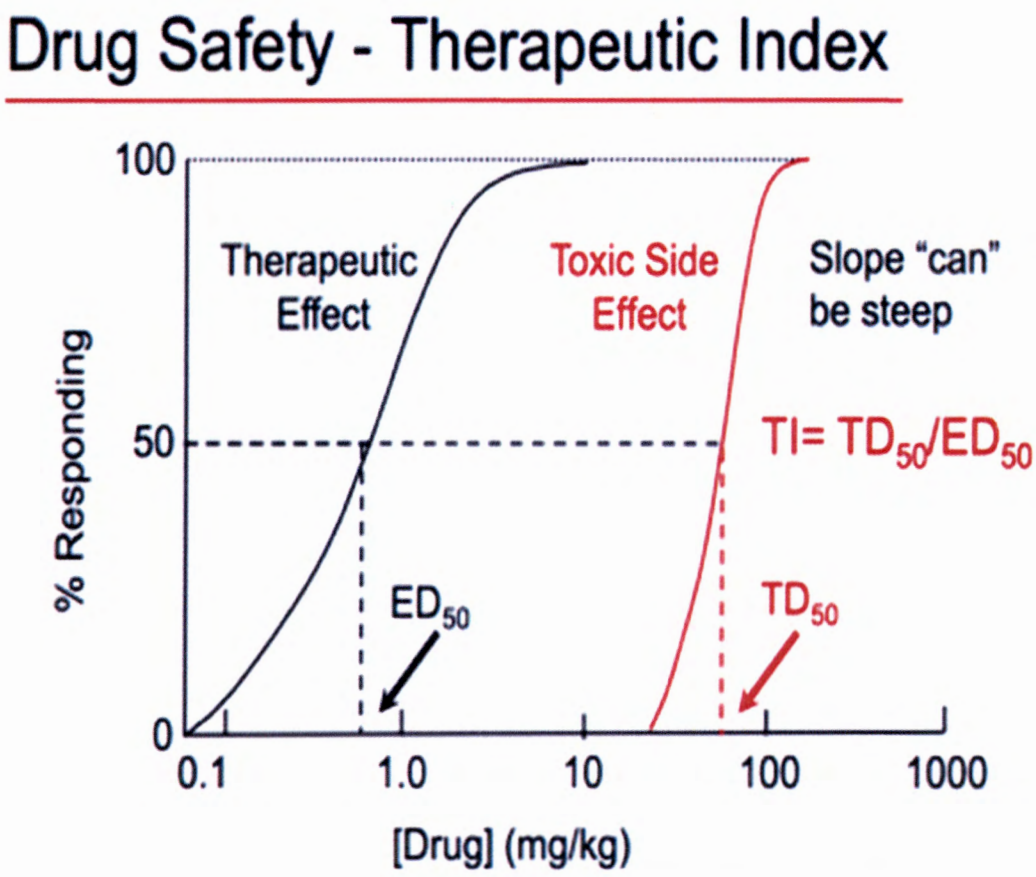

Figure 2: Plot of human response with change in concentration of drug (Ketakin, 1997)

Squibb (2002) in his publication presents a list of elements that are regarded as toxic or sometimes referred to as non-essential elements.

Table 2: List of Toxic Elements (Squibb, 2002)

Toxic Element symbol	Toxic element name
As	Arsenic
Ag	Silver
Au	Gold
Be	Beryllium
Cd	Cadmium
Cs	Caesium
Li	Lithium
Hg	Mercury
Pb	Lead
Sn	Tin
Sr	Strontium

The toxic elements have varying negative effects on the human body. For example, lead causes liver and kidney damage, mental retardation as well as abnormalities in fertility and pregnancy (Squibb, 2002).

1.1.4 Site Location

The Princess mine dump is one of the mine dumps of a previously active gold mine in the Witwatersrand Mining Basin. The dump forms an L- shape with a park (Victory Park) inside the shape. At the edge of the dump are houses. Figure 3 gives a better insight into the place (the empty ground with no houses or vegetation in Figure 3 is the dump).

Figure 3: An aerial view of the Princess mine dump

Soil and water samples from the Princess mine dump were collected, prepared and then analyzed so as to identify the radionuclides and toxic elements in the water which are transferred from the dump.

1.2 Problem Statement

When mining companies shut down, the greatest issue becomes the waste generated from the whole mining program (commonly referred to as mine tailings). The mine tailings get blown by the winds and are washed by rains into water systems. Radon (Rn), a gas generated by tailings, can travel up to thousands of kilometers in a light breeze (Davies &Mundalamo, 2010).

The slime dams and mine dumps of the Gauteng and the North West Provinces leak uranium and its daughters (Durand, 2012).The effluents from the mines contain radium, polonium, thorium, uranium and isotopes of lead. Pollution of the country's soil and water resources affect the food chain and consequently the health of the population and surrounding ecosystems. These elements are not just toxic but are also radioactive and therefore become a threat to the people staying near the dump. Exposure pathways to humans can be through one of the following (Davies &Mundalamo, 2010):

- Ingestion of earth crops that have high concentrations of the radionuclides from the soil;
- Consumption of fish swimming in contaminated water;
- Consumption of meat/milk from cows grazing in contaminated land or drinking the contaminated water;
- Inhalation of dust or particulate matter from the dump;
- Direct contact with soil materials from the dump.

The following diagram (Figure 4), taken from the South African National Nuclear Regulator (NNR) regulatory guide (RG-002), gives further insight into the exposure pathways.

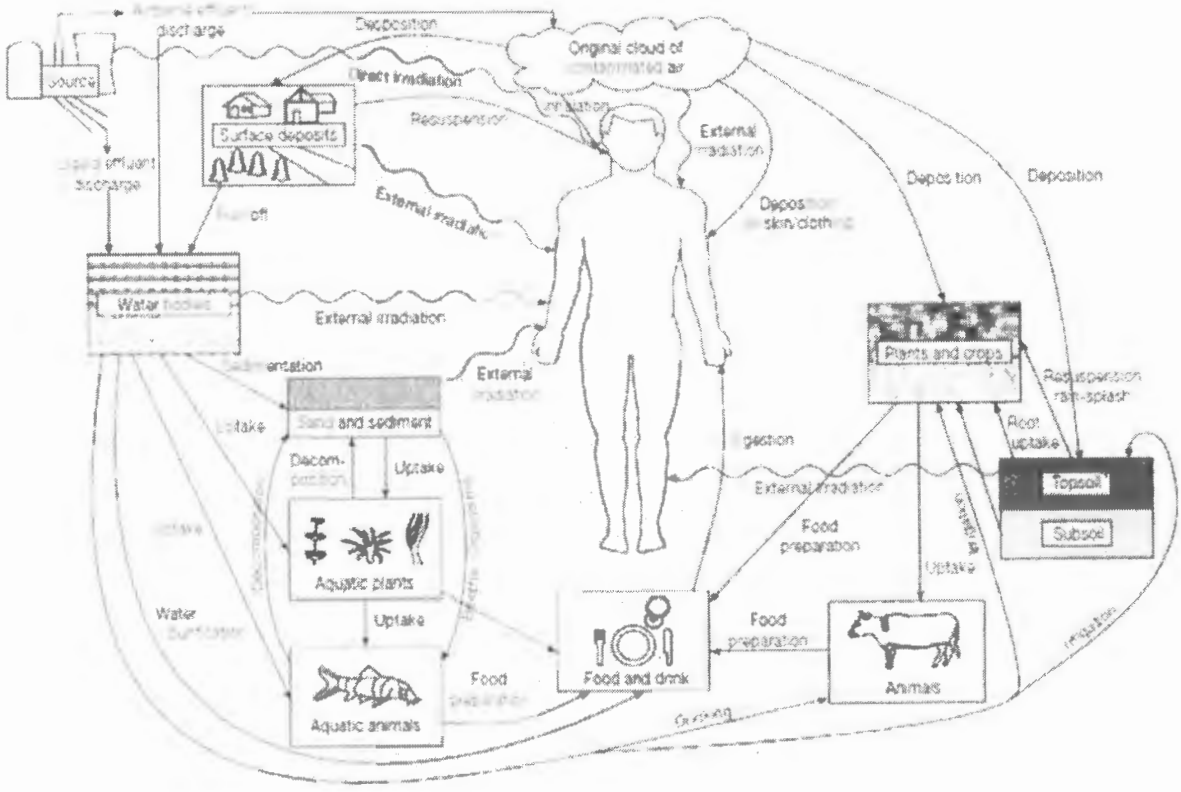

Figure 4: Different exposure pathways to the general public (NNR regulatory guide (RG-002))

CHAPTER 2: RESEARCH AIMS AND OBJECTIVES

2.1 Research Aims

During the gold mining process, several tons of rock are extracted from underground and processed to obtain gold. Once the milling process and extraction of gold is done the mill tailings are then placed on mine dumps in the environment. There are an estimated 7000 hectares of such dumpsites with large populations living close by (Lindsay et al., 2004).

The aims of this project are to investigate the transfer of radionuclides and toxic elements from soil around the Princess mine dump to water, and determine the potential radiological and toxicological impact on humans.

2.2 Research Objectives

The research objectives are as follows:

- To determine the activity of selected radionuclides in the soil samples using the High Purity Germanium detector;
- To identify the heavy elements present in water and their concentrations using inductively coupled plasma mass spectrometer and compare the concentrations against the soil results obtained from the HPGe detector to determine the transfer factors for the radionuclides;
- To identify selected radionuclides and measure their activity concentrations using an alpha spectrometer;
- To compare the results of the concentrations of different radionuclides from the dump obtained using the different equipment against water samples collected around Mafikeng in an area where people reside where there is no uranium or gold mine dump.

2.3 Justification

People come up with many different myths and perceptions concerning the threat to their health due to being located near mine tailings. Mara Kardass-Nelson, a health journalist for Mail and Guardians Centre published a story of a lady who claimed she witnessed a flood acid mine drainage sweep her furniture away. For any action to be taken on the mine dump, first there should be some data collected that will be analyzed so as to determine

the concentration levels of the radioactive elements in the soil and in the slime dams. Determination of the radionuclides in the dump and their concentrations will assist in assessing whether there is any potential radiological and toxicological impact on humans. Fayazi (2005) did a water quality survey around the Princess mine dump with the aim of determining the dump's negative effects on the water resources. The main focus of this study was on the sulphate (SO_4) concentration, hydrogen ion concentration (pH), Iron (Fe) concentration and selected trace elements (Cd, Cr, Co, Cu, Pb, Mn, Ni, Zn, and Al). The sulphate concentration in surface water analyzed was higher compared to that of ground water investigated. The oxidation of pyrite which was found in the mine dump increased the sulphate concentration. Fayazi did not go to the extent of measuring uranium and thorium concentrations in the water and compare them to the concentrations in the soil so as to determine the transfer factors. As far as we know such a study has not been previously done at this Princess mine dump. This study is also of national importance in that the data collected at this dump can be used to compare with or update or compliment data collected in other areas so as to come up with a national database on radioactivity levels at the different dumping sites.

CHAPTER 3: LITERATURE REVIEW

3.1 Background Information on Radioactivity

The International Atomic Energy Agency, in its IAEA safety glossary (IAEA, 2007), defines radioactivity as the phenomenon whereby atoms undergo spontaneous random disintegration, usually accompanied by the emission of radiation.

The discovery of radioactivity resulted from the discovery of X-rays by Wilhelm Conrad Roentgen in 1895 by shining light rays onto photographic plates (World Nuclear Association, 2013). In 1896 Becquerel decided to repeat the X-ray experiment carried out by Roentgen. He prepared several photographic plates to ensure that there is repetition of the results. He left the plates in the drawer yet the uranium crystal was still attached to the plates. Since it was a cloudy day, there was no sunlight but when he checked the plates the results obtained were the same as when there was sunlight in the X-ray experiment. The only explanation Becquerel could come up with was that the rays produced were produced internally by the crystal that contained uranium which was attached to the plates (World Nuclear Association, 2013).

Marie S. Curie and her husband Pierre did some further research and analysis of the observation done by Becquerel on the materials and their new property. They extracted uranium from its ore and to their surprise the remaining ore after uranium extraction still showed more activity than the pure uranium. They named this new material property and behavior *radioactivity*. Their study led to the discovery of the elements polonium and radium (CPEP, 2003).

Ionizing radiation is radiation that is composed of particles that individually carry enough kinetic energy to liberate an electron from an atom or molecule thus ionizing it. Radiation emitted by radioactive materials is also referred to as ionizing radiation, due to the manner in which it interacts with matter. This ionizing radiation can be in the any of the three main types (Martins, 2006):

- Alpha particles;
- Beta particles;
- Gamma rays.

3.2 Radionuclide Decay

Atoms undergo radioactive transformations because they are not stable, that is, the protons and neutrons in the nucleus are not arranged in the lowest potential energy states possible. So, when the nucleus undergoes a rearrangement it happens in such a way that the excess energy is emitted and the nucleus gets transformed to an atom of a new element. The number of disintegrations per unit time, which is referred to as the decay rate, is proportional to the number of radioactive nuclei in the sample. This statement can be expressed mathematically as;

$$\frac{dN}{dt} = -\lambda N, \qquad (2)$$

where; - N is the number of radioactive nuclei in the sample

- λ is called the decay constant, which is the probability per unit time that a given radioactive nucleus will decay.

- λ = decay constant = $\frac{\ln 2}{T_{1/2}} = \frac{0.693}{T_{1/2}}$

- $T_{1/2}$ is known as the half-life of the radionuclide, which is the time it takes for a radionuclide to decay to half its initial activity.

- Activity = $^{decays}/_{time} = -\frac{dN}{dt} = \lambda N$

For purposes of this mini-dissertation, three decay mechanisms will be discussed in detail; alpha decay, beta decay (beta minus, beta plus and electron capture) and gamma emission.

3.2.1 Alpha Decay

Alpha decay occurs when the parent nucleus emits an alpha particle. It occurs almost exclusively to heavy nuclei($Z > 83$). An alpha particle is actually a helium nucleus which is made up of two protons and two neutrons (^{4}He). Therefore, the resultant daughter product (from an alpha decay) is four (4) mass units lighter and two (2) fewer units of electric charge (CPEP, 2003). Since the atomic numbers of the parent and daughter nuclei change (not the same), they are therefore different elements and as such will have different chemical properties (Mehta, 2005). These particles can damage human cells if they are

exposed to them directly considering their high energies. Direct exposure to these alpha particles can be achieved through ingestion. An alpha particle can be easily stopped by even the top layer of a human skin. Equation (3) shows the release of an alpha particle.

$$^{A}_{Z}X \rightarrow {}^{A-4}_{Z-2}Y + {}^{4}_{2}\alpha, \quad (3)$$

where; - X is the parent nuclide

- Y is the daughter nuclide

- α is the alpha particle

- A is the mass number (number of proton + neutrons)

- Z is the atomic number

3.2.2 Beta Decay

Beta decay can be either through the emission of a β^- particle, β^+ particle or electron capture. Therefore, a beta particle can either be an electron or a positron, which travels at very high speeds as it gets emitted or ejected by the decaying radionuclide. The beta particles have energies less than those of alpha particles. Their energies range from 5 keV to 4000 keV and are smaller in size, compared to an alpha particle, since it is just an electron or positron but have a large range when travelling through a material (Mehta, 2005). This property of beta particles enables them to penetrate the skin of a human being.

3.2.2.1 β^- Emission

A beta minus emission occurs when the unstable isotope has an excess number of neutrons to that of protons in the nucleus, so it then produces negatrons (electron) to be in a more stable state. In such a case, the excess neutron(s) is transformed into a proton (which stays inside the nucleus) and the electron is emitted as the negatron (β^-) and an antineutrino. The antineutrino has no charge and mass (Mehta, 2005; Martins, 2006). This process is summarized in equation (4).

$$^{A}_{Z}X \rightarrow {}_{Z+1}{}^{A}Y + \beta^- + \bar{\nu}, \quad (4)$$

where; - X is the parent nuclide

-Y is the daughter nuclide

- β^- is the emitted electron

- $\bar{\nu}$ is the antineutrino

- A is the mass number and Z is the number of protons.

3.2.2.2 β^+ Emission

A beta positive emission occurs when the unstable isotope has an excess number of protons to that of neutrons in the nucleus, so it then produces a positron (positive electron) to be in a more stable state. In such a case, the excess proton is transformed into a neutron (which stays inside the nucleus) and the electron is emitted as the positron and a neutrino (Mehta, 2005; Martins, 2006) as presented in equation (5).

$$p \rightarrow n + \beta^+ + \nu, \tag{5}$$

where; - p is proton

- n is the neutron produced

- β^+ is the positron emitted

- ν is the neutrino

3.2.2.3 Electron Capture

Electron capture is another way in which a nucleus rich in protons gets to reduce the number of protons so as to attain stability. During electron capture, an electron from the innermost orbit (90% of the time it is from the K-shell) is absorbed and this results in one of the protons being converted into a neutron. This process is accompanied by the emission of an X-ray which is characteristic of the product nuclide as shown in equation (6) (Mehta, 2005; Martins, 2006)

$$e^- + p \rightarrow n + \nu, \tag{6}$$

3.2.3 Gamma Emission

A gamma ray is emitted by a nucleus which decays rapidly to ground state from an excited state. This process (gamma emission) often occurs after either an alpha decay or beta decay has taken place (CPEP, 2003). During a gamma emission the number of protons and neutrons in the nucleus does not change thus the parent and daughter have the same

number of protons and same mass number. Gamma rays travel at the speed of light when they are emitted from a decaying radionuclide. They occur in the form of photons. Gamma radiation is in actual fact electromagnetic radiation (Sang, 1992). Gamma rays have discreet energies, frequency and wavelength and these three are related through equation (7);

$$E = hf = hc/\lambda\,, \qquad (7)$$

where; - E = energy

- h = Planck's constant

- f = frequency of gamma radiation

- c =speed of light

- λ = wavelength

An example of a gamma emission by an excited atom of ^{22}Na is given in Figure 5.

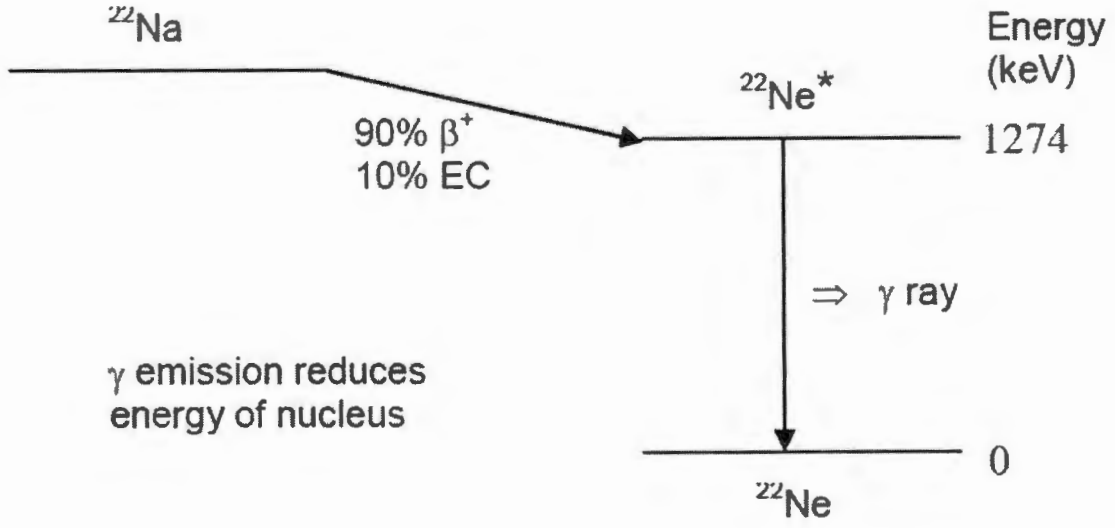

Figure 5: Example of a gamma emission by an excited atom of ^{22}Na (Sang, 1992)

The gamma particles have no charge and no mass but they are the most penetrating of the three (Sang, 1992).

The penetration ability of alpha, beta particles and gamma ray can be summarized by Figure 6.

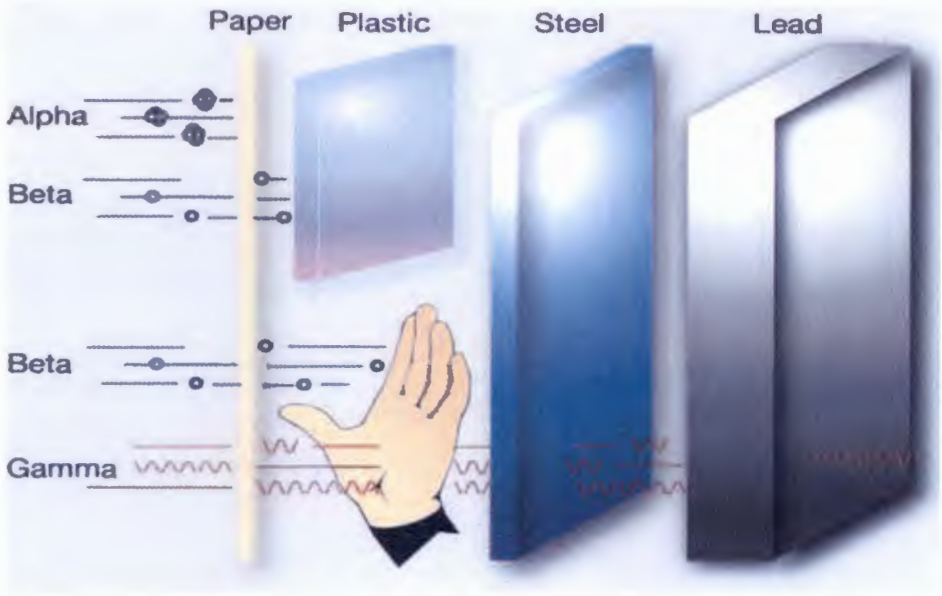

Figure 6: Penetration power of alpha and beta particles, and gamma ray (IAEA, 2008)

3.3 Decay Chains

Section 3.2 gives an introduction to radionuclide decay. Most NORMs decay through a series of transformations. During these transformations, the radionuclide gives off or emits some energy or particles and as a result it becomes other nuclides (Saqan et al., 2001). The nuclide that decays is referred to as the parent and the resultant new nuclide that the parent decays to, is referred to as the daughter nuclide. These series of transformations continue as long as the resultant nuclide is unstable until a stable nuclide is reached. There are three major transformation series: Uranium series, Actinium series and Thorium series and they are listed in appendix 1. These series form what is called the decay chain of the NORM parent radionuclide.

3.4 Dose Measurement and Calculation

Ionizing radiation has varying effects on matter depending on (among other things); the type of ionizing radiation, amount of energy being deposited and target matter. Unfortunately, ionizing radiation cannot be detected directly through human senses. Appropriate technology (detectors, radiation meters, gauges, etc.) is used for direct

measurement of the energy that the radiation concerned deposited in that particular part of body or organ. Another alternative is to calculate the dose absorbed by the organ (Martins, 2006).

3.4.1 Absorbed Dose

Absorbed dose is defined in the IAEA Safety Standards Series No. GSR Part 3 (2011) as the average amount of radiation energy imparted to or absorbed by an organ or body. Absorbed dose helps relate the radiation energy absorbed to the extent of radiation damage. The absorbed dose can be evaluated in one of two ways:

1. Through direct measurement
2. Through performing calculations

Absorbed dose, D, can be expressed mathematically through equation (8);

$$D = \frac{d\bar{E}}{dm}, \tag{8}$$

where; - $d\bar{E}$ is the mean energy imparted by ionizing radiation to matter,

- dm is the mass of matter contained in infinitesimal volume.

The SI unit for absorbed dose is joule per kg and is referred to as the gray (Gy).

3.4.2 Equivalent Dose

The extent of radiation damage to tissue or organ depends on a number of factors which include;

- The source of the radiation energy or the type of ionizing radiation,
- The distance between the source and the organ receiving the dose,
- The organ absorbing the radiation energy.

Equivalent dose is a radiation protection quantity that takes into account (consideration) all the above listed (in the bullets) factors together with the absorbed dose. Of note is that, for the same absorbed dose, the effects are more likely and more severe in some tissues than in other parts of the human body, and some radiation is more severely damaging than other ionizing photons. The weighting factors are introduced as a way of taking into consideration the varying effects of radiation on different tissues. The weighting factors

help to improve the relationship between the dose quantities applied in radiation protection and the effects. The two weighting factors are the tissue weighting factor and the radiation weighting factor (ICRP, 2007).

Thus, equivalent dose in an organ or tissue, H_T, is given in equation (9) as;

$$H_T = \sum_R w_R D_{T,R}, \quad (9)$$

where; - $D_{T,R}$ is the average absorbed dose deposited in organ or tissue T by ionizing radiation of type R

- w_R is the radiation weighting factor for ionizing radiation type R

- $\sum_R$ –means that the sum is performed over all types R of radiation involved

The radiation weighting factors for the different radiation types are given in Table3.

Table 3: Radiation weighting factors, w_R (ICRP, 2007)

Type of radiation and energy range	**w_R**
Photons	1
Electrons and muons	1
Protons	2
Alpha particles, fission fragments, heavy nuclei	20
Incident neutrons	For neutrons w_R is given by the function $w_R(E_n)$ which is shown in detail in equation 10 and Figure 7

$$w_R(E_n) = \begin{cases} 2.5 + 18.2 \exp\left[-\dfrac{\{\ln(E_n)\}^2}{6}\right] & \text{for } E_n < 1\ MeV \\ 5.0 + 17.0 \exp\left[-\dfrac{\{\ln(2E_n)\}^2}{6}\right] & \text{for } 1\ \text{MeV} \le E_n \le 50\ \text{MeV}, \\ 2.5 + 3.25 \exp\left[-\dfrac{\{\ln(0.04E_n)\}^2}{6}\right] & \text{for } E_n > 50\ MeV \end{cases} \quad (10)$$

Figure 7 shows the energy dependence of the radiation weighting factor for neutrons as it has been given ($w_R(E_n)$) in equation 10.

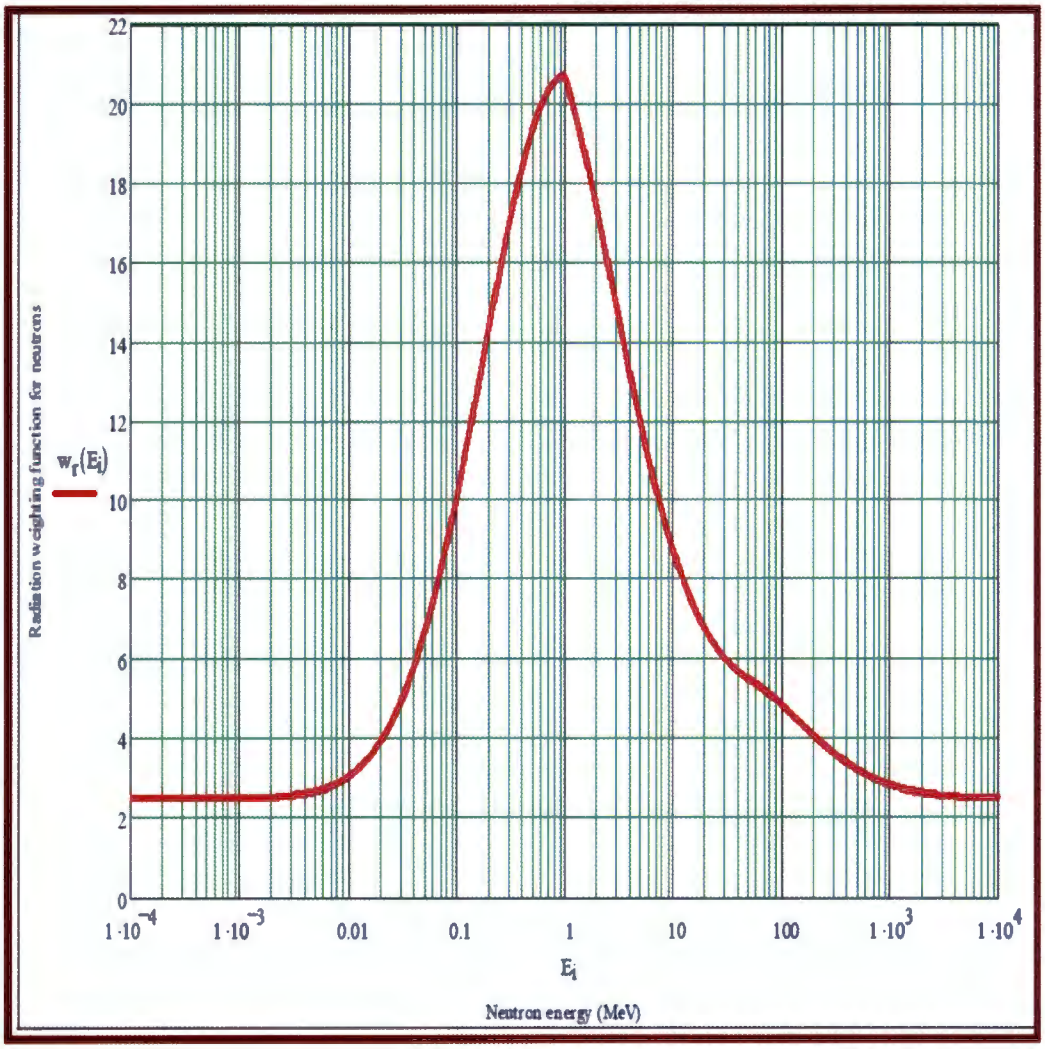

Figure 7: Plot of dependence of radiation weighting factor with energy for neutrons (ICRP, 2007)

3.4.3 Effective Dose

Effective dose is the quantity that is used when more than one tissue is exposed. It is applicable when one focuses on the risk of radiation-related cancer and when the dose rates are low. It is the summation of all the equivalent doses with each of them multiplied by the appropriate tissue weighting factor (Mehta, 2005).

Thus the effective dose, E, is defined mathematically in equation (11) as;

$$E = \sum_T [w_T H_T], \tag{11}$$

where; - H_T is the equivalent dose in organ or tissue T

- w_T is the tissue weighting factor

Using the definition of equivalent dose as given in earlier discussion above in equation (9) to substitute for H_T in equation (11) gives;

$$E = \sum_T w_T \left[\sum_R [w_R D_{T,R}]\right], \tag{12}$$

The values of the tissue weighting factors w_T, as prescribed in the Safety Standards series No. GSR part 3 (IAEA, 2011), are listed in Table 4.

Table 4: Tissue weighting factors (IAEA, 2011)

Tissue	w_T	$\sum_T w_T$
Bone marrow Breasts Colon Lung Stomach	0.12	0.60
Gonads	0.08	0.08
Bladder Esophagus Liver Thyroid	0.04	0.16
Bone surface Brain Salivary glands Skin	0.01	0.04
Summed value for 14 remaining tissues		0.12
total		1.00

3.5 Effects of Varying Levels of Dose to the Body

The South African National Nuclear Regulator (NNR) has set out a procedure to follow when assessing the safety of the public from exposure to radiation. The process is summarized through the following flow chart.

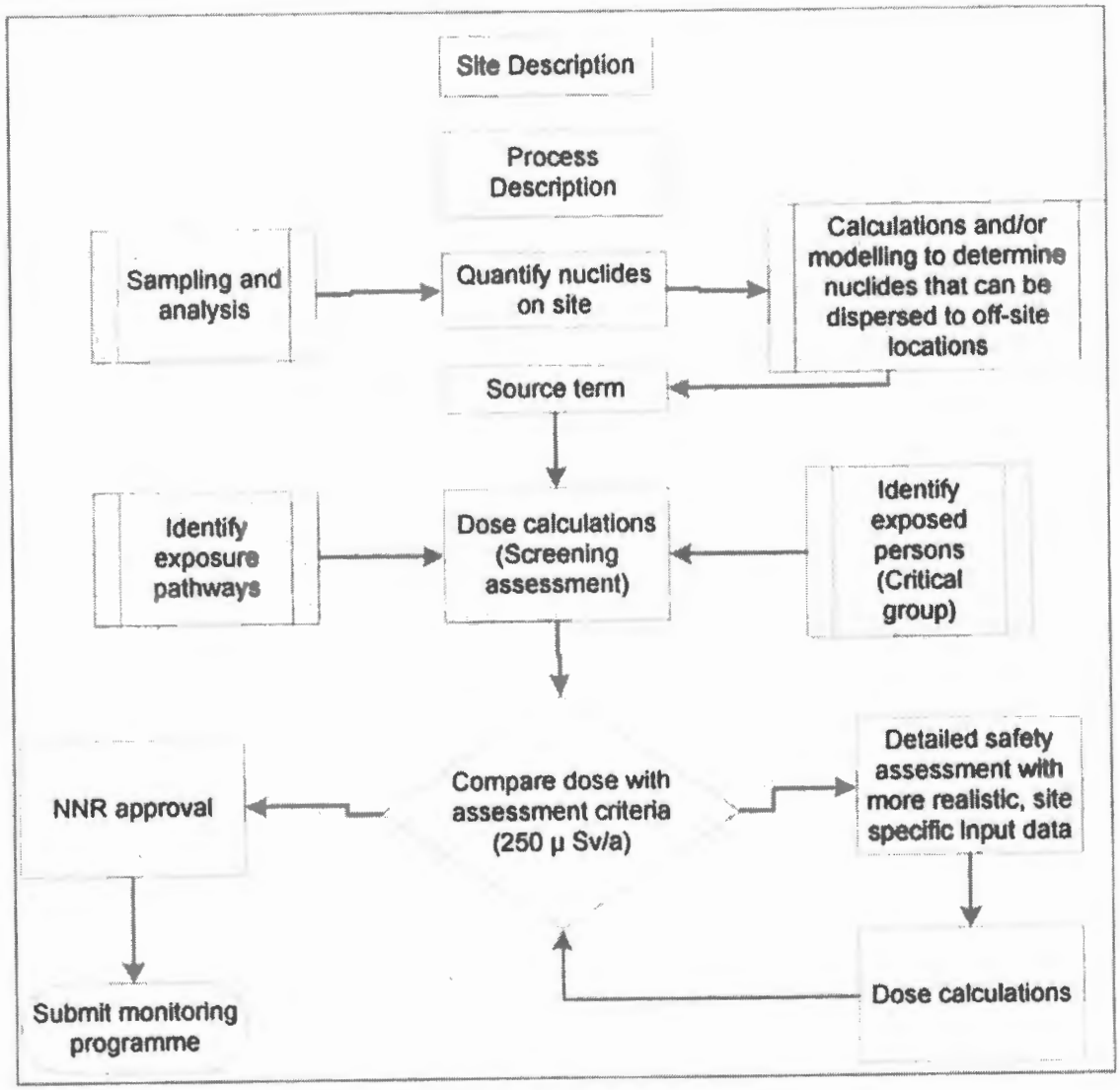

Figure 8: The public safety assessment process (NNR regulatory guide (RG-002))

Previously the South African Department of Water Affairs and Forestry (now South African Department of Water Affairs) (DWAF, 2002) gave a description and the effects of different dose levels to the body as presented in Table 5.

Table 5: Description and Effects of Different Doses and Dose Rates (DWAF, 2002)

Dose	*Description / Effects*
0.3 to 0.6 mSv/a	This is the typical range of dose rates from artificial sources of radiation, mostly medical.
0.2 to 0.8 mSv/a	This is the range of worldwide average annual radiation dose from ingestion of foodstuff and water. Variations about the mean values by factors 5 to 10 are not unusual for many components of exposure from natural sources.
2.4 mSv/a (approximately)	The normal average background radiation from natural sources. Approximately half of this exposure is from radon in air.
13 mSv/a	This is the highest known average annual dose from background radiation that occurs in the Kerala and Madras states in India where a population of over 100 000 people is exposed to this level.
20 mSv/a	This dose averaged over 5 years is the limit for regulated practices and working activities such as the nuclear industry employees and mining and mineral processing workers, who are closely monitored.
50 mSv/a	This dose is conservatively the lowest dose rate where there is any evidence of cancer being caused. It is also the dose rate that arises from natural background levels in several places. Above this, the probability of cancer occurrence (rather than the severity) increases with dose.

Dose	*Description / Effects*
100mSv	This dose accumulated over some time, would probably cause a fatal cancer many years later in 5 of every 100 persons exposed to it (i.e. if the normal incidence of fatal cancer were 25%, this dose would increase it to 30%).
1 000 mSv	This dose received as a short-term dose would probably cause (temporary) illness such as nausea and decreased white blood cell count, but not death. Above this dose the severity of illness increases with dose.
Between 2 000 and 10 000 mSv	This dose over a short-term would cause severe radiation sickness with increasing likelihood that this would be fatal.
≥10 000 mSv	This dose in a short-term dose would cause immediate illness and subsequent death within a few weeks.

3.6 Theory on Calculation of ^{238}U and ^{232}Th from Daughter Nuclides

If the parent has a very long half-life compared to its daughters in a decay chain, the activities of the natural radio isotopes can be measured and the concentration of the parent can be calculated from that of its daughters. In such a case, secular equilibrium is assumed.

3.6.1 Radioactive Equilibrium

Krane (1998) states that equilibrium in a decay series is said to be reached when the parent nuclide and its daughter(s) begin to decay at the same rate. The condition for equilibrium to be reached or achieved is that the half-life of the daughter nuclide should not be longer than the half-life of the parent nuclide. If the daughter has a longer half-life than

the parent, then equilibrium will not be reached (Krane, 1998). Three types of decay equilibrium are observed: secular equilibrium, transient equilibrium and no equilibrium.

3.6.1.1 No Equilibrium

If the daughter nuclide is longer lived than the parent nuclide, no equilibrium is reached. In this case the parent decays until it is negligible thus leaving the daughter nuclide to decay by its own half-life (L'Annunziata, 2012). This condition is expressed as;

$$\text{If } \lambda_{\text{parent}} > \lambda_{\text{daughter}} \quad \text{then no equilibrium is reached.}$$

The condition can alternatively be presented as;

$$\text{If } t_{1/2\,(\text{parent})} < t_{1/2(\text{daughter})}, \text{ then no equilibrium.}$$

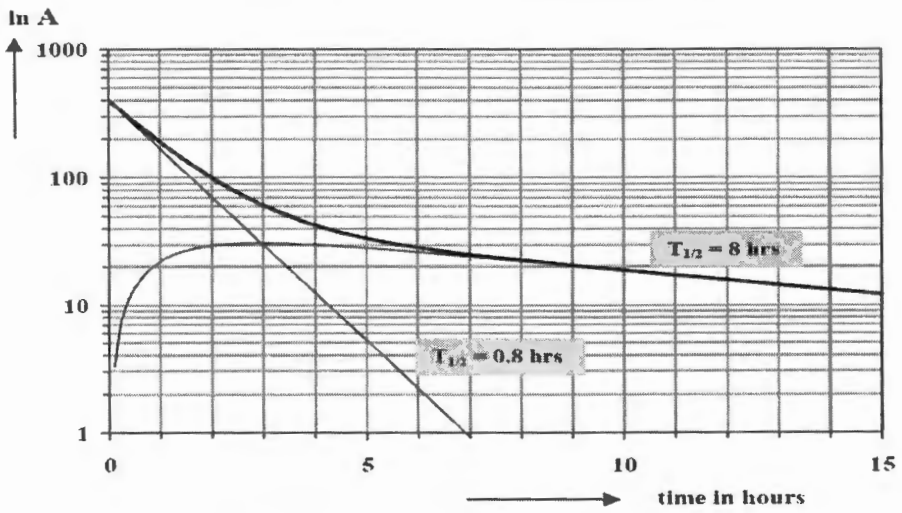

Figure 9: Plot of activity with time showing the condition where no equilibrium is reached (Krane, 1998)

3.6.1.2 Transient Equilibrium

The condition for transient equilibrium is that the parent should have a half-life greater than that of its daughter and the ratio of $\lambda_{\text{parent}}/\lambda_{\text{daughter}}$ should be within the range 10^{-4} and 1 (L'Annunziata, 2012).

Mathematically;

$$\lambda_{parent} < \lambda_{daughter} \quad \text{And} \quad 10^{-4} < \frac{\lambda_{parent}}{\lambda_{daughter}} < 1$$

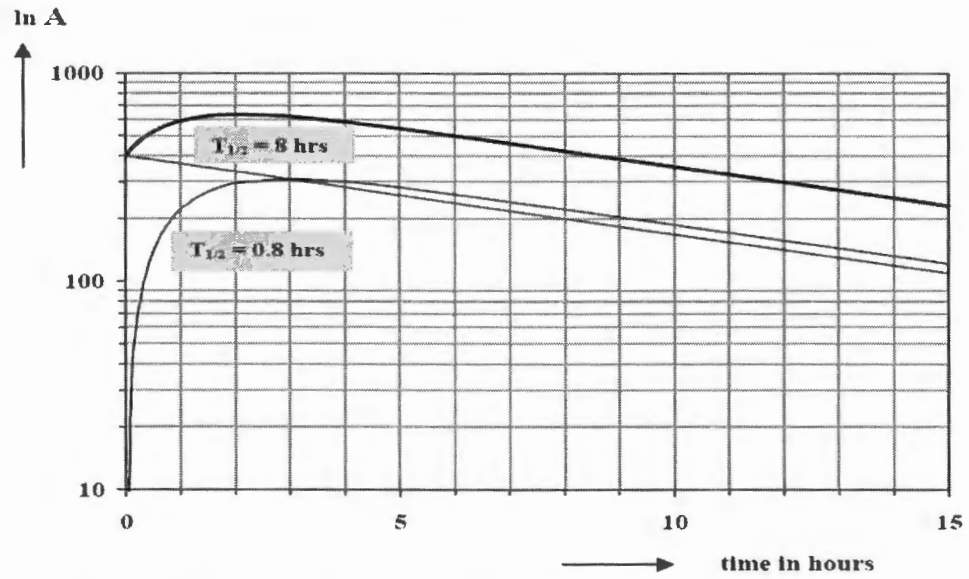

Figure 10: Plot of activity with time to show the transient equilibrium condition
(Krane, 1998)

3.6.1.3 Secular Equilibrium

Secular equilibrium is a steady state condition whereby the parent nuclide and its daughter have equal activities. The parent is long-lived while the daughter is short-lived. For secular equilibrium to be assumed, the ratio of $\lambda_{parent}/\lambda_{daughter}$ should be less or equal to 10^{-4}. This means that $\lambda_{parent} \ll \lambda_{daughter}$.

Therefore, to calculate the concentration of the parent, equation (13) is used (Saqan et al, 2001).

$$N_p\lambda_p = N_d\lambda_d, \qquad (13)$$

where; - N_p and λ_p are the number of atoms in a given sample and the decay constant of the parent, respectively.

- N_d and λ_d are the number of atoms in the same sample and the decay constant of the daughter, respectively.

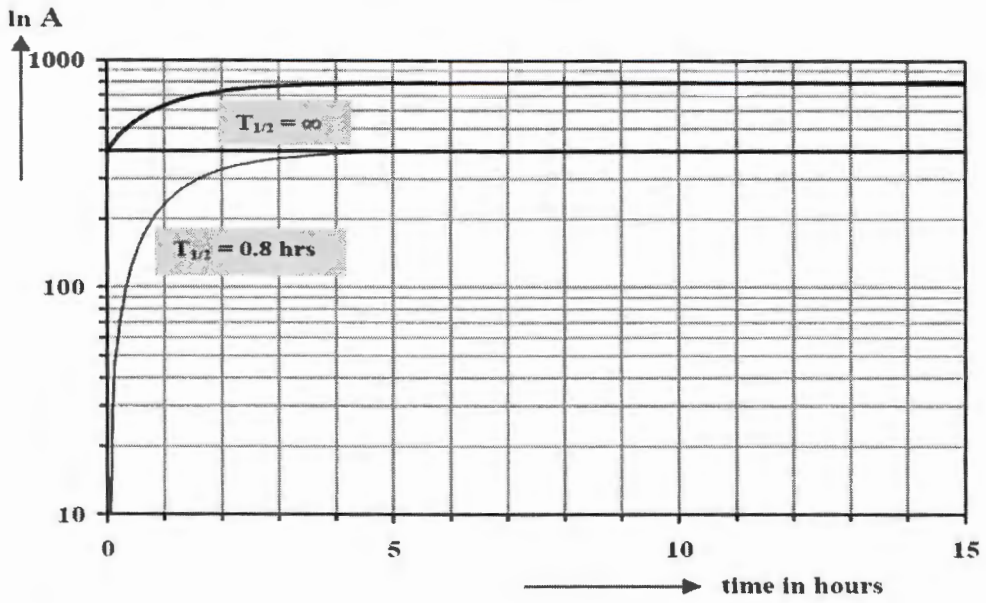

Figure 11: Plot of activity with time showing secular equilibrium being reached (Krane, 1998)

Ngigi (2009) states that it is difficult to directly measure ^{238}U concentration levels using its gamma line at 49.5 keV. However, if it is in secular equilibrium with its daughters the gamma lines of its daughters can be used. For example, the 63.3keV gamma line and the 92.6keV doublet gamma line of ^{234}Th and the ^{234m}Pa gamma line at 766.4 keV can be used to calculate the concentration of the parent ^{238}U (Saidou et al, 2008).

3.7 Measurement of Radioactivity

When radiation interacts with matter there are a number of effects that are observed or that accompany that particular interaction (Knoll, 1999). These effects can include, among others, emission of photons, charged particles and heat. The instruments used to measure or detect the amount of radioactivity make use of this property of effects during interaction with matter and radiation can be detected, intensity can also be measured and radiation spectra can be obtained (Knoll, 1999). Different types of detectors can be characterized by the nature of the interaction of radiation with matter.

3.7.1 Classification of Detectors Used to Measure Radiation

A lot of studies have been done in identifying radionuclides either in dust, soil, water and/or vegetation all over the world. Different studies use different equipment depending on availability of equipment and aim of that particular study.

Different authors have come up with many different ways of categorizing detectors used to measure radiation and they base them on many different characteristics. However, in our discussion we shall use the classification of NUREG-1575 (NUREG-1575, 2009) who came up with three classes for the many different kinds of detectors out there. The three types are: Gas-Filled Detectors, Scintillation Detectors and Solid State Detectors.

3.7.1.1Scintillation Detectors

These detectors are based upon the use of various phosphors (scintillators) which emit light in proportion to the quantity and energy of the radiation they absorb. Different scintillation materials are used to detect different types of radiation. These materials include: NaI(Tl), CsI(Tl) crystals, plastics, or liquids. Thallium-activated sodium iodide (NaI (Tl)) is the most widely used inorganic scintillator (Knoll, 1999).

3.7.1.2Gas-Filled Detectors

Gas filled detectors have become the most commonly used detectors around the world and include gas- ionization chamber, gas-flow proportional, and Geiger-Muller (GM) (NUREG-1575, 2009). These detectors have been made or designed in such a way that they are able to detect alpha, beta, photon and neutron radiation.

3.7.1.3Solid State Detectors

Solid state detectors are often semi conducting devices which measure the conduction of electrons across an otherwise non conducting medium (Wiles, 2002). A crystal composed of an electron-rich sector and an electron-deficient sector is used. The solid state detector systems use silicon or germanium crystals together with semi-conductor technology. The crystal material's insulating properties help to prevent thermal generation of noise. To achieve these insulating properties, the semi-conductor detectors are cooled to extreme temperatures (NUREG-1575, 2009). For example, the HPGe detector is cooled with liquid nitrogen to –180 °C.

3.7.2 The High Purity Germanium Detector (HPGe)

The germanium semiconductor detectors were introduced in 1962 (Khandaker, 2011). These detectors are the best choice for high energy resolution gamma-ray spectrometry studies or measurements. Gamma ray spectrometry is based on the knowledge that each gamma ray photon has a discrete energy, and this energy is characteristic of the source isotope (IAEA, 2003). By measuring the energies of gamma ray photons, we can determine the source of the radiation.

A typical gamma spectrometry system consists of a Germanium (Ge) detector, liquid nitrogen or mechanical cooling system, preamplifier, detector bias supply, linear amplifier, analog-to-digital converter (ADC), multichannel storage of the spectrum, and data readout devices (www.ortec-online.com). HPGe detectors are made by highly refining the element germanium and growing it into a crystal. To increase the efficiency of the detector, it is housed within a shield which helps reduce radiation from the background. To construct the shield, a dense material which will be able to absorb a large portion of gamma ray background is used. Lead is usually the ideal material used to construct the shield. Ambient photons interact with the lead material to generate some X-rays. To counter the X-ray effect generated, the lead shielding material is graded with a two part thin metal shield such as tin and copper (www.ortec-online.com). Photons from the sample get emitted and they interact with the germanium crystal to produce a pulse. The amplitude of the pulse is proportional to the energy of the photon absorbed by the germanium.

Advantages of HPGe over Other Detectors for Gamma Ray Spectrometry

The HPGe has a very high resolving power compared to other detectors. For example, the HPGe has 20-30 times better resolution than sodium iodide (NaI) detectors (IAEA, 2003). Due to this very superior resolving power, HPGe provides sufficient information to accurately and reliably identify radionuclides from their passive gamma ray emissions without any chemical change or destruction of the sample (Busto et al., 2002). HPGe detectors are resistant to information (signal) degradation caused by changes in background radiation, shielding, multiple radionuclide interference, and temperature variations. It is also much more effective than NaI detectors in stand-off radionuclide identifications such as are encountered in vehicle or shipping container inspections.

3.7.3 The Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The ICP-MS is one of the most sensitive analytical techniques for elemental determination (Bosnak&Pruszkowski, 2008). The Inductively Coupled Plasma (ICP) source converts the atoms of the elements in the sample to ions. These ions are then separated and detected by the mass spectrometer. The advantages of the ICP-MS over other analytical methods are:

- it is able to provide us with isotopic ratios of a sample,
- detection limit for most of elements analyzed using ICP-MS is better, compared to Atomic Absorption Spectroscopy, for example.

3.7.4 Alpha Spectrometry

Alpha spectrometry is used in many different fields. For example, it is used for the investigation of groundwater, surface water and seawater processes through the measurement of uranium and radium isotopes. The energy of an alpha particle is related to the half-life of the parent nuclide; the highest alpha particle energies have the longest half-lives (Vajda et al., 2012). A short half-life implies a high decay constant due to the inverse relationship as earlier indicated in equation (2).

$t_{1/2} = \frac{\ln 2}{\lambda}$, where $t_{1/2}$ is the half life and λ is the decay constant.

Examples of this relationship can be seen in the radionuclide ^{212}Po which has a decay constant of 0.299 μs^{-1} and energy of 8784.37 keV and ^{213}Po with decay constant of 4.2 μs^{-1} and energy of 8375.9 keV. This relationship between the alpha particle energy and its half-life can be presented using an empirical equation which expresses a law that was recognized by Geiger-Nuttal in 1991 (Vajda et al., 2012). The equation is given in equation (14) as;

$$\log \lambda = A + B \log E_{\alpha}, \qquad (14)$$

where ; - λ is decay constant, as already mentioned

- E_{α} is the alpha particle energy

- A and B are constants

The advantages of alpha spectrometry are that it is a very sensitive technique since it has a very high counting efficiency yet at the same time has low intrinsic background. It also has quite a good range of radionuclides that can be identified using it. Lastly, it allows for different sample types to be analyzed. Its limitation is that the radionuclides that one is interested in need to be first separated from the matrix sample since alpha particles have a short range (Vajda et al., 2012).

3.8 Literature Search (on radioactivity and radionuclides in water and soil)

Al-Amir et al. (2012) investigated tap water that had been collected from highly populated areas in Amman and Aqaba in Jordan. The aim of the study was to assess potential public impact of radiation by measuring gross alpha and beta activity as well as uranium and radium radionuclides. Liquid scintillation counting was used to deduce the gross activities.

Ortega et al. (1996) studied natural radioactivity in drinking water in Catalonia, Spain. The study focused on gross alpha and beta emitted by ^{234}U, ^{235}U, ^{238}U, ^{226}Ra, ^{228}Ra, ^{230}Th, ^{232}Th, ^{210}Pb and ^{210}Po activity. Average concentration of the radionuclides ranged from 10 to 100mBq/ℓ. Some of the water samples showed a high degree of disequilibrium among the members of the uranium series. The ZnS scintillation counter was used for the gross alpha counting. Gross beta activity measured was mostly as a result of the presence of ^{40}K in the water samples.

Rangel et al. (2002) studied the radioactivity in bottled water in Mexico. A liquid scintillation detector was used to measure the gross alpha and beta activities. The bottled water investigated was both purified water and mineral water. All the samples of purified water had beta activity values lower than 1.0Bq/ℓ which is the beta activity limit for potable drinking water. Three water sample brands exceeded the alpha activity limit of < 0.1 mBq/ℓ.

Wallner et al. (2008) measured the activity concentrations of ^{228}Ra, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{238}U and ^{234}U in Austrian mineral water using liquid scintillation counting. The measured activities were then used to calculate the committed effective dose for adults and babies. The calculations (results) were then compared to the limit of 0.1 mSv/a given in the EC Drinking Water Directive. The highest committed effective dose for adults was found to be 0.02 mSv/a. For babies, the limit was exceeded by two mineral water brands while two other brands had doses very close to the indicative value.

Duenas et al. (1997) have studied the levels of natural radioactivity in spring waters in Spain. Bottled water from all over Spain was analyzed to determine the level of gross alpha and gross beta activities. An alpha/beta counter of low background multiple detector type with four gas-flow window counters about 5cm in diameter was used to do the gross alpha and gross beta measurements.

Santawamaitre et al. (2011) investigated the levels of naturally occurring radioactivity in surface soils along the Chao Phraya river basin in Thailand. A hyper pure germanium (HPGe) detector was used for gamma ray spectroscopy measurements. This study was aimed at investigating the activity concentrations of the radionudides in the ^{238}U and ^{232}Th decay chains and that of ^{40}K. Results obtained from gamma measurements indicated that ^{238}U activity concentration was in the range 55.3-65.2 Bq/kg, ^{232}Th had activity range of 60.7-69.1Bq/kg and ^{40}K had activity range of 393-478Bq/kg. These reported activity concentrations were found to be higher than the upper range of the world mean values identified by UNSCEAR (2000).

Mohanty et al. (2004) did a study of natural radioactivity and radiation exposure at Chhatrapur beach, India. The HPGe detector was used to measure the average activity concentrations of the radioactive radionuclides ^{232}Th, ^{238}U and ^{40}K. The activity concentrations for large samples measured for ^{232}Th, ^{238}U and ^{40}K were 2500±1850Bq/kg, 230±140Bq/kg and 120±35 Bq/kg, respectively. This showed that the beach was a high natural background radiation area.

Skipperud et al. (2013) did a study in the uranium mine in Taboshar and at Digmai tailings dump. The study was aimed at determining the environmental impact of radionuclides and trace elements in the mine and tailings dump. In addition to soil sample measurements, sampling of water, fish and vegetation was done to come up with a convincing conclusion of the environmental impact. Different samples were analyzed using a number of instruments which include; Inductively Coupled Plasma Mass Spectrometry, Liquid Scintillation Counting, HPGe Gamma Spectrometry, Alpha Spectrometry and Instrumental Neutron Activation Analysis.

Naicker et al. (2003) studied soil, surface and ground water at the Natalspruit stream and areas adjacent to it. Natalspruit is in the Witwatersrand region of South Africa which is

known for gold mining activities. The soil, taken within the mining district, was analyzed for toxic elements using the X-Ray Fluorescence and the water samples were analyzed using the Atomic Absorption Spectrophotometer. This study revealed that the area has high concentration levels of heavy metals.

Agbalagba et al. (2013) used gamma spectroscopy to determine the concentrations of naturally occurring radionuclides measured in hand dug wells, boreholes and river waters collected from three oil mineral leases (OML) 30, 58 & 61 oil and gas fields onshore of the Niger delta. The average activity concentrations of ^{226}Ra, ^{228}Ra and ^{40}K were found to be 8.9 $\pm$ 1.0Bq/ℓ, 8.1 $\pm$ 0.9Bq/ ℓ and 39.8 $\pm$ 3.3Bq/ ℓ, respectively for hand dug wells, 4.4 $\pm$ 0.8Bq/ ℓ,4.6 $\pm$ 0.5Bq/ ℓ and 28.5 $\pm$ 3.0Bq/ ℓ for borehole water, and 8.2 $\pm$ 1.0Bq/ ℓ, 6.7 $\pm$ 0.7Bq/ ℓ and 32.1 $\pm$ 3.5Bq/ ℓ for river water, respectively. These average activities were above the WHO permissible levels for hand dug wells, borehole water and river water (1.0, 0.1 and 10 Bq/ ℓ, respectively). The estimated committed effective dose due to intake of the sampled water for all the age groups was calculated and found to be higher than the maximum permissible limit set by the ICRPof 0.1mSv/yr. However, the hazard indices calculated were within the tolerable levels.

Kleinschmidt et al.(2011) conducted a survey of the radioactivity in groundwater in rural and remote communities in Queensland, Australia. The survey was aimed at providing a baseline of radiation exposure that may be impacted upon by exposure pathways associated with the supply, treatment, use and wastewater treatment of the resource.^{238}U, ^{226}Ra, ^{222}Rn, ^{228}Ra, ^{224}Ra and ^{40}K were measured and found to contain activity concentration levels of up to 0.71 Bq/ ℓ, 0.96 Bq/ ℓ, 108 Bq/ ℓ, 2.8 Bq/ ℓ, 0.11 Bq/ ℓ and 0.19 Bq/ ℓ, respectively. In this survey it was recommended that further research needed to be carried out so as to assess the potential radiation exposures other than that due to the ingestion of water.

El-Mageed et al.(2013) studied the natural radioactivity of ground and hot spring water in some areas of Yemen.Ground water samples were taken from Assalamia-Alhomira and Juban areas while hot spring water was sampled at Dempt area. In their study, analysis was done so as to determine the concentration of ^{226}Ra, ^{232}Th and ^{40}K. Ground water samples from Juban area had average activity concentrations of 2.95 Bq/ℓ, 0.72 Bq/ℓ and 34.9 Bq/ℓ for ^{226}Ra, ^{232}Th and ^{40}K, respectively. Ground water from Assalamia-Alhomira

had undetectable levels of ^{40}K, 4.04 Bq/ℓ and 1.81 Bq/ℓ for ^{226}Ra and ^{232}Th, respectively. The conclusion made from the study was that the results obtained after calculations of annual effective dose equivalent were higher than the WHO recommended limit for drinking water.

In Croatia, Rozmaric et al. (2012) investigated bottled drinking water (spring and mineral) for the availability and activity concentrations of radionuclides and also determined their contribution to radiation dose. The radionuclides of interest in the study were ^{234}U, ^{238}U, ^{226}Ra, ^{228}Ra, ^{210}Po and ^{210}Pb. The activity concentrations were used to calculate the average total annual effective ingestion doses for the different age groups (infants, children, and adults). The results obtained were compared with the European Commission recommendations and found to be below the reference dose level.

Natural radionuclides in drinking waters in Serbia have been investigated by Jankovic et al. (2012). They measured the gross alpha and beta activities and ^{3}H, ^{226}Ra, ^{232}Th and ^{40}K activities in bottled mineral water that is produced locally in Serbia. Results showed that the activity of ^{226}Ra, ^{232}Th and ^{40}K were below the minimum detectable activity. The ^{3}H concentration in the bottled water ranged from 0.023 ± 0.012 to 0.046 ± 0.006 Bq/ℓ. All the alpha and beta emitting radionuclides had natural activities within the range recommended by the World Health Organisation.

Clulow et al. (1998) conducted a study in Canada whereby they measured the activity concentration of radionuclides in water, sediments and fish tissues. Sampling was done from four lakes in watershed affected by uranium mining and milling operations at Elliot Lake. Radionuclides of interest were ^{210}Pb, ^{210}Po, ^{230}Th and ^{232}Th. From the study, the lakes Quirke, McCarthy, McCabe and Whiskey had higher concentrations of radionuclides than Elliot.

Arogunjo et al. (2009) have investigated Uranium and Thorium levels in soils, mineral sands, water and food samples in a tin mining area in Nigeria with elevated activity. High-purity germanium detectors (HPGe) were used in the determination of the concentrations in soil and mineral sands. To determine uranium and thorium in liquids and foodstuffs consumed locally in the mining area, the high resolution sector field inductively coupled plasma mass spectroscopy (HR-SF-ICP-MS) was used. The activities of uranium and

thorium measured in the soils and mineral sands from Bisichi ranged from 8.7 kBq/kg to 51 kBq/kg for ^{238}U and from 16.8 kBq/kg to 98 kBq/kg for ^{232}Th, respectively. The results obtained from the study revealed the pollution potential of the mining activities to the surrounding areas. This is because the activity concentrations of uranium and thorium were found to be higher when compared to that of areas in Nigeria which were used as controls. These values were also higher than the values reported in literature for areas with very high natural background levels.

Ryan et al. (2008) inspected the old Rockhole Mine area in Kakadu National Park to determine if there was an amount of tailings from the former South Alligator uranium (U) mill being uncovered by wet season rain and road works. Sediment, water and freshwater mussels' samples were collected from the South Alligator River, near and at the confluence of Rockhole Mine Creek, and next to the exposed tailings. Radionuclide activities and isotopic ratios were determined by alpha and/or gamma spectrometry. For ^{238}U, ICP-MS was used together with a conversion factor of 1Bq of ^{238}U = 80.962 µg of natural Uranium.

Salbu et al. (2013) assessed the environmental impact of radionuclides and trace elements associated with the Kurday mining site in Kazakhstan. Sampling included, at site fractionation of water, as well as sampling of water, fish, sediment, soils and vegetation. The results obtained showed that the concentrations of uranium and associated trace metals were enriched in the Pit Lake and in the artesian water. However, the concentrations decreased downstream away from the mining area. From the results obtained in the study it was concluded that measures such as restricted access to the Pit Lake as well as dietary restrictions with respect to drinking water and intake of fish should be taken to reduce the environmental exposure risk.

Lind et al. (2013) determined the environmental impact of radionuclide and metal contamination at the former uranium site in KadjiSai, Kyrgyzstan. The study was carried out over a period of two years (2007 and 2008). To assess the environmental impact of these radionuclides and metals, gamma and radon dose rates were measured, and samples were taken from vegetation, sediments and soils, water and fish. The results obtained indicated that water from the Issyk-Kul Lake had generally low concentrations of radionuclides and trace elements but the concentration of arsenic (As) was found to be

surprisingly very high. Within the KadjiSai area, the concentration of uranium in water was found to be within the WHO recommended limits for drinking water. Studies carried out on the fish, indicated that there was an uptake of uranium and arsenic by the fish. The overall conclusion made from the investigation was that the results showed low radiological risk and no detrimental health effects or impact to the public residing within the area.

Tripathi et al. (2008) did an assessment of environmental radioactivity at mining, processing and tailings management facility at Jaduguja, India. These uranium mines at Jaduguja supply fuel to nuclear power plants. For their study, grab water samples were collected from nearby rivers while ground water was collected from wells and boreholes near the tailings ponds and areas away from the tailings ponds. About 1 kg of soil samples were also taken for analysis. Results obtained from this study indicated that in surface water, the concentrations of natural uranium and ^{226}Ra varied from 0.3 – 54.9 µg/ℓ and 5 – 283 mBq/ℓ, respectively. Ground water sources in the vicinity of the tailings ponds had uranium and ^{226}Ra concentration levels similar to the regional average of 3.6 µg/ℓ and 23 mBq/ℓ, respectively. Analysis of the ground water away from the tailings ponds revealed that there was no transfer of radionuclides from the tailings ponds to the ground water.

The Beatrice Gold Belt in Zimbabwe started its operation in 1900 and was in operation (mined for gold) until it was abandoned towards the year 2000. The belt has four mines; Beatrice, Joyce, Argyle and Roma. The mines are all located under 5 km from the Mupfure River, therefore run-off from the mines ad their dumps can easily reach the main river system. Ravengai et al. (2005) investigated the water quality in the abandoned gold mining belt of Beatrice. The surface water showed slight contamination with respect to Pb, Zn and Ni. This contamination was attributed to the mine dumps. Conclusion made from the study was that for now the low contamination could indicate that the acid mine drainage was proceeding at a slow rate or that it is still in its initial stages.

Lindsay et al. (2004) proposed the use of a mobile gamma ray detector (Solid state detector: NaI (Tl) to quantitatively assess the flux of radon from large mine dumps at the gold mines in South Africa. This method was proposed as a solution to the problem encountered when determining radon fluxes. Analysis of soil samples from mine dumps using gamma ray spectrometry indicates that 30% of the formed radon may escape resulting in the ^{238}U decay series secular equilibrium being disturbed.

Ngigi (2009) did a study at the Princess mine dump. The aim of the study was to identify an effective, appropriate and applicable technologies to treat the contaminated surface water from the Princess dump. To come up with such technology there was need to first investigate the water so as to assess the extent of water pollution attributed to the dump. Sampling was done at selected areas around the mine dump and the chemical analysis was performed on the data to ascertain if the quality concentration of the water from the mine dump was within the Target Water Quality Range (TWQR) as determined by the Department of Water Affairs (Ngigi, 2009). Results obtained indicated that pollution from the mine dump was seriously affecting the water quality in the environment around the site.

Fayazi (2005) did a water quality survey around the Princess mine dump with the aim of determining the dump's negative effects on the water resources. The main focus of this study was on the sulphate (SO_4) concentration, hydrogen ion concentration (pH), Iron (Fe) concentration and selected trace elements (Cd, Cr, Co, Cu, Pb, Mn, Ni, Zn, and Al). The sulphate concentration in surface water analyzed was higher compared to that of ground water investigated. The oxidation of pyrite which was found in the mine dump increased the sulphate concentration.

Though a number of studies have been carried out around the world on radioactivity and radionuclides in water and in soil, few studies have been reported in literature that have been done in South Africa. Studies that have been done at the Princess mine dump in Roodepoort (by Ngigi and Fayazi) have focused mainly on the quality of the water in that area and solutions for the water pollution. Ngigi and Fayazi did not go to the extent of measuring uranium and thorium concentrations in the water and compare them to the concentrations in the soil so as to determine the transfer factors. Therefore, this project's main aim was to identify and determine the transfer of radionuclides and toxic elements from the Princess mine dump to water in the Roodepoort area, South Africa and determine the potential radiological and toxicological impact on humans.

CHAPTER 4: METHODS OF INVESTIGATION

This section gives a detailed description of the sampling points that were selected, the sample preparation procedures and how the data was acquired using different equipment available at the labs.

4.1 Sampling

Figure 12: Map showing the sampling points around the dump marked with yellow pins and red alphabets

4.1.1 Soil Sampling

Sampling points were marked using a GPS in and around the area and were denoted with letters from A to Z as shown by the yellow pins in Figure 12. Soil samples from the ground were taken at different depths. The soil samples that were taken from the top soil (15 cm) were labeled with suffix 1; for example A1 means top soil taken at GPS point A. Those taken from the bottom, which is 100 cm below the top soil, were labeled with suffix 2.For

example; A2 means a sample taken 100 cm below at GPS point A. The soil samples were packaged in sturdy plastic sample bags and labeled accordingly with a permanent marker.

4.1.2 Water Sampling

Water sampling was done twice; once during the dry season and also during the rainy season. Water samples were collected right at the dump and along the stream (after the drainage pipe), before it joins other water sources. Figure 13 shows the water at the dump and just before it goes into the drainage pipe that travels underground from the mine dump. This choice of sampling was done so as to allow the researchers to consider the dump as the only source of pollution. During the dry season, three sampling points were chosen and marked A1004, Z1004 and Z1005. During the wet season, six water sampling points were chosen and marked as A, C, E, Z1, Z2 and Zm as can be seen in Figure 12 with points A, Z1 and Z2 being the exact sampling points as A1004, Z1004 and Z1005, respectively. The GPS coordinates are given in appendix 6.

Figure 13: One of the water sampling points which is the entrance to the drainage pipe from the mine dump.

4.2 Sample Preparation

4.2.1 Gamma Spectroscopy

The collected soil samples were fine silt and thus did not need any grinding. About 250 g of soil was then put in plastic bottles and sealed for over 20 days to ensure equilibrium between ^{226}Ra and its daughter nuclides was reached. The soil samples were weighed using an analytical scale. The same procedure was repeated for some samples but with the soil sealed in marinelli beakers for comparison.

4.2.2 Mass Spectroscopy

The soil samples were digested using Aqua regia method (Chen&Ma, 2001) where 1 gram of soil sample was weighed into a microwave sample holders then 3ml of industrial nitric acid followed by 9 ml of industrial hydrochloric acid was added. All the samples were then put in a multiwave 3000, Anton paar microwave oven, manufactured by Perkin Elmer for digestion. The samples were then emptied into 100 ml volumetric flasks and filled to the mark using distilled water and left over night. The following day, the samples were filtered and were ready for ICP-MS measurement.

The water samples were collected and filtered into sample bottles and 1.25 ml nitric acid was added per liter of sample at pH2 to avoid the adsorption of radionuclides on the walls of the sample bottle (Montana et al., 2013). The water bottles were then kept in a refrigerator.

For digestion purposes a pipette was used to measure out 5 ml of water collected during the rainy season into the sample holders then 1 ml of nitric acid followed by 3 ml of hydrochloric acid was added. Digestion was done in the microwave and the process repeated as for the soil samples.

4.2.3 Alpha Spectrometry

To obtain the first order estimate of the total activity, the water samples collected during the dry season were screened for gross alpha/beta activity.

The following separation techniques were used to prepare the different radionuclides for analysis using alpha spectrometer.

Uranium radionuclides: ^{238}U, ^{234}U and ^{235}U

The solid phase extraction was used to first extract the radionuclides from the water. A cation exchange resin was used for further extraction before analyzing with alpha spectrometer. The water sample, 200 ml in volume, was acidified with HNO_3 and pre-concentrated to a volume of 10 ml. This pre-concentrated sample was loaded on a pre-conditioned Truspec resin. Dilute HNO_3 and dilute hydrochloric acid were used to rinse the sample after loading it on the resin. The first eluent was obtained after the analytes had been eluted with 15 ml of 0.1 M hydrochloric acid /0.01 M hydrofluoric acid. The eluent was then loaded on a pre-conditioned cation exchange resin for purification. Before eluting with 15 ml of 2 M hydrochloric acid to make the second eluent, 10 ml of 0.1 M hydrochloric acid/0.01 M hydrofluoric acid was used to rinse the eluent. A volume of 0.1 ml of lanthanum oxide, 0.5 ml concentrated hydrofluoric acid and titanium chloride were added to the second eluent for the formation of a co-precipitate of uranium and lanthanum fluoride precipitate. A filter paper was then used to filter out the precipitate. The filtrate was then dried and analyzed using an alpha spectrometer.

A ^{232}U tracer was used to evaluate the extraction yield of this method.

Thorium radionuclides: ^{230}Th, ^{227}Th and ^{228}Th

Like with the uranium radionuclides, the solid phase extraction was used to first extract the thorium radionudides from the water. A cation exchange resin was used for further extraction before analyzing with alpha spectrometer.

The water sample, 200 ml in volume, was acidified with HNO_3 and then pre-concentrated to a volume of 10 ml. This pre-concentrated sample was loaded on a pre-conditioned Truspec resin. Dilute HNO_3 and dilute hydrochloric acid were used to rinse the sample after loading it on the resin. The first eluent was obtained after the analytes had been eluted with 15 ml of 2 M hydrochloric acid. The eluent was then loaded on a pre-conditioned cation exchange resin for purification. Before eluting with 15 ml of 2 M H_2SO_4 to make the second eluent10 ml of 0.1 M hydrochloric acid /0.01 M hydrofluoric acid was used to rinse the eluent. A volume of 0.1 ml of lanthanum oxide, 0.5 ml concentrated hydrofluoric acid were added to the second eluent for the formation of a co-precipitate of thorium and lanthanum fluoride precipitate. A filter paper was then used to filter out the precipitate. The filtrate was then dried and analyzed using an alpha spectrometer.

A ^{229}Th tracer was used to evaluate the extraction yield of this method.

Radium radionuclides: ^{226}Ra, ^{223}Ra and ^{224}Ra

Barium solution was added into 500 ml of water sample to extract the radium radionuclides. The extraction of the radium radionuclides was through co-precipitation with Barium sulphate in an acidic solution. To enhance precipitation, 0.1 M Ethylenediaminetetraacetic acid (EDTA) was added into the solution. The extract was analyzed using an alpha spectrometer.

A ^{133}Ba tracer was used to evaluate the extraction yield of this method.

Polonium radionuclide: ^{210}Po

The water sample, 200 ml in volume, was acidified with dilute hydrochloric acid. To prevent the co-precipitation of polonium with iron, ascorbic acid was added as a reducing agent. A silver disk was dropped into the solution to enhance the polonium being deposited spontaneously on to the surface of the silver disk. The solution was stirred for 4 hours to enhance the deposition of polonium onto the silver disk. The disk was then removed and dried before it was analyzed for polonium using an alpha spectrometer.

4.3 Sample Data Acquisition

To acquire data from the samples collected, three instruments were used; the High Purity Germanium Detector {resolution (FWHM) at 122 keV (^{57}Co) is 0.85 keV and at 1332.5 keV (^{60}Co) is 1.86 keV and relative efficiency for energy 1.33 MeV relative to (NaI) Tl is 36%}, the Inductively Coupled Plasma Mass Spectrometer and the alpha spectrometer.

4.3.1 Soil Samples

For the measurement of the radioactivity in the soil samples, a Portable Detection Unit based on HPGe Coaxial Detector (Baltic Scientific Instruments GCD-35190) was used to measure the gammas emitted by the radionuclides present in the soil.

4.3.2 Water Samples

4.3.2.1 Alpha Spectrometry

The dry season water samples were screened for gross alpha/beta activity using a gas proportional counter. Selected radionuclides in the uranium and thorium series (discussed under sample preparation) were analyzed for, using alpha spectrometry.

4.3.2.2 ICP-MS

The rainy season water samples were run using the NexION 300Q (Perkin Elmer) ICP-MS. Figure 14 is a picture taken at the lab at Animal Health at North-West University in Mafikeng where the analysis was done.

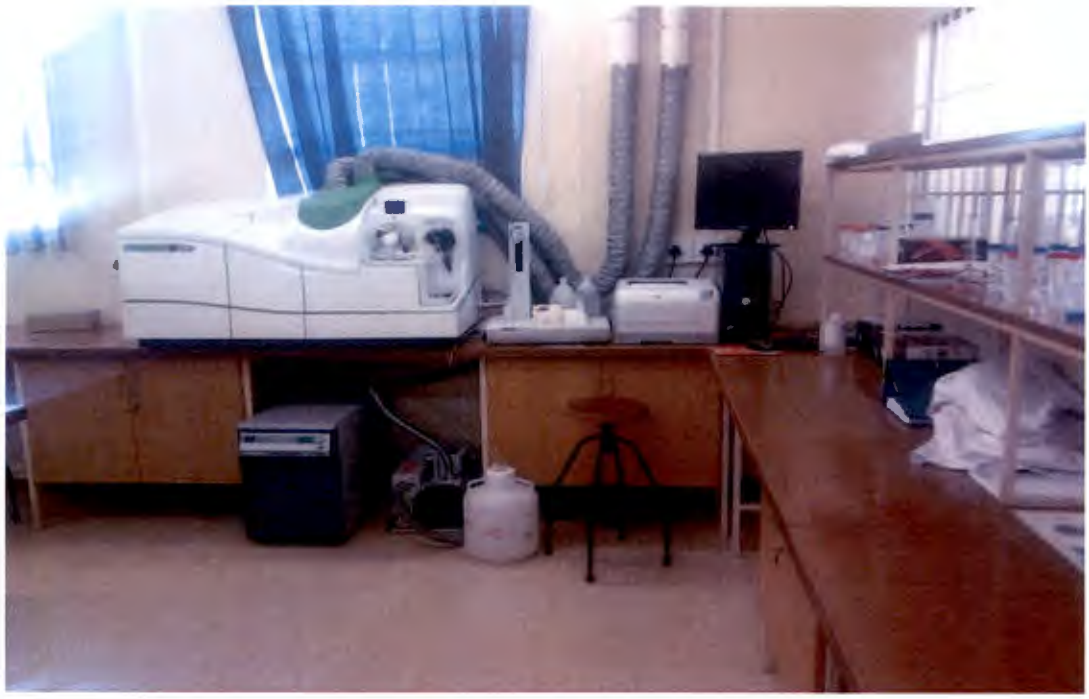

Figure 14: NexION 300Q ICP-MS (Perkin Elmer) used for the water analysis

4.4 Sample Data Analysis

The data obtained from gamma spectrometry was analyzed using software known as IDENTIFY. This software identifies the peaks using their energies obtained and labels the peak with the nuclide responsible for each peak and the corresponding activity. The knowledge of secular equilibrium was used to calculate the activity of the long-lived parents from their daughter radio isotopes since ^{238}U and ^{232}Th have relatively low gamma-ray intensities following their decay.^{226}Ra, ^{214}Pb and ^{214}Bi activities and gamma-lines were used to determine ^{238}U activity concentration, while ^{228}Ac, ^{212}Pb, ^{212}Bi and ^{208}Tl were used to determine ^{232}Th activity concentration.

Results obtained from the alpha spectrometer were tabulated and the radionuclide activities were used to calculate the yearly dose to the public due to ingestion of the water.

The printouts from the ICP-MS gave the concentrations of the elements in water in µg/ℓ and were then entered into a spreadsheet and used for calculation of yearly doses for different age groups.

To calculate the transfer factors (TF) the following equation was used (Dobrin, 2006):

$$TF = \frac{\text{radionuclide activity per unit mass in water (Bq/kg)}}{\text{radionuclide activity per unit mass in soil (Bq/kg)}}, \quad (15)$$

CHAPTER 5: RESULTS AND DISCUSSION

The Department of Water Affairs has set out water quality guidelines and presented them in different volume numbers for;

- Domestic water use
- Recreational water use
- Industrial water use
- Agricultural water use – irrigation
- Agricultural water use – livestock watering
- Agricultural water use – aqua culture
- Aquatic ecosystems
- Field guide

For purposes of this research discussion, not all the above will be checked with respect to the water quality at our sampling site. Domestic water use, recreational water use, agricultural-irrigation and agricultural-livestock watering will be the four water quality criteria investigated.

5.1 Domestic Water Use

The Strahlengschutz-Komission (SSK) has set an annual dose limit of 0.500 mSv for tap water in areas where the resources are affected by former uranium activities. The WHO, on the other hand, has set the screening value at 0.100 mSv/a.
(www.dwaf.gov.za/iwqs/radioact/DWAFGuideline/section2.htm).

Table 6 presents the concentrations of uranium and thorium in water samples obtained from the ICP-MS measurements.

Table 6: Uranium and Thorium concentrations in µg/ℓ

	A	C	E	Z1	Z2	Zm
Th	1.69E+02	1.53E+02	1.81E+01	1.02E+01	1.82E+01	1.13E+01
U	5.17E+03	1.55E+02	1.26E+03	8.68E+02	1.27E+03	6.85E+02

Table 7 presents the activity concentrations (in mBq/ℓ) of uranium and thorium in the water samples collected.

Table 7: Uranium and Thorium concentrations in mBq/ℓ

	A	C	E	Z1	Z2	Zm
Th	6.96E+02	6.30E+02	7.47E+01	4.21E+01	7.50E+01	4.65E+01
U	6.39E+04	1.92E+03	1.56E+04	1.07E+04	1.57E+04	8.46E+03

The thorium and uranium concentrations at all the sampling points are presented in the Figures 15a and 15b, respectively.

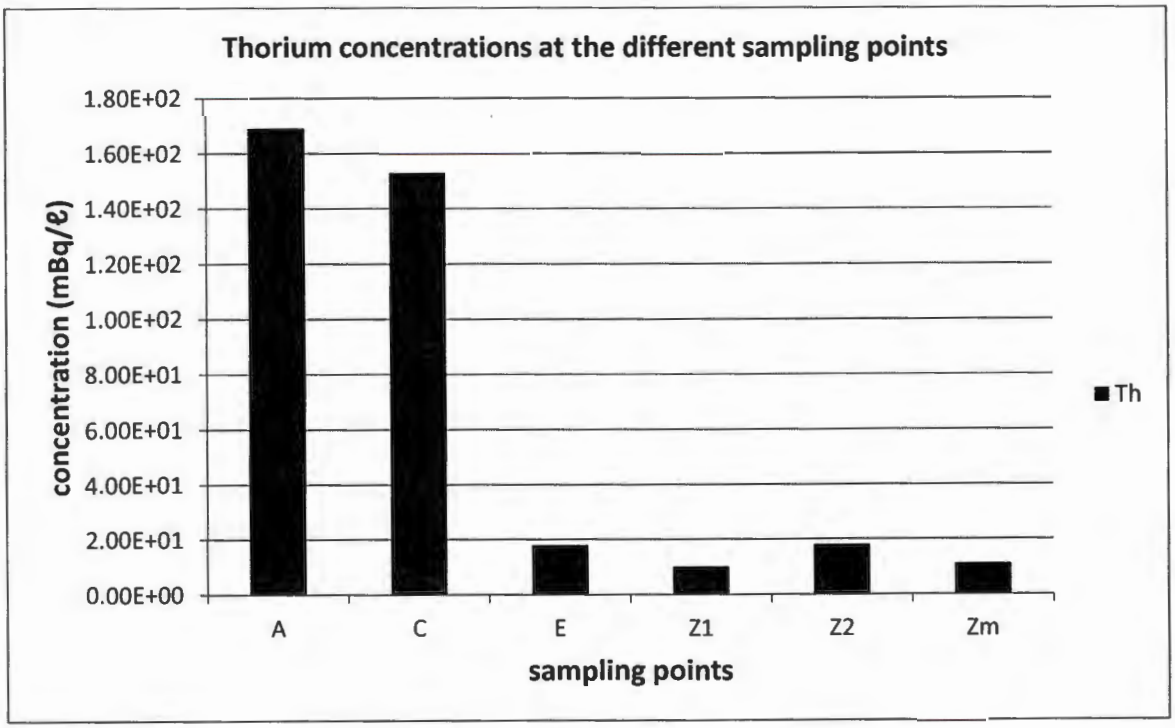

Figure 15a: Plot of Thorium concentrations in mBq/ℓ

From the plot in Figure 15a it can be noted that sampling points A and C have considerably high concentrations compared to the other points. This difference in activity concentration can be explained by the fact that points E, Z1, Z2 and Zm are located close to each other and are down the drainage about 1 km away from the mine dump when compared to points A and C which are very close to the dump. The high concentration at A than at C yet C is on the dump can be attributed to leaching. The radionuclides get washed from the top of the dump down to the sides or bottom part of the dump. There is a possibility that either thorium does not wash out easily with flowing water or it sticks on the walls of the drainage pipe as the water flows along it before joining other sources. Thorium is known to have low solubility in natural water. Even during radioactive decay of ^{234}U, the thorium generated in solution rapidly hydrolyses and adsorbs to nearest solid surface (www.dwaf.gov.za/iwqs/radioact/DWAFGuideline/section2.htm)

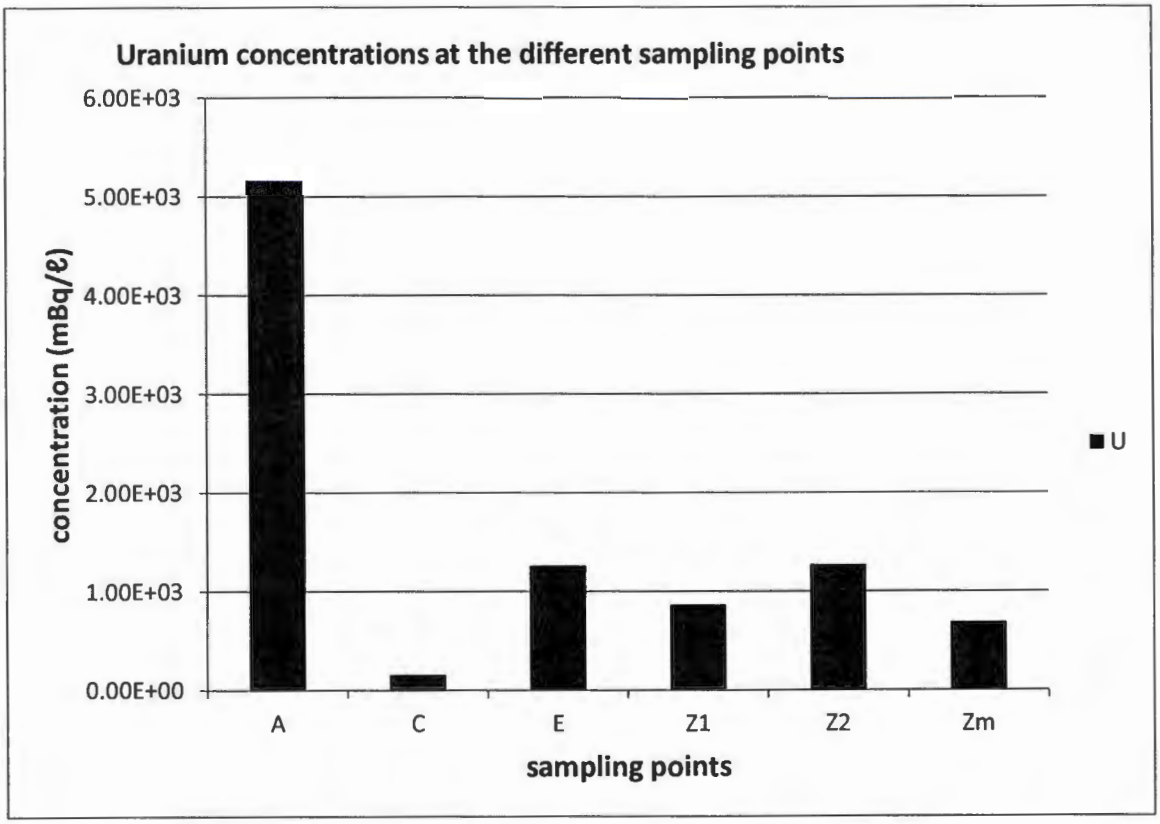

Figure 15b: Plot of Uranium concentrations in mBq/ℓ

From Figure 15b one notices that the plot of uranium concentration at the different sampling points follows the same trend as that of thorium discussed in Figure 5a except for

the point C which in the case of uranium is lower than all the other sampled points. The uranium seems to be oxidized to the 6+ oxidation state. This is because in this oxidation state uranium forms soluble uranyl complex ions which play a most important role in uranium transportation.
(www.dwaf.gov.za/iwqs/radioact/DWAFGuideline/section2.htm)

The uranium and thorium concentrations in Table 7 were used together with the dose conversion factors presented in appendix 2 and the South African consumption rates in appendix 3 to calculate the annual dose that can be received by the public considering the different age groups if they so happened to ingest water from the sampled points. The effective dose was calculated using the guidelines given by the Department of Water Affairs (DWAF, 2002) through the equation;

Annual effective dose (Sv/a) = (radioactivity concentration in water (Bq/L)) × (consumption of water (L/a)) × (radiation dose conversion factor (Sv/Bq)), (15)

The detailed calculations of the dose are given in appendix 4 for all the sampling points and are therefore summarized in Table 8.

Table 8: Uranium and Thorium yearly dose (mSv/a) for different age groups

sampling points	U and Th Yearly Dose for the different Groups (mSv/a)						
	< 1a	1-2a	2-7a	7-12a	12-17a	> 17a	average life-time (years)
A	10.20	4.29	3.33	3.27	5.53	4.52	**5.19**
C	1.32	0.26	0.20	0.19	0.29	0.27	**0.42**
E	2.33	1.03	0.80	0.78	1.33	1.08	**1.23**
Z1	1.58	0.70	0.54	0.53	0.91	0.74	**0.83**
Z2	2.35	1.03	0.80	0.79	1.34	1.09	**1.23**
Zm	1.27	0.56	0.43	0.42	0.72	0.59	**0.67**

Figure 16 is a plot of the dose results given in Table 8 with the aim of giving a much clearer picture of the difference in the dose rates for different groups as one compares the different sampling points.

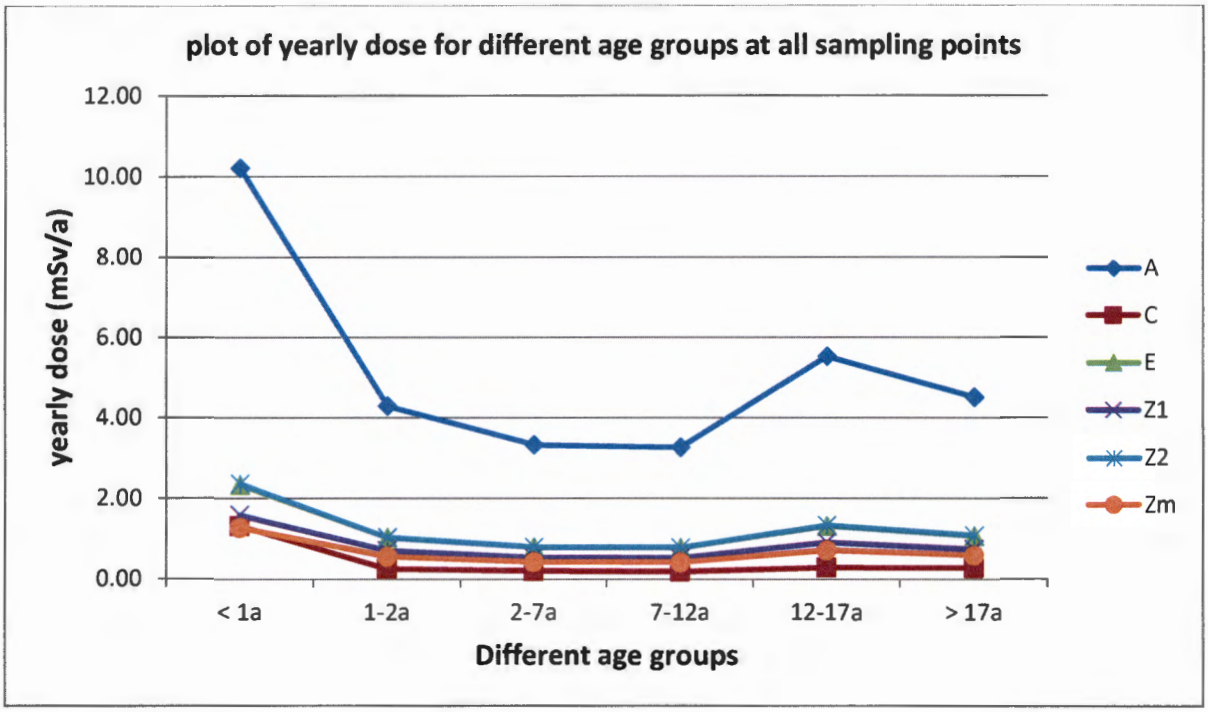

Figure 16: A plot of the yearly dose for the different age groups compared at all sampling points

From the plot in Figure 16 it can be seen that the yearly dose that can be received by people due to consumption of the untreated water at all the sampling points varies between 0 mSv/a to about 2 mSv/a for all age groups except at sampling point A. Sampling point A shows quite high doses which exceed 10 mSv/a for infants< *1a*. These high doses may be attributed to the fact that the water sampling point A is right at the bottom of the dump yet the other sampling points are further away from the dump at varying distances.

The alpha spectrometry analysis was performed in a SANAS ISO 17025 accredited testing laboratory (T0111). The radionuclides and their concentrations measured are presented in Table 9 below.

Table 9: Activity concentrations of nuclides in filtered samples (mBq/L)

Field code	A 1004			Z 1004			Z 1005		
Lab code	CARST-X001			CARST-X002			CARST-X003		
Nuclide	Value	Unc.	MDA	Value	Unc.	MDA	Value	Unc.	MDA
^{238}U	17800	300	11	18100	300	9.7	15700	200	7.7
^{234}U	16800	300	11	16700	200	9.7	14700	200	7.7
^{230}Th	387	60	32	767	117	38	844	136	170
^{226}Ra	43.9	6.1	2.3	39.7	4.5	1.4	46.0	5.0	1.5
^{210}Po	8.28	2.52	2.1	23.9	4.6	7.0	17.3	4.4	9.7
^{235}U	817	13	0.52	832	12	0.44	722	10	0.35
^{227}Th	163	10	4.1	223	12	1.8	180	25	35
^{223}Ra	147	12	3.1	143	9	1.8	142	10	2.0
^{232}Th	24.0	4.3	8.9	59.8	6.3	1.8	51.3	13.0	21
^{228}Th	54.4	5.6	5.2	78.5	7.4	7.1	89.9	16.9	21
^{224}Ra	8.86	3.96	4.8	10.7	3.4	2.9	19.3	4.7	3.1
Gross alpha	15200	1300	1400	10100	800	760	12000	1000	850
Gross beta	12700	800	600	11900	700	650	11900	700	680

The activity concentrations in Table 9 were used to calculate the dose rates according to the guidelines in the National Nuclear Regulator licensing guide LG-1032. For purposes of calculation the following radioactive equilibria were assumed:

^{238}U up to ^{234m}Pa (= ^{238}U) ^{226}Ra up to ^{214}Bi (= ^{226}Ra) ^{210}Pb and ^{210}Po (= ^{210}Po)

^{235}U up to ^{231}Th (= ^{235}U) ^{231}Pa up to ^{227}Th (=^{227}Th) ^{223}Ra and ^{211}Pb (= ^{223}Ra)

^{228}Ra up to ^{228}Th (= ^{228}Th) ^{224}Ra up to ^{212}Bi (= ^{224}Ra)

The calculated dose rates are presented in Table 10.

Table 10: Dose rate calculations (mSv/a)

Sample ID		Age Group					
Field code	**Lab code**	**< 1a**	**1-2a**	**2-7a**	**7-12a**	**12-17a**	**> 17a**
A 1004	**CARST-X001**	5.1	1.7	1.3	1.2	2.1	1.6
Z 1004	**CARST-X002**	6.3	1.9	1.4	1.4	2.3	1.8
Z 1005	**CARST-X003**	5.7	1.7	1.3	1.2	2.1	1.6

The ICP-MS results showing the concentrations of toxic elements are presented in Table 11.

Table 11: Concentrations of toxic elements in water (µg/ℓ)

	A	C	E	Z1	Z2	Zm	Reference value
As	9.36E+01	2.86E+02	4.15E+02	9.79E+01	5.72E+02	9.50E+01	**5.00E+02**
Cd	4.94E+01	9.94	8.72	0	1.78	0	**2.00E+01**
Hg	2.78	2.5	2.54	4.28	3.1	3.48	**3**
Li	1.99E+02	6.05E+02	1.54E+02	1.14E+02	1.95E+02	8.90E+01	**no value**
Pb	5.01E+01	5.67E+02	2.70E+02	6.50E+01	1.03E+02	6.49E+01	**1.00E+02**
Sn	1.18E+01	5.92	1.09E+01	1.18E+01	1.27E+01	5.64	**5.00E+03**
Al	4.80E+05	no value	1.63E+05	2.08E+05	2.84E+05	1.50E+05	**5.00E+03**

The concentrations that exceed the reference values given (Peterson, 1999) are:

- At sampling point A, only cadmium and aluminium exceed the limit,
- At point C, lead is the only element that exceeded the limit. However, it is worth noting that for aluminium measurement no value was recorded by the ICP-MS,
- Aluminium and lead exceeded the limit in water sampled at point E,
- Water samples taken at Z1 and Zm both had exceeding limit concentrations of mercury and aluminium,
- Z2 had more elements exceeding the limit than all the other sampled points, with arsenic, mercury, lead and aluminium having concentrations above reference values.

Figures 17a to 17f present the toxic element concentrations discussed in Table 11 at each sampling point. Aluminium was excluded because it showed very high concentrations and thus made it difficult for other element concentrations to show in one graph due to the scale.

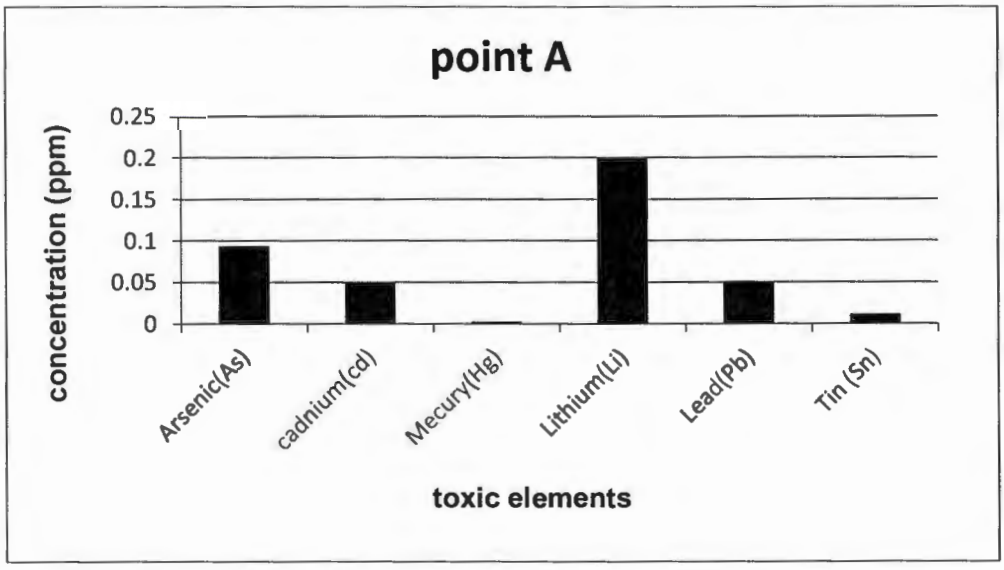

Figure 17a: Plot of varying concentrations of selected toxic elements at sampling point A

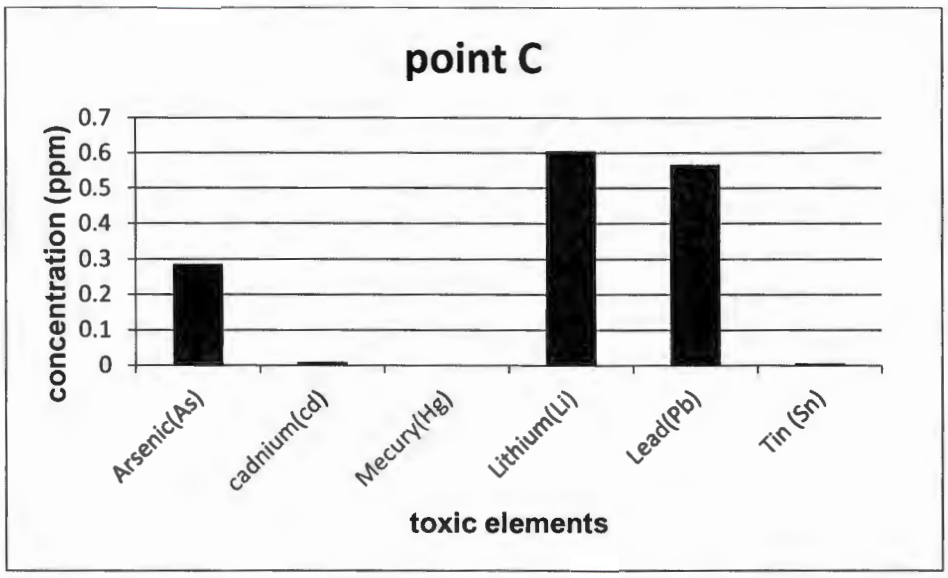

Figure 17b: Plot of varying concentrations of selected toxic elements at sampling point C

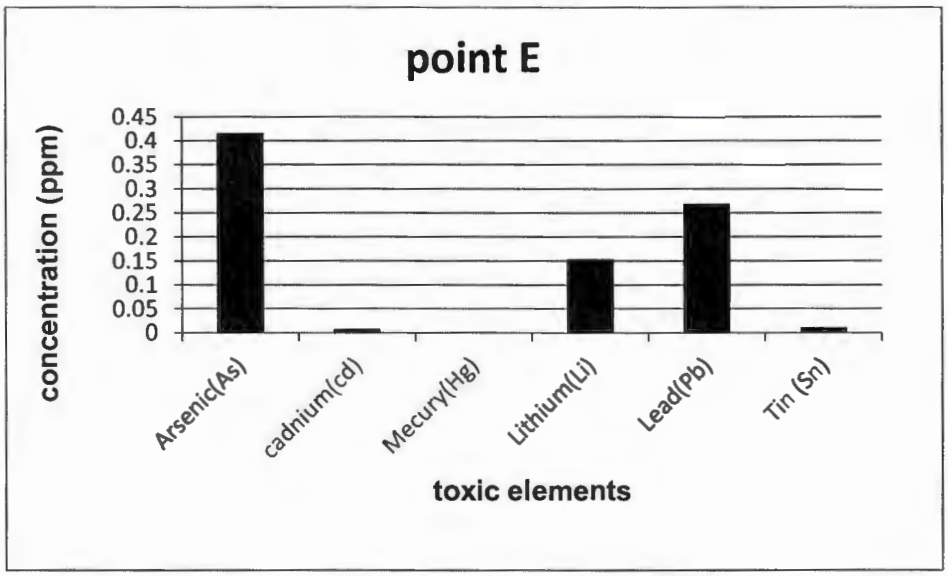

Figure 17c: Plot of varying concentrations of selected toxic elements at sampling point E.

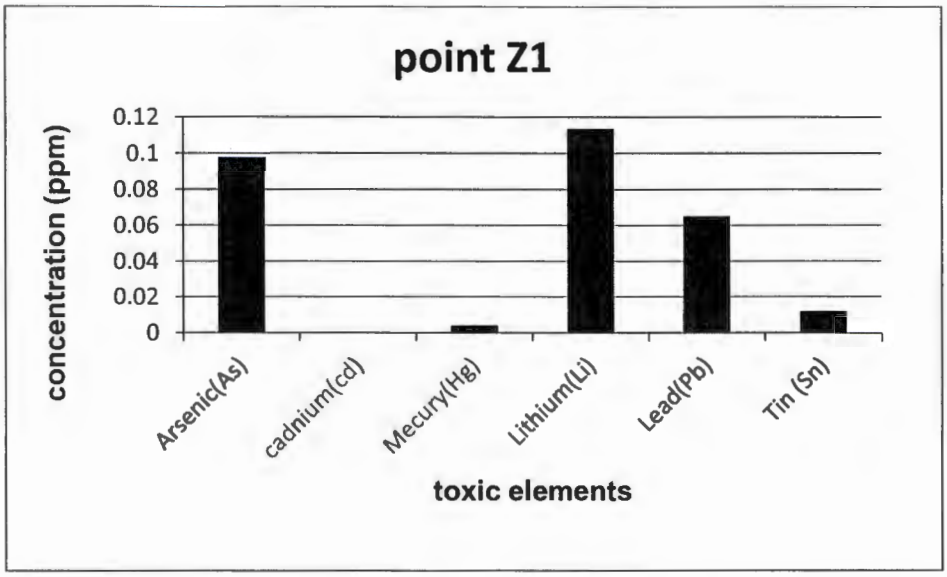

Figure 17d: Plot of varying concentrations of selected toxic elements at sampling point Z1

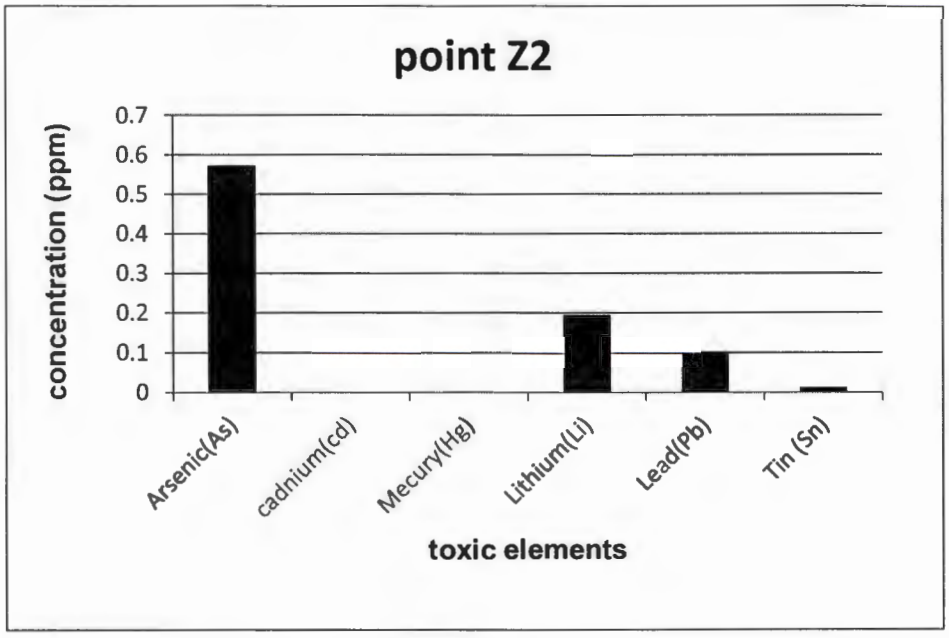

Figure 17e: Plot of varying concentrations of selected toxic elements at sampling point Z2

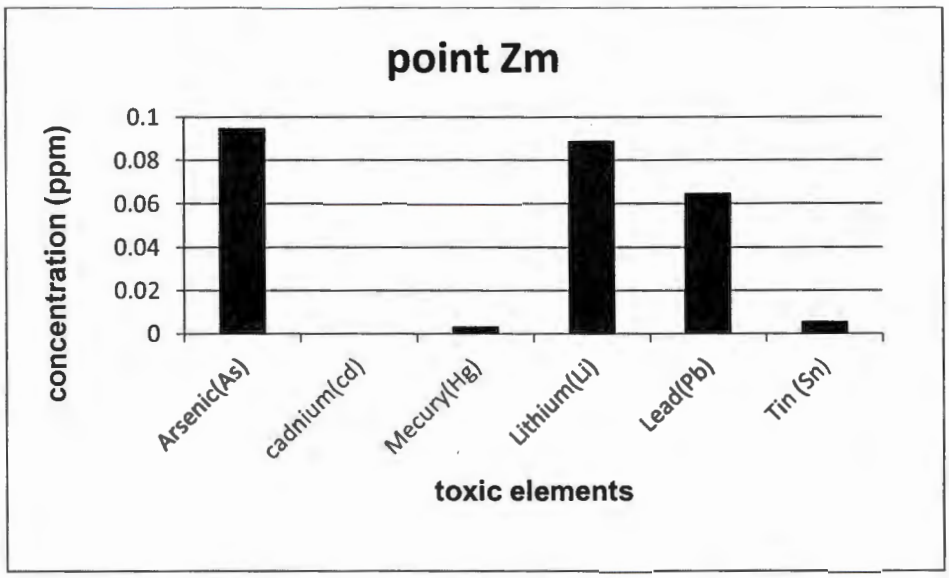

Figure 17f: Plot of varying concentrations of selected toxic elements at sampling point Zm

There seems to be a slight difference in concentration between the sampling points. Of note is point Z2 which shows a high concentration of all the toxic elements when comparing it with the points closest to it (Z1 and Zm). Z2 is the water sampling point furthest from the mine dump; therefore, these results suggest that the toxic elements are being trans-located as the water flows.

5.2 Agricultural Water Use - Irrigation

To decide whether the water from our study area can be used by the residents for irrigation purposes, the concentrations of selected toxic elements were compared against the FAO standards given for irrigation quality (www.dwaf.gov.za/iwqs/radioact/DWAFGuideline/section2.htm). The comparison is presented in Table 12.

Table 12: Selected water quality criteria for irrigational water (mg/ℓ)

Element	FAO	A	C	E	Z1	Z2	Zm
Aluminium	5.0	480.25	No value	163.32	208.22	284.48	150.11
Arsenic	0.1	0.09	0.29	0.42	0.10	0.57	0.09
Cadmium	0.01	0.05	0.01	0.009	0	0.001	0
Chromium	0.1	1.32	8.20	0.73	0.84	4.65	0.70
Copper	0.2	3.00	1.81	1.17	0.88	1.40	0.68
Manganese	0.2	39.47	37.53	7.58	6.40	11.00	4.82
Nickel	0.2	15.04	2.01	5.33	4.15	6.93	3.32
Zinc	2.0	21.10	4.87	21.02	6.61	12.17	5.38

From the comparison in Table 12, it can be seen that aluminium, chromium, copper, manganese, nickel and zinc exceed the FAO set limit at all the sampling points. Cadmium is within the limits at all sampling points except for sampling point A. This implies that the water from these sampled points does not meet the requirements or set guidelines and as such cannot be used for irrigation purposes.

5.3 Agricultural Water Use - Livestock Watering

The Department of Water Affairs (DWAF, 1996) in volume 5 of the water quality guidelines gives the limits that have been set for water to be considered fit to be consumed by livestock. Table 13 gives a list of the elements that are considered in the water quality guide and are compared against those that were measured from the different sampling points to see how they compare.

Table 13: The comparison of limit set for water to be consumed by livestock against concentrations at each sampling point

element	DWA limit (mg/l)	A (mg/l)	C (mg/l)	E (mg/l)	Z1 (mg/l)	Z2 (mg/l)	Zm (mg/l)
Al	0-5 NAE 5-10 neurotoxicity	480.25	Not measured	163.32	208.22	284.48	150.11
As	0-1 NAE 1-1.5 ACE	0.093	0.29	0.42	0.097	0.57	0.095
B	0-5 NAE 5-50 ACE	0.19	1.79	0.29	0.20	0.70	2.19
Cd	0-0.01 NAE 0.01-0.02 ACE	0.049	0.009	0.008	0	0.002	0
Ca	0-1000 NAE 1000-2000 ACE	1920.63	4440.69	1250.35	986.40	1407.83	770.93
Cl	0-1500 NAE	151.01	984.08	0	533.23	140.88	271.73
Cr	0-1 NAE 1-2 ACE	1.31	8.20	0.73	0.84	4.65	0.70
Co	0-1NAE 1-2 ACE	7.52	0.84	3.21	2.42	4.19	1.81
Cu	0-0.5 NAE	3.00	1.81	1.17	0.88	1.40	0.69

	1-2 ACE						
Fe	0-10 NAE 10-50 ACE	419.97	1901.84	979.91	634.71	1172.27	466.49
Pb	0-0.1 NAE 0.1-0.2 ACE	0.05	0.57	0.27	0.065	0.10	0.065
Mg	0-500 NAE 500-1000 ACE	90.38	223.32	75.56	63.80	91.48	42.36
Mn	0-10 NAE 10-50 ACE	39.47	37.53	7.58	6.40	11.00	4.82
Hg	0-1 NAE 1-6 ACE	0.0027	0.0025	0.0025	0.0043	0.0031	0.0035
Mo	0-0.01 NAE 0.01-0.02 ACE	0.029	0.030	0.028	0.16	0.056	0.078
Ni	0-1 NAE 2-5 ACE	15.04	2.01	5.33	4.15	6.93	3.32
Se	0-50 NAE 50-75 ACE	0.077	0.063	0.033	0.034	0.034	0.032
Na	0-2000 NAE 2000-2500 ACE	100.04	77.60	71.18	114.72	91.17	95.37

V	0-1 NAE 1-2 ACE	0.020	3.36	0.085	0.040	0.089	0.023
Zn	0-20 NAE 20-40 ACE	21.10	4.87	21.02	6.61	12.17	5.38

NAE stands for No Adverse Effects

ACE stands for Adverse Chronic Effects

From the comparisons done on Table 13, it can be noted that As, B, Cl, Mg, Hg, Se and Na are all below the DWA set limits at all the sampling points. V and Cd exceed the DWA limit only at sampling points C and A, respectively. A majority of the elements under consideration exceed the limits set by DWA. Therefore, the water is not fit to be consumed by livestock.

Table 14 presents the thorium and uranium activity concentrations of samples A, B1, B2, H1, H2, G1 and G2 which are the soil sampling points at the dump but closest to the first water sampling point A.

Table 14: Concentrations of uranium and thorium in soil samples close to the water sampling points

Sample ID	Uranium (Bq/kg)	Error	Thorium (Bq/kg)	Error
A	1.88E+02	4.95E+01	2.93E+01	6.57E+00
B1	1.02E+02	3.21E+01	1.59E+01	3.46E+00
B2	1.33E+02	3.62E+01	2.10E+01	4.69E+00
G1	8.21E+01	2.53E+01	1.46E+01	3.23E+00
G2	1.50E+02	4.10E+01	1.55E+01	3.41E+00
H1	1.33E+02	3.66E+01	1.54E+01	3.39E+00
H2	1.17E+02	3.20E+01	1.47E+01	3.34E+00
average	**1.29E+02**	**3.61E+01**	**1.81E+01**	**4.01E+00**

Table 15: Comparison of concentration of Uranium and Thorium at two water points with that in soil

	Uranium (Bq/kg)	Thorium (Bq/kg)
soil	1.29E+02	1.81E+01
Rainy season water at Point A	6.39E+01	6.96E-01
Rainy season water at Point Z2	1.57E+01	7.50E-02
Dry season water at Point A	1.78E+01	3.87E-01
Dry season water at Point Z2	1.57E+01	8.44E-01

The results in Table 15 show that the concentration of uranium and thorium in the soil is higher compared to the water whether it is the dry season or rainy season. The high counting error in the soil results may be attributed to the 24 hours counting time. Point A is located just next to the mine dump yet point Z2 is located furthest from the mine down-stream. From the above values we can conclude that there is transfer of the radionuclides from the soil to water. The same concentration for uranium in water at point Z2 was measured for both seasons which implies that the movement of uranium at point Z2 is the same throughout the year. This is further confirmed by the transfer factors of uranium and thorium at water point A which were calculated and found to be 49.4% and 3.9%, respectively in the rainy season. At water point Z2 the transfer factors in rainy season were found to be 12.1% and 0.4% for uranium and thorium, respectively. These results show that as we go further away from the mine dump there are less radionuclides being transferred into the water. In the dry season the transfer factors were calculated and found to be 13.8% and 2.1% at point A for uranium and thorium, respectively. At point Z2 the transfer factors were found to be 12.1% and 4.7% for uranium and thorium, respectively. These transfer factors suggest that there is more transfer of radionuclides during the rainy season than when it is dry. However, at point Z2 it seems that during the dry season the thorium gets more concentrated in the water than during the rainy season.

5.4 Comparison to Mafikeng Water

Tap water from around Mafikeng in an area where people reside and where there is no uranium or gold mine dump was sampled and run using the ICP-MS so as to compare with the results of the concentrations of different radionuclides from the Princess mine dump. The Mafikeng area was named BRTC and the results for selected elements are listed in Table 16.

Table 16: Selected elements concentration from water sampled at BRTC (µg/ℓ)

Element	Concentration (µg/ℓ)
As	12.92
Cd	0.00
Hg	2.62
Li	6.54
Pb	85.60
Sn	17.74
Th	0.00
U	0.00

The water from BRTC had no uranium and thorium concentration detected by the ICP-MS. Of note is that only Sn has a concentration higher in BRTC water than the water from all the sampling points at Princess dump.

Fayazi (2005) in 2003 did a study around the Princess mine dump where they investigated major cations and anions and selected trace elements. The results from the study are compared with those obtained in this research in Table 17 (appendix 5 gives all the results from Fayazi in tabular form). The sampling points being considered are point labeled DV-2 (Fayazi, 2005) and sampling point Z1 from this current study. According to GPS details provided by Fayazi point DV-2 is located where Z1 in our study is thus the comparison can be made of the same sampling point.

Table 17: A comparison of data with that collected by Fayazi (µg/ℓ)

	Ca	Mg	K	Na	Cd	Cr	Co
DV-2	4.60E+04	1.69E+05	7.00E+03	4.90E+04	<40E+00	7.50E+02	7.90E+03
Z1	9.86E+05	6.40E+04	1.18E+05	1.15E+05	0.00E+00	8.38E+02	2.40E+03
	Mn	**Ni**	**Zn**	**Al**	**Si**	**V**	**Sr**
DV-2	1.50E+04	1.30E+04	1.20E+04	3.68E+05	5.10E+04	<1E+03	6.00E+02
Z1	6.40E+03	4.10E+03	6.60E+03	2.08E+05	6.00E+03	4.00E+01	7.28E+02
	Cu	**Fe**	**Pb**	**Ba**	**B**	**Mo**	
DV-2	4.00E+03	1.48E+06	4.20E+02	3.00E+02	< 1000	< 300	
Z1	8.83E+02	6.35E+05	6.50E+01	2.99E+02	2.03E+02	1.58E+02	

The results displayed in Table 17 show that there is a slight difference in the concentrations of the elements with most of the elements from Fayazi (2005) being at higher concentrations. This can be attributed to the fact that there is over 10 year gap between the two studies and as such the elements could have been translocated during rains.

5.5 Limitations of the Study

In the during of the study sampling was initially planned to be carried out four times but eventually only done once in the dry season and also once in the rainy or wet season due to the volatile nature of the residents at the sampling points.

5.6 Future Work

This study only focused on mainly uranium and thorium transfer from the dump to the water. However, it would be of great interest to study the behavior of all the radionuclides that can be identified in soil and water and observe if secular equilibrium is not disturbed in the soil and water.

CHAPTER 6: CONCLUSION

The aim of this study was to identify and determine the transfer of radionuclides and toxic elements from the Princess mine dump to water in the Roodepoort area, South Africa, and also determine the potential radiological and toxicological impact on humans.

Thorium and uranium were identified in the soil from the mine dump and also from the water sampled at the dump and down the drainage before it joins other water sources. This, therefore, confirmed that thorium and uranium are being transferred from the mine dump to water in the area. The same concentration for uranium in water at point Z2 was measured for both seasons (dry and rainy season) which implies that the movement of uranium at point Z2 is the same throughout the year. The transfer of the radionuclides is further confirmed by the transfer factors of uranium and thorium at water point A which were calculated and found to be 49.4% and 3.9%, respectively in the rainy season. At water point Z2 the transfer factors in rainy season were found to be 12.1% and 0.4% for uranium and thorium, respectively. These results show that as we go further away from the mine dump there are less radionuclides being transferred into the water. In the dry season the transfer factors were calculated and found to be 13.8% and 2.1% at point A for uranium and thorium, respectively. At point Z2 the transfer factors were found to be 12.1% and 4.7% for uranium and thorium, respectively. These transfer factors suggest that there is more transfer of radionuclides during the rainy season than when it is dry.

Water samples were analyzed using an alpha spectrometer equipped with alpha spectrometer Genie software and ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Po, ^{235}U, ^{227}Th, ^{223}Ra, ^{232}Th, ^{228}Th and ^{224}Ra were the radionuclides identified.

Doses due to ingestion of the untreated water were estimated in this study using the literature given conversion factors and were found to be above the 0.100 mSv/a limit set by WHO. Thus using these estimates it can be concluded that the dose that the public can receive from drinking this untreated water from the sampled sites poses a potential radiological health risk since it is above the recommended limit. The reference value of 0.25 mSv/a, which has been set as the dose limit by the NNR was exceeded by almost all the water samples analyzed (both those sampled during dry and those sampled during

rainy season). Only the age groups 2-7a and 7-12a for water sampled at point C have dose rates below this limit.

Focusing on the toxicity of the water, one may highlight that the toxic elements concentrations from the sampling sites exceed the limit set by the FAO. Therefore, the water that was investigated in this study is not good for agricultural use, for example irrigation and livestock watering, unless it undergoes treatment before it is utilized.

The study achieved the aim of this research which was set out as objectives in section 2.2 as the activity of radionuclides in soil samples was determined using HPGe detector, heavy elements present in water were identified using ICP-MS, alpha spectrometry was used to identify selected radionuclides and their activity concentrations and ,finally, the water results from the mine dump water samples obtained from the different equipment was compared with that of a residential place where there was no uranium or gold mine dump.

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APPENDICES

Appendix 1: Uranium, Thorium and Actinium series, respectively (Blundy & Wood, 2003).

^{238}U decay series

Nuclide	Half-life	Major Gamma Radiation Energies (MeV) and Intensities
^{238}U ↓ α	4.5×10^9 a	0.04955 (22.46%) 0.1135 (0.013%)
^{234}Th ↓ β	24.1 d	0.0924 (16.2%)
^{234m}Pa (99.86%) ↓ β	1.18 min	0.0435 (1.42%) 1.001 (0.856%)
^{234}U ↓ α	2.38×10^5 a	0.0532 (28.7%)
^{230}Th ↓ α	7.52×10^4 a	**0.068 (0.38%)**
^{226}Ra ↓ α	1602 a	0.1862 (5.962%)
^{222}Rn ↓ α	3.825 d	0.511 (0.078%)
^{218}Po ↓ α	3.05 m	0.837 (0.0011%)
^{214}Pb ↓ β	26.8 m	0.2952 (27.3%) 0.3519 (46.96%)
^{214}Bi (99.98%) ↓ β	19.7 m	0.609 (46.4%) 1.1203 (15.14%)
^{214}Po ↓ α	164 μs	0.799 (0.0105%)
^{210}Pb ↓ β	22,3 a	0.047 (80.2%)
^{210}Bi ↓ β	5.02 d	0.305 (0.000084%)
^{210}Po	138.3 d	0.803 (0.00124%)

↓ α	
^{206}Pb	stable

^{235}U decay series (Actinium series)

Nuclide	Half-life	Major Gamma Radiation Energies (MeV) and Intensities
^{235}U	7.13×10^8 a	0.144 (13.5%)
↓ α		0.186 (63.4%)
^{231}Th	24.64 h	0.059 (75.1%)
↓ β		0.084 (23.4%)
^{231}Pa	3.43×10^4 a	0.300 (4.25%)
↓ α		0.303 (2.62%)
^{227}Ac	21.8 a	0.0693 (0.0076%)
(98.8%) ↓ β		
^{227}Th	18.17 d	0.236 (12.6%)
↓ α		
^{223}Ra	11.68 d	0.1542 (28.2%)
↓ α		0.2695 (25.5%)
^{219}Rn	3.92 s	0.2712 (13.3%)
↓ α		0.4018 (7.12%)
^{215}Po	1.83 ms	0.4389 (0.06%)
↓ α		
^{211}Pb	36.1 m	0.4048 (4.3%)
↓ β		0.4272 (2.13%)
		0.832 (3.6%)
^{211}Bi	2.16 m	0.351 (16.16%)
(98.7%) ↓ α		
^{207}Tl	4.79 m	0.8978 (0.269%)

↓β

^{207}Pb stable

Minor branchings omitted

^{232}Th decay series

Nuclide	Half-life	Major Gamma Radiation Energies (MeV) and Intensities
^{232}Th	1.39 ×10^{10} a	0.064 (0.26%)
↓ α		
^{228}Ra	5.75 a	0.0264 (28%)
↓ β		
^{228}Ac	6.13 h	0.0578 (72.5%)
↓ β		0.338 (11.7%)
		0.911 (26.5%)
^{228}Th	1.913 a	0.0844 (26.4%)
↓ α		
^{224}Ra	3.64 d	0.241 (5.26%)
↓ α		
^{220}Rn	55.6 s	0.550 (0.118%)
↓ α		
^{216}Po	0.14 s	0.805 (0.0019%)
↓ α		
^{212}Pb	10.64 h	0.2386 (81.6%)
↓ β		0.3001 (4.66%)
^{212}Bi → (36%)	60.5 m	0.0399 (26.0%)
(64%) ↓ β		0.727 (6.74%)
↓ α		
	304 ns	No gamma
^{212}Po ↓		
↓ α	3.1 m	0.583 (86.7%)
^{208}Tl		2.6145 (100%)
↓ ↓ β		
	Stable	
^{208}Pb ←		

Appendix 2: Dose conversion factors, E(g), for ingestion by various age groups of the public(DWAF, 2002)

Radionuclide	$< 1a$	1 – 2a	2 – 7a	7 – 12a	12 – 17a	$> 17a$
	E (g)	E (g)	E (g)	E (g)	E (g)	E (g)
^{238}U	3.4E-07	1.2E-07	8.0E-08	6.8E-08	6.7E-08	4.5E-08
^{234}Th	4.0E-08	2.5E-08	1.3E-08	7.4E-09	4.2E-09	3.4E-09
^{234}U	3.7E-07	1.3E-07	8.8E-08	7.4E-08	7.4E-08	4.9E-08
^{230}Th	4.1E-06	4.1E-07	3.1E-07	2.4E-07	2.2E-07	2.1E-07
^{226}Ra	4.7E-06	9.6E-07	6.2E-07	8.0E-07	1.5E-06	2.8E-07
^{214}Pb	2.7E-09	1.0E-09	5.2E-10	3.1E-10	2.0E-10	1.4E-10
^{214}Bi	1.4E-09	7.4E-10	3.6E-10	2.1E-10	1.4E-10	1.1E-10
^{210}Pb	8.4E-06	3.6E-06	2.2E-06	1.9E-06	1.9E-06	6.9E-07
^{210}Bi	1.5E-08	9.7E-09	4.8E-09	2.9E-09	1.6E-09	1.3E-09
^{210}Po	2.6E-05	8.8E-06	4.4E-06	2.6E-06	1.6E-06	1.2E-06
^{235}U	3.5E-07	1.3E-07	8.5E-08	7.1E-08	7.0E-08	4.7E-08
^{231}Pa	1.3E-05	1.3E-06	1.1E-06	9.2E-07	8.0E-07	7.1E-07
^{227}Ac	3.3E-05	3.1E-06	2.2E-06	1.5E-06	1.2E-06	1.1E-06
^{227}Th	3.0E-07	7.0E-08	3.6E-08	2.3E-08	1.5E-08	8.8E-09
^{223}Ra	5.3E-06	1.1E-06	5.7E-07	4.5E-07	3.7E-07	1.0E-07
^{232}Th	4.6E-06	4.5E-07	3.5E-07	2.9E-07	2.5E-07	2.3E-07
^{228}Ra	3.0E-05	5.7E-06	3.4E-06	3.9E-06	5.3E-06	6.9E-07

^{228}**Th**	3.7E-06	3.7E-07	2.2E-07	1.5E-07	9.4E-08	7.2E-08
^{224}**Ra**	2.7E-06	6.6E-07	3.5E-07	2.6E-07	2.0E-07	6.5E-08

Appendix 3: South African annual consumption rates (DWAF, 2002)

Foodstuff	annual consumption (kg fresh weight)					
	< 1a	**1-2a**	**2-7a**	**7-12a**	**12-17a**	**> 17a**
Freshwater fish	0.5	1	5	10	10	25
Meat	10	20	50	75	100	100
Poultry	7.5	15	35	60	75	75
Eggs	3	6	15	25	30	30
Cereals and grains	45	60	75	90	128	150
Root crops	51	68	85	102	145	170
Other vegetables, fruits, nuts	39	52	65	78	111	130
Water (L)	200	260	300	350	600	730
Milk (L)	300	300	300	300	300	250

Appendix 4: Detailed annual effective dose calculations for each sampling point

POINT A	Yearly Dose for the different Groups (Sv/a)					
Nuclide	**< 1a**	**1-2a**	**2-7a**	**7-12a**	**12-17a**	**> 17a**
U-238	4.3E-3	2.0E-3	1.5E-3	1.5E-3	2.6E-3	2.1E-3
U-235	32.2E-6	15.6E-6	11.7E-6	11.4E-6	19.3E-6	15.8E-6
U-234	4.7E-3	2.1E-3	1.7E-3	1.6E-3	2.8E-3	2.3E-3
Th-232	6.40E-04	6.26E-05	4.87E-05	4.04E-05	3.48E-05	3.20E-05
Th-228	5.15E-04	5.15E-05	3.06E-05	2.09E-05	1.31E-05	1.00E-05
total	**10.20E-3**	**4.29E-3**	**3.33E-3**	**3.27E-3**	**5.53E-3**	**4.52E-3**

POINT C	Yearly Dose for the different Groups (Sv/a)					
Nuclide	**< 1a**	**1-2a**	**2-7a**	**7-12a**	**12-17a**	**> 17a**
U-238	129.6E-6	59.5E-6	45.7E-6	45.4E-6	76.6E-6	62.6E-6
U-235	967.7E-9	467.3E-9	352.5E-9	343.5E-9	580.6E-9	474.3E-9
U-234	141.0E-6	64.4E-6	50.3E-6	49.4E-6	84.6E-6	68.2E-6
Th-232	579.60E-06	7.37E-05	6.62E-05	6.39E-05	9.45E-05	1.06E-04
Th-228	466.2E-06	6.06E-05	4.16E-05	3.31E-05	3.55E-05	3.31E-05
total	**1.32E-3**	**258.7E-6**	**204.1E-6**	**192.1E-6**	**291.9E-6**	**270.2E-6**

POINT E	Yearly Dose for the different Groups (Sv/a)					
Nuclide	**< 1a**	**1-2a**	**2-7a**	**7-12a**	**12-17a**	**> 17a**
U-238	1.1E-3	483.2E-6	371.7E-6	368.6E-6	622.5E-6	508.7E-6
U-235	7.9E-6	3.8E-6	2.9E-6	2.8E-6	4.7E-6	3.9E-6
U-234	1.1E-3	523.4E-6	408.8E-6	401.1E-6	687.6E-6	553.9E-6
Th-232	68.72E-06	8.74E-06	7.84E-06	7.58E-06	11.21E-06	12.54E-06
Th-228	55.28E-06	7.19E-06	4.93E-06	3.92E-06	4.21E-06	3.93E-06
total	**2.33E-3**	**1.03E-3**	**796.1E-6**	**784.0E-6**	**1.33E-3**	**1.08E-3**

POINT Z1	Yearly Dose for the different Groups (Sv/a)					
Nuclide	**< 1a**	**1-2a**	**2-7a**	**7-12a**	**12-17a**	**> 17a**
U-238	722.3E-6	331.4E-6	254.9E-6	252.8E-6	427.0E-6	348.9E-6
U-235	5.4E-6	2.6E-6	2.0E-6	1.9E-6	3.2E-6	2.6E-6
U-234	786.0E-6	359.0E-6	280.4E-6	275.1E-6	471.6E-6	379.9E-6
Th-232	38.73E-06	4.93E-06	4.42E-06	4.27E-06	6.32E-06	7.07E-06
Th-228	31.15E-06	4.05E-06	2.78E-06	2.21E-06	2.37E-06	2.21E-06
total	**1.58E-3**	**702.0E-6**	**544.5E-6**	**536.3E-6**	**910.5E-6**	**740.8E-6**

POINT Z2	Yearly Dose for the different Groups (Sv/a)					
Nuclide	**< 1a**	**1-2a**	**2-7a**	**7-12a**	**12-17a**	**> 17a**
U-238	1.1E-3	486.3E-6	374.0E-6	370.9E-6	626.5E-6	512.0E-6
U-235	7.9E-6	3.8E-6	2.9E-6	2.8E-6	4.7E-6	3.9E-6
U-234	1.2E-3	526.8E-6	411.5E-6	403.7E-6	692.0E-6	557.5E-6
Th-232	69.00E-06	8.76E-06	7.88E-06	7.61E-06	11.25E-06	12.59E-06
Th-228	55.50E-06	7.22E-06	4.95E-06	3.94E-06	4.23E-06	3.94E-06
total	**2.35E-3**	**1.03E-3**	**801.2E-6**	**789.0E-6**	**1.34E-3**	**1.09E-3**

POINT Zm	Yearly Dose for the different Groups (Sv/a)					
Nuclide	**< 1a**	**1-2a**	**2-7a**	**7-12a**	**12-17a**	**> 17a**
U-238	571.1E-6	262.0E-6	201.6E-6	199.9E-6	337.6E-6	275.9E-6
U-235	4.3E-6	2.1E-6	1.6E-6	1.5E-6	2.6E-6	2.1E-6
U-234	621.5E-6	283.9E-6	221.7E-6	217.5E-6	372.9E-6	300.4E-6
Th-232	42.78E-06	5.44E-06	4.88E-06	4.72E-06	6.98E-06	7.81E-06
Th-228	34.41E-06	4.47E-06	3.07E-06	2.44E-06	2.62E-07	2.44E-07
total	**1.27E-3**	**557.9E-6**	**432.8E-6**	**426.1E-6**	**722.6E-6**	**588.6E-6**

Appendix 5: Data collected by Fayazi in 2003 (Fayazi, 2005)

Constituents	DV-1	DV-1	DV-2	DV-2	DV-3	DV-4	DV-5	DV-6	DV-7	DV-8	DV-9	DV-10	DV-S1	DV-S2	DV-S3	DV-S4	DV-Dam	Constituents
(mg/l)																		(mg/l)
EC(mS/m)	411	391	605	803	1 394	34	20	61	256	27	737	669	8	127	334	1 121	16	EC (mS/m)
TDS	4 806	4 224	10 368	13 560	33 520	194	176	512	2 578	220	20 378	10 978	84	1 004	4 548	22 462	116	TDS
TAL (As CaCO3)	31	170	<10	<10	<10	41	36	<10	46	25	<10	<10	<10	<10	<10	<10	42	TAL (as CaCO3)
Cl	34	36	28	16	89	17	6	13	23	14	700	425	10	<3	<3	7	8	Cl
F	0.1	0.1	0.1	0.2	<0.1	0.2	0.4	0.3	0.4	0.2	<0.1	<0.1	0.2	0.2	0.1	0.1	0.3	F
SO4	2 900	2 600	5 000	7 425	17 800	104	50	276	349	163	9 600	6 650	25	400	2 340	12 650	24	SO4
Ca	422	376	46	72	54	23	20	42	531	22	15	83	3.6	6.4	12	61	15	Ca
Mg	470	349	169	185	786	3	2	19	88	4	220	153	0.4	12	35	161	3.4	Mg
K	14	16	7	6	2	6	6	8	25	5	0.5	6	2	0.2	0.5	0.2	3.4	K
Na	111	105	49	48	206	20	16	31	45	27	5	37	3	3	3	6	14	Na
NH4=N	14	14	1	0.2	21	0.6	0.8	1.3	3	0.5	4	2	<0.1	0.4	1	1.8	0.3	NH4=N
TKN	14	10	10	7.7	14	2.5	2.8	5	3	3	6	9	<1	<1	3.5	7.4	<1	TKN
NO3=N	<0.1	0.3	<0.1	<0.1	<0.1	1	2	3	3	3	1	1	<0.1	0.4	0.4	<0.1	0.4	NO3=N
NO2=N	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.3	0.2	0.2	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NO2=N
Ortho P	<0.1	<0.1	0.1	1.5	4.4	0.2	4	<0.1	5	0.5	14	0.3	0.2	0.2	1.9	8.9	<0.1	Ortho P
Total P	<0.1	<1.0	2.2	3.7	1.5	<1	5	<1	<1	1	6	2	<1	<1	2.9	8.5	<1	Total P
pH (Units)	8.2	5.9	2.9	3.1	2.2	8.4	6.8	4.2	8.6	8.2	2.2	3	5.3	2.7	2.4	2.4	7.1	pH (Units)
Cd	<0.04	<0.04	<0.04	0.07	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.28	0.16	<0.04	<0.04	<0.04	0.16	<0.04	Cd
Cr	<0.03	<0.03	0.75	1.54	1.8	<0.03	0.05	0.03	0.03	<0.03	8.8	0.8	<0.03	0.32	1.66	4.64	<0.03	Cr
Co	0.23	3.14	7.9	14.8	29	0.08	0.06	1	0.12	0.26	15.7	7.7	<0.04	0.65	3.02	17.51	<0.04	Co
Cu	0.04	0.03	4	6.1	2.5	0.06	0.54	0.66	0.06	0.28	17.03	4.02	<0.03	1.05	3.66	12.47	<0.03	Cu
Fe	70	10.5	1 490	1 516	3 078	9.5	36	9.5	0.7	0.71	3 053	1 633	0.53	40.74	421.9	2 714	1.12	Fe
Pb		0.19	0.42	0.76	0.99	0.08	<0.06	<0.06	0.11	0.06	0.6	0.36	0.29	0.35	0.49	1.05	0.2	Pb
Mn	109	185	15	****	77.7	****	****	****	****	****	****	****	0.13	0.32	3.29	9.27	<0.06	Mn
Ni	0.13	0.85	13	18.04	44	0.06	0.12	0.89	0.19	0.11	26.1	13.9	<0.06	1.23	5.17	31.83	0.05	Ni
Zn	1.01	0.52	12	19.3	39.5	1.8	1.03	2.2	0.1	1.21	22.3	11.3	0.03	1.16	6.25	39.8	0.3	Zn
Al	0.1	<0.1	368	442	1 148	0.4	0.7	8.4	2.1	0.9	730	362	0.4	59.4	149	1 099	****	Al
Si	5.4	****	51	****	116	2.7	4.3	3.7	5.1	3.5	29	44	****	****	****	****	****	Si
V	<1	****	<1	****	<1	****	****	****	****	****	****	****	<1	<1	<1	<1	****	V
Ba	0.1	****	0.3	****	0.8	****	****	****	****	****	****	****	<0.1	<0.1	0.1	0.5	****	Ba
B	<1	****	<1	****	<1	<1	<1	<1	1	<1	<1	<1	<1	<1	<1	<1	****	B
Mo	<0.3	****	<0.3	****	<0.3	****	****	****	****	****	****	****	<0.3	<0.3	<0.3	<0.3	****	Mo
Sr	1.2	****	0.6	****	<0.1	<0.1	<0.1	<0.1	1.6	<0.1	<0.1	0.5	<1	<1	<1	0.9	****	Sr
As		****	****	****	****	<1	<1	<1	<1	<1	2.3	<1	<1	<1	<1	1.9	****	As
Oil&Grea.	85	<10	<10	<10	<10	<10	<10	<10	<10	14	<10	<10	****	****	****	****	<10	Oil&Grea.
Phenols	0.08	0.1	<0.05	<0.05	<0.05	0.05	<0.05	****	****	0.29	<0.05	<0.05	****	****	****	****	<0.05	Phenols
Surfactants	<10	****	<10	****	<10	****	****	****	****	****	****	****	****	****	****	****	****	Surfactants
Samling ID	DV-1	DV-1	DV-2	DV-2	DV-3	DV-4	DV-5	DV-6	DV-7	DV-8	DV-9	DV-10	DV-S1	DV-S2	DV-S3	DV-S4	DV-Dam	Samling ID
Date	30 Sept.03	13 Nov.03	30 Sept.03	11 Dec.03	30 Sept.03	30 Sept.03	18 Nov. 03	18 Nov. 03	18 Nov. 03	18 Nov. 03	18 Nov. 03	########	25 Nov.03	25 Nov.03	25 Nov.03	25 Nov.03	11 Dec. 03	Date

Appendix 6: GPS coordinates for the water sampling points

Sample Name	latitude	longitude	elevation
Point A	-26,1578	27,8540	1645,0
Point C	-26,1610	27,8560	1727,1
Point E	-26,1618	27,8559	1737,1
Point Z1	-26,1573	27,8516	1699,9
Point Zm	-26,1574	27,8519	1692,7
Point Z2	-26,1618	27,8521	1691,8