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Radionalytical chemistry in support of the naturally occurring radioactive material (NORM) industries in South Africa

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Chapter 1 INTRODUCTION

1.1 Background

Humans are exposed to ionizing radiation from a number of sources, of which the largest proportion (about 75%) comes from natural sources – see Figure 1-1. These include external sources of radiation (*e.g*. from soil), as well as inhalation and ingestion of radioactive materials, which occur everywhere in the environment. According to the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) the average global radiation dose received by an individual from natural sources is 2.4 $mSv.a^{-1}$; with regional variations from 1-13 $mSv.a^{-1}$ (UNSCEAR, 2000).

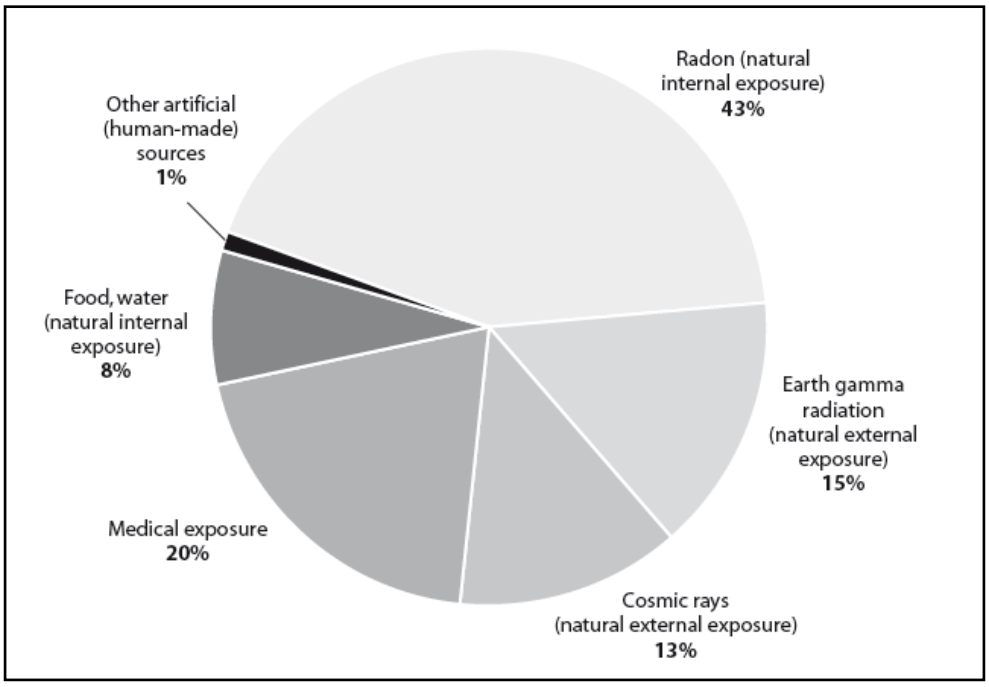


Figure 1-1: Sources of radiation contributing to public exposure (UNSCEAR, 2000)

The naturally occurring radioactive elements Uranium and Thorium are widely distributed in ores and minerals the earth's crust. Exploitation of the mineral resources containing U and Th may result in elevated concentrations of the natural nuclides in products, residues, waste and the environment at industries involved with processing of these raw materials (International Atomic Energy Agency, 2003a). This can result in exposure to the public via different pathways, of which the most important are:

— Emission of gamma rays from the ground and building materials (external)
— Transfer of radioactivity to water and plants (ingestion)
— Release of the gaseous element radon into the atmosphere (inhalation).

Naturally Occurring Radioactive Material (NORM) present in the environment has created a scientific interest in NORM and the study of their behaviour. The term NORM is used to describe situations where the potential exposure to ionising radiation from materials containing naturally occurring radionuclides has increased as a result of human activities compared to the situation where those materials were left undisturbed. Knowledge of radionuclide activity in environmental media is required to (1) identify the sources of the radionuclides, (2) estimate the radiation dose received by individuals, (3) evaluate the dose contribution through consumption of food from farms in the vicinity of the industries, (4) check compliance with radioprotection norms, (5) assess the efficiency of techniques for the elimination of incorporated radionuclides and (6) establish the background radiation of areas planned to be exploited. Dose assessments are usually based on models, which in turn rely on accurate analytical measurements. Appropriate radio-analytical techniques to be used for this purpose are the main focus of this thesis.

Mineral resources in South Africa contain significant concentrations of radionuclides from the natural uranium- and thorium decay series. This may result in exposure to communities living around areas where the minerals are exploited. Industries of concern include the building-, coal-, phosphate-, and mineral sands industry and gold mining. The type of plant operation, the treatment of effluents, as well as the socio-economic habits of people living in the vicinity of the mining- and mineral processing operations will influence exposure. The industry operator is responsible for radiation protection of both people and the environment in relation to all industrial and mining activities. This responsibility includes assessing the actual or potential radiological impact arising from operation and, where required, undertaking sampling and measurements to collect the necessary data to enable such assessment. The radiological impact of all operations in SA is monitored as part of the license obligations, imposed by the South African Nuclear Energy Act and enforced by the South African National Nuclear Regulator (NNR) (South African government, 1999a).

Legislation in South Africa allows for an annual radiation dose of $1 mSv.a^{-1}$ to the public, similar to the internationally accepted standard (International Commission on Radiological

Protection, 1991). The sum of the contributions from every individual nuclide from all possible sources is considered for the annual dose. The NNR recommends the evaluation of an individual nuclide at the level of 0.025 $mSv.a^{-1}$ to enable them to assess the total dose to the public from all sources at the level of 1 $mSv.a^{-1}$ (National Nuclear Regulator, 2013). This present some challenges to the radioanalytical laboratory to measure the various radionuclides in a variety of matrices at the required sensitivity for proper dose evaluation. The required sensitivity of the radiometric techniques depends on the type of sample and the purpose for which the data has to be used.

1.2 Problem statement

It is important for industry and regulatory bodies in a country to understand the occurrence of NORM within a specific process and to identify locations with enhanced concentrations of NORM. In this regard it is important to assess the potential sources of NORM, processes contributing to increased concentrations and release of NORM into the environment, and the resulting exposure to humans. The best process to follow by industries to determine whether regulatory control with regard to radioactivity is required is to establish a monitoring programme and conduct a survey to determine the radionuclide content of potential sources of NORM. This is where the radio-analytical laboratory plays an important role in analyzing samples from various sources in the industrial processes and environmental media. Based on the radio-analytical results a decision is made to proceed with the radiological assessment to determine impact on workers and the public. The analytical results used must be reliable since any decisions made may have a significant impact on human health and the environment. The thesis addresses the need to produce radio-analytical data, which are appropriate for the intended use.

The question to be answered in this study is: How can radiometric techniques utilized effectively to support NORM industries in South Africa to comply with regulatory requirements in order to minimize the environmental impact of the industries?

1.3 Aims and Objectives

The broad aim of this study is to give an indication of the radiological impact of some of the NORM industries in South Africa, with main focus the impact on humans. To achieve this, the results of samples analysed at the radio analytical laboratory at the South African Nuclear

Energy Corporation (NECSA) were used. The focus of the submitted work is on the analytical techniques, measurement and the results obtained. Radiological impact assessments for each industry, where all potential sources and pathways are considered to determine the levels of radiation exposure from each scenario, are not within the scope of this thesis; however to illustrate the use of radiological data some case studies are included.

In general, the overall objective of this study is to investigate how radiometric techniques can support industries in radiological assessments to comply with regulations in order to restrict the radiological impact on humans and the environment. In specific terms, this study focuses on the following objectives:

- To investigate the implementation of radiometric techniques.
- To assess the advantages and limitations of the radiometric techniques utilized at the radio-analytical laboratory of NECSA.
- To demonstrate the application of the analytical methodology in support of environmental monitoring programmes of NORM industries.
- To present radio-analytical data for samples of environmental media in the vicinity of selected NORM industries.
- To determine the potential radiological impact of South African NORM industries.

1.4 Significance of the study

The justification for this research is founded on the following:

- There has been an increase in public concern of the radiological impact of NORM industries. To address these concerns reliable analytical data is required, which can only be obtained by the sensitive and specific methods for radionuclide determination discussed here.
- There is a lack of scientific published information on radioactivity of materials from NORM industries in SA. Data for Southern Africa in international databases compiled by the IAEA are scarce. Many samples from various industries in South Africa are analysed routinely for radioactivity but the analytical results are mostly used in unpublished reports. Some of this existing data are presented in the thesis.
- Potential human exposure due to ingestion of contaminated water and foodstuffs in the environment around mining areas, have received press attention in South Africa

on many occasions. Available data can be used to address these concerns.

— Environmental protection and the impact of radioactivity on non-human biota has become an important field of study worldwide in recent years. To date, no official research has been done in SA. National guidance on protection of non-human species currently lags behind international guidance. The importance of reliable analytical data to support models used for assessing ionising radiation exposure and absorbed dose rates to animals and plants are illustrated in the thesis.

— Models are used as tool to predict the concentrations in plants and animals from soil concentration. The predicted data do not necessarily match measured values obtained by analysis of water, fish and plants. Models rely on theoretical transfer values. Existing values recommended by the NNR for South African use were compiled from international documents, but have never been experimentally confirmed. Some preliminary work in this regard is presented in the thesis.

— In areas with enhanced radioactivity due to either natural occurrence or historical contamination, it is difficult to decide if increased levels are the result of industrial activities or just natural variations. Data from a region with no mining activities may give an idea of variations of natural background and serve as a baseline against which possible future industrial activities can be compared. Baseline maps are important, and have never been done in SA. Results for background media are presented here.

1.5 Scope and limitations of the thesis

The scope of the study is restricted to natural radioactivity. There are a number of NORM industries, which may significantly contribute to radioactivity in the environment. This study focuses prominently on the building-, coal-, phosphate-, and mineral sands industry and gold mining. Activities such as releases from nuclear power stations and nuclear fuel cycle facilities, which can result in artificial radioactive contamination of the environment, are excluded.

The first phase of a monitoring programme for any industry focuses on gathering information on the radionuclide content of the various sources from the industrial process *e.g.* waste products. The potential radiological impact on workers and the public is determined using the results and default intake values. A large number of samples were analysed for this purpose. In this work only the possible radiological impact on the public is considered;

impact on workers is excluded.

For a second phase survey the impact of secondary intake *i.e*. the consumption of meat and milk of cattle grazing on, or crops growing in contaminated soil, or through intake from fish, are considered. Some of the work presented here focus on aspects of these transfer pathways of secondary intake. The possible effect of radioactivity on non-human biota is also briefly addressed.

There are a number of pathways that contribute to the overall dose obtained by man. In this study mainly the ingestion pathway is considered. Measurement of radionuclide concentrations in air, and the resulting dose due to inhalation of radon, is not addressed, since RA does not perform measurements of radon and radon progeny in surface air. Data on the radiological quantity of various water sources in South Africa, including bottled water, surface and groundwater, is presented. Results for other samples including fish and foodstuff, non-human biota species, soil, sediment and other solid material, are also presented.

In many countries the analytical data of environmental assessments is accessible to the general public. Unfortunately, with the exception of monitoring of the radiological status of South Africa's water resources by the Department Water Affairs and Sanitation (DWS, 2006), there is no state-funded national radioactivity monitoring programme to assess the radiation exposure to the public in South Africa. Even though a vast amount of analytical results was available for the thesis, the use of this data is restricted due to permission issues. It is therefore necessary to present the case studies in a very general manner. The origin of samples is only explicitly mentioned in the text when collected from non-mining properties and received from an independent source *e.g.* universities.

1.6 Thesis outline

This thesis consists of six chapters. In Chapter 1 a short background of the proposed study is given. The problem statement, objectives, scope and limitations, as well as the significance of the study, are also stated.

Chapter 2 contains the literature review and includes general information on natural occurring radionuclides, radiological protection and dose evaluation, protection of the environment and applicable regulations. Typical occurrence of natural radionuclides in water,

plants and food, sediment and soil, humans and mammals, and in the coal-, building-, phosphate-, mineral sands- and gold mining industry are discussed. The chapter is concluded with a review of radiometric techniques.

The research method and limitations are stated in Chapter 3. The experimental development and implementation of appropriate analytical techniques is described in Chapter 4. Validation reports, which contain the details of the experimental work performed by the author when implementing the procedures, form an integral part of this study. Some reports are available in Appendix D.

Chapter 5 presents findings and analysis of the research. Case studies, in which the analytical data are successfully applied, are presented. The chapter is divided into sub-sections in which the radioactivity results of environmental media and various NORM industries are presented. The results for each industry are summarized, followed by a discussion of the main findings and trends, and then connected with the literature surveyed and any correlations that have emerged in the data are highlighted.

Chapter 6 summarizes the important conclusions that can be drawn from the results presented in this thesis and makes some recommendations for further consideration.

Chapter 2 LITERATURE REVIEW

In this chapter general information about the naturally occurring radionuclides and occurrence in various environmental compartments and non-nuclear industries are discussed. Theory is provided on applicable legislation for the protection of the public and environment and dose assessment methodology. The chapter is concluded with an overview of available radio-analytical methods for accurate and sensitive measurements of naturally occurring radionuclides.

2.1 Naturally Occurring Radioactive Material (NORM)

According to the International Atomic Energy Agency (IAEA), NORM "encompasses all naturally occurring radioactive material where human activities have increased the potential for exposure in comparison with the unaltered situation. Concentrations of radionuclides may or may not have been increased" (IAEA, 2003a). This material is subject to control by regulatory bodies.

Natural radionuclides is present in the Earth's crust and generally only occur in low or moderate concentrations in NORM *e.g.* in phosphate sedimentary rocks, although higher concentrations may be present in some NORM such as monazite sands and uranium ores. Human activities that exploit natural resources can enhance natural radionuclide concentrations either by creating by-products or residues through raw material processing or through increased bio-availability in the environment.

Low level exposure arising from NORM has been a topic of interest over many decades, due to the fact that more than 70% of the radiation dose to man can be from exposure to natural sources. Various concentrations of natural radionuclides are present in all environmental media *i.e*. rock, soil, water, food, air and the human body. Concentrations of natural radioactivity in foodstuffs and humans had been recorded as early as 1965 (Hill, 1965). Measurement of the radioactivity content of food and water samples, and other environmental media, is required to assess the potential radiation dose and is especially important in areas where human activities have increased the levels of these nuclides.

Figure A-1 (Appendix A) gives the three natural decay series, also known as the naturally occurring radionuclides, which are the nuclides of concern found in NORM. The radiological

properties of these radionuclides, as obtained from the NUDAT database, are summarized in Table A-1 in Appendix A (NUDAT, 2017).

2.1.1 Properties of decay chains and radioactive equilibrium

The elements in the decay chains are usually immobile in solids such as soil, rocks and ore, leaving the mixture of radionuclides relatively undisturbed. The radionuclides are said to be in secular equilibrium, which means that all the radionuclides in the specific decay chain have similar activity concentrations (Friedlander *et al*., 1981). In soils the ^{232}Th series nuclides will mostly be in equilibrium, whereas equilibrium in the ^{238}U series may be disturbed due to the formation and emanation of ^{222}Rn into the atmosphere (Linsalata, 1994). The radioactive equilibrium in soil can also be disturbed due to chemical or physical processes, such as leaching or erosion.

Disequilibrium in water is very often found due to a difference in precipitation and dissolution behaviour of the decay chain elements. Industrial activities can also have a large impact on enhancement of the radioactivity concentrations of certain nuclides. As indicated below in the ^{238}U series disequilibrium is most likely to occur between ^{234}U and ^{230}Th, ^{230}Th and ^{226}Ra, ^{226}Ra and ^{222}Rn; and also between the short-lived ^{222}Rn progeny and ^{210}Pb. Disequilibrium may also occur between ^{210}Pb and ^{210}Po. Within the ^{232}Th series the major points of disequilibrium occur between ^{232}Th and ^{228}Ra and between ^{228}Ra (^{228}Ac) and ^{228}Th. ^{228}Th and its progeny is assumed to be in equilibrium (Linsalata, 1994).

^{238}U series: $^{238}\text{U} = {}^{234}\text{U} \neq {}^{230}\text{Th} \neq {}^{226}\text{Ra} \neq {}^{222}\text{Rn} \neq {}^{210}\text{Pb} \neq {}^{210}\text{Po}$……

^{232}Th series: $^{232}\text{Th} \neq {}^{228}\text{Ra} = {}^{228}\text{Ac} \neq {}^{228}\text{Th} \neq {}^{224}\text{Ra} = {}^{212}\text{Pb}$……..

Because of the lack of equilibrium in biological and many environmental samples the individual analysis of all these nuclides is desirable. One of the first indicators of possible human influence in an area is the lack of secular equilibrium among natural decay radionuclides.

Isotopic ratios

^{238}U /^{235}U ratio: In natural uranium ^{235}U will always be present in a constant ratio relative to ^{238}U. The natural isotopic ratio is 21.7.

^{238}U/^{234}U ratio: The ratio in ores, rocks and soil would be close to 1.0. Higher concentrations

of ^{234}U compared to ^{238}U are often found in water.

$^{238}U/^{226}Ra$ ratio: In soil apparent loss of ^{238}U are sometimes observed due to higher mobility of U compared to Ra.

$^{210}Pb/^{226}Ra$ ratio: Overabundance of ^{210}Pb relative to ^{226}Ra is caused by deposition of the nuclide originated by decay of radon gas.

$^{232}Th/^{238}U$ ratio: The average Th/U mass ratio in the earth's crust is about 2.7, which is a natural activity ratio of $^{238}U/^{232}Th$ of 1.12 (UNSCEAR, 2000).

$^{232}Th/^{228}Th$ ratio: This ratio gives an indication of when a Th specimen was purified.

$^{230}Th/^{232}Th$ ratio: This ratio can give an indication of the $^{238}U/^{232}Th$ concentrations in samples where U was not actually measured. For geologically old and undisturbed material ^{230}Th is always in equilibrium with ^{238}U and the same ratio as for $^{238}U/^{232}Th$ of about one is expected. In Th-bearing material such as mineral sands $^{230}Th << ^{232}Th$, since this material contains less U than Th.

$^{232}Th/^{228}Ra$ ratio and $^{230}Th/^{226}Ra$ ratio: Due to chemical differences between Th and Ra this ratio will deviate from unity. Th is more particle-reactive and are less soluble than Ra.

2.1.2 Uranium

Occurrence and properties

Uranium, a silver-gray heavy metal with atomic element 92, is commonly found in various mineral deposits in nature. It will be present in environmental media mainly due to emissions from the nuclear industry, release from waste and tailings, combustion of coal, use of phosphate fertilizers and leaching from natural deposits (UNSCEAR, 2016).

Uranium most commonly occurs in nature as the uranyl ion, UO_2^{2+}, in the hexavalent valence state (Gindler, 1962). In the +6 state U is mobile due to formation of uranyl complexes, whereas it remains immobile in the +4 state precipitating as UO_2. It is chemically reactive forming several compounds with other elements.

Natural uranium consists of the three isotopes, ^{238}U, ^{235}U and ^{234}U in mass concentration ratios as indicated in Table 2-1. When secular equilibrium exists, the activity of ^{234}U and ^{238}U

would be equal, but the masses would differ. The activity per unit mass (specific activity) for natural uranium is 25.4 mBq per µg.

Table 2-1: Standard composition of uranium

Isotope	U-238	U-235	U-234	Ratio 238/235	Ratio 238/234
Half-life	4.468×10^{9}	7.037×10^{8}	2.470×10^{5}		
Natural 1 µg = 25.346 mBq					
Mass %	99.274	0.7205	0.00545	138	1.82E+04
Activity %	48.85	2.30	48.85	21.3	1
mBq per µg U	12.34	0.576	12.43		

Principle emissions

Due to its long half life and low intensity gamma emission of 48 keV, the external radiation risk from ^{238}U is low. As an alpha emitter the main risk is from ingestion. Table A-3 (Appendix A) shows the principal emissions of the three most important uranium isotopes. The three isotopes have similar dose coefficients, based on similar retention time in body tissue and similar alpha particle energies.

^{238}U has a low specific activity, due to its long half-life. Therefore the chemical concentration of ^{238}U, at a concentration which represents a radiological risk, is also significant and has to be considered. Uranium is of concern both because of its chemical- and radio toxicity. The specific activity values in Table A-1 (Appendix A) are used to convert from activity concentration to chemical concentration units. The relationship between the mass, M and activity, A, of a radionuclide is given by equation 2-16.

Uranium in soil and sediment

The concentration of natural radionuclides in the earth's crust depends on the type of rock; phosphates and granites are particularly rich in uranium. U is released to the environment through natural processes such as erosion of soil and leaching to ground- and surface water. The U in soil can be taken up by animals and plants resulting in exposure to humans through ingestion (Longworth *et al*., 1998).

The activity concentration of ^{238}U in soil can vary up to three orders of magnitude (Ewers *et*

al., 2003) depending on location, with concentrations as high as 6200 $Bq.kg^{-1}$ reported in sedimentary rock in Brazil (UNSCEAR, 2016). The Uranium concentration in undisturbed normal soil ranges from 1 to 10 $mg.kg^{-1}$, with an average of 3 $mg.kg^{-1}$ quoted in some sources (76 $Bq.kg^{-1}$ U; 37 $Bq.kg^{-1}$ ^{238}U) (UNS, 2008), and more recently reported as 1.2 $mg.kg^{-1}$ (30 $Bq.kg^{-1}$ U) (UNSCEAR, 2016). Concentrations in South African soils may be higher, because of its association with gold deposits.

U in sediment can be absorbed onto clay particles or associated with organic matter. When included in the crystal lattice of the sediment grains, the U-series nuclides are expected to be in equilibrium. Since U is more soluble than thorium, it is often found in lower concentrations than Th in solids.

Uranium in water

U concentration in water depends on many factors such as the presence of chemicals and complexing agents in the aquifer and the concentration in the host aquifer rock. Uranium is found in U^{4+} states (immobile state) in a rock and in a more reducing environment. Once released in the presence of oxygen uranium changes to U^{+6} oxidation state (the mobile state). The stability of the uranyl carbonate complex and the long half-life allows for U to be transported long distances under oxidizing conditions.

The UNSCEAR reference value for ^{238}U in water is very low ~1$mBq.L^{-1}$ (UNSCEAR, 2000). In most surface water, the uranium concentrations range from less than 0.1 to 10 $\mu g.L^{-1}$ (~2 to 250 $mBq.L^{-1}$) but it can reach values of several $mg.L^{-1}$ in areas where natural radioactive minerals are abundant. As shown in Table A-17 (Appendix A), high concentrations of U are often found in surface, as well as groundwater worldwide with several sources exceeding the WHO guidance levels indicated in Table 2-4.

Disequilibrium of uranium in water

Due to their long half-lives ^{234}U and ^{238}U are usually in secular equilibrium in a mineral matrix, rock or ore. This equilibrium can be disturbed by chemical and physical processes involving water. Waters in contact with rocks rich in uranium often contains excess ^{234}U, due to mechanical weathering and preferential leaching of ^{234}U from the granite bedrock. Solubility and mobilization of the decay product ^{234}U are enhanced by alpha recoil

(Ivanovich, 1994).

Generally the activity concentration ratio of $^{234}U/^{238}U$ in natural water is greater than unity and ratios of up to 20:1 have been reported (Shabana & Kinsara, 2014). Lower ratios (<1.5) are found in samples with higher uranium concentrations (> 200 $mBq.L^{-1}$) (UNSCEAR, 2016). The $^{234}U/^{238}U$ ratio can give an indication of the origin of the uranium observed in water –a ratio close to one indicating possible contamination of the water by U-bearing ores (Skwarzec *et al*., 2001).

Because of the disequilibrium between ^{234}U and ^{238}U found in water, isotopic analysis is important to accurately estimate dose from uranium. The dose can be underestimated based on measurement of ^{238}U only (*e.g*. by a chemical technique) and assuming equilibrium. Due to its longer half-life, the mass of U is largely determined by ^{238}U, whilst the activity of all three uranium isotopes will contribute to the total activity in the water (see Table 2-1). Consequently, the concentration of each of the three uranium isotopes has to be known, for accurate conversion from mass to activity or vice versa.

Uranium in plants and food

Concentrations of uranium in air are typically very low (about 0.001 $mBq.m^{-3}$) and deposition is therefore not an important contributor to plant concentrations (UNSCEAR, 2000). Given that U is relatively mobile in soil, root uptake becomes important. Because of its ability to absorb to cell walls U is not very mobile in plant tissue. U concentrations are often much lower in leafy- than in root vegetables (UNSCEAR, 2016).

Intake of uranium in food varies as indicated in Table A-18 (Appendix A), with reported intakes as high as 178 mBq ^{238}U per day (14.3 µg of uranium). The average intake seems to be about 1.2 $µg.d^{-1}$ (33 $mBq.d^{-1}$), contributing to a very low annual dose of 0.64 µSv. Studies conducted in the Unites States found the largest intake to be from certain kinds of fish, vegetables and cereal products (Fisenne *et al.*, 1987), whereas concentrations in meat and milk are typically very low: Meat: 0.8-20 $mBq.kg^{-1}$; and milk: 0.012-15 $mBq.L^{-1}$ (UNSCEAR, 2016). Intake from drinking water is 0.2 $µg.d^{-1}$ (5 $mBq.d^{-1}$) (UNSCEAR, 2000), which is small compared to other foodstuff. Even though not the main source of ingested uranium, the contribution of drinking water may not always be negligible because high concentrations may occur in some water sources.

Uranium in humans and mammals

The main pathways for uranium from the environment to humans include inhalation of airborne dust particles and ingestion of drink and food. The estimated intake of U through inhalation is generally low (4.5 $mBq.a^{-1}$) compared to intake from ingestion, contributing to an annual dose of 0.046 µSv (UNSCEAR, 2016). As an alpha emitter, uranium can cause damage to DNA if it reaches the cell nuclei. However, chemical toxicity of U usually dominates in human and ecological risk assessment.

2.1.3 Thorium

Occurrence and properties

Thorium has a half-life of $1.4x10^{10}$ years and occurs naturally (as ^{232}Th with 100% natural abundance). In the environment Thorium is absorbed onto clays and other soil colloids and is also present as a trace constituent in silicate and phosphate minerals. High concentrations of naturally occurring thorium (as ThO_2) is incorporated in monazite (20%) and zircon (3-9%) (IAEA, 2006).

There are six Th isotopes in the natural environment: ^{234}Th, ^{228}Th, ^{230}Th, ^{232}Th, ^{231}Th and ^{227}Th. The potential hazard is mostly from the α-emitting nuclides ^{228}Th, ^{230}Th and ^{232}Th due to their long half-lifes. ^{232}Th and ^{228}Th are present in thorium minerals, whereas ^{230}Th is associated with natural uranium. ^{230}Th is highly radiotoxic for intake (Table A-5, Appendix A), while ^{232}Th due to its low specific activity is less so. The contribution of ^{230}Th in radiological dose assessments should therefore not be ignored. Exposure to ^{232}Th and decay products will be mainly from ingestion through diet, inhalation of contaminated dust particles and external gamma radiation. The latter can contribute significantly to dose, for example, in building materials rich in natural radioactivity.

A "natural" isotopic composition cannot be assumed for thorium found in nature, as the $^{230}Th/^{232}Th$ activity ratio can vary widely between ores. $^{230}Th/^{232}Th$ activity ratios ranging from 0.738 to 1.96 have been reported (Fretzdorff *et al.*, 2003). In an ore secular equilibrium of ^{232}Th with all its decay products is expected. This equilibrium is disrupted when thorium metal is separated from the ore, and is not achieved again shortly, due to the relatively long half-life of 5.75 years of the immediate daughter ^{228}Ra.

The behaviour of Th in ion exchange separations is influenced by the strong tendency of the positive ion, Th^{4+}, to form complexes. The low solubility of Th is utilized for radiochemical separation from other elements. Th precipitates as the oxalate, phosphate and with lanthanum fluoride (Hyde, 1960).

Less research has been done for thorium compared to the large amount of published research for uranium. However, scientific interest in thorium has increased in recent years, mostly with respect to mining operations of thorium-rich minerals such as zircon and monazite.

Thorium in soil

Thorium is fairly abundant in the earth's crust occurring naturally in many minerals. Due to its higher abundance compared to U, high ^{232}Th mass concentrations are expected in soil. Concentrations vary from 2-12 $mg.kg^{-1}$ with a world median concentration average of 8 $mg.kg^{-1}$ (33 $Bq.kg^{-1}$) (UNSCEAR, 2008). In monazite regions in the southwest coast of India, the concentrations of Th in the soil are as high as 400-4000 $mg.kg^{-1}$ (Dang *et al.*, 2000).

The average natural mass ratio Th/U expected is about 2.7, whereas due to the higher specific activity of ^{238}U, the radioactivity ratio of $^{238}U/^{232}Th$ is about 1.12. Despite the higher abundance of Th, it is less mobile and seldom present in soluble form in ground- and surface water. Tetravalent thorium strongly sorbs onto rock minerals and soil, and high concentrations are expected in sediment compared to water. It also has a strong tendency to attach to particles (Nour *et al*., 2002).

Thorium in water

Even though mining operations may release thorium into surface water the concentrations will be lower compared to other elements such as U, due to its low solubility. The world average concentration in water is 0.03 $\mu g.L^{-1}$ (0.12 $mBq.L^{-1}$), which is much lower than that of U (UNSCEAR, 2000). Higher concentration can be expected in water from regions with high natural Th, such as monazite areas.

Because of their relative insolubility in water, thorium isotopes would normally not be encountered at concentrations exceeding the gross alpha screening level in water and regulations in most countries therefore do not routinely require analysis. Since elevated ^{230}Th concentrations has been found in some waters from the South African mining industry

(Figure 2-1), measurement of the thorium isotopes is routinely included in the scope of nuclide specific analysis of water when monitoring for compliance purposes.

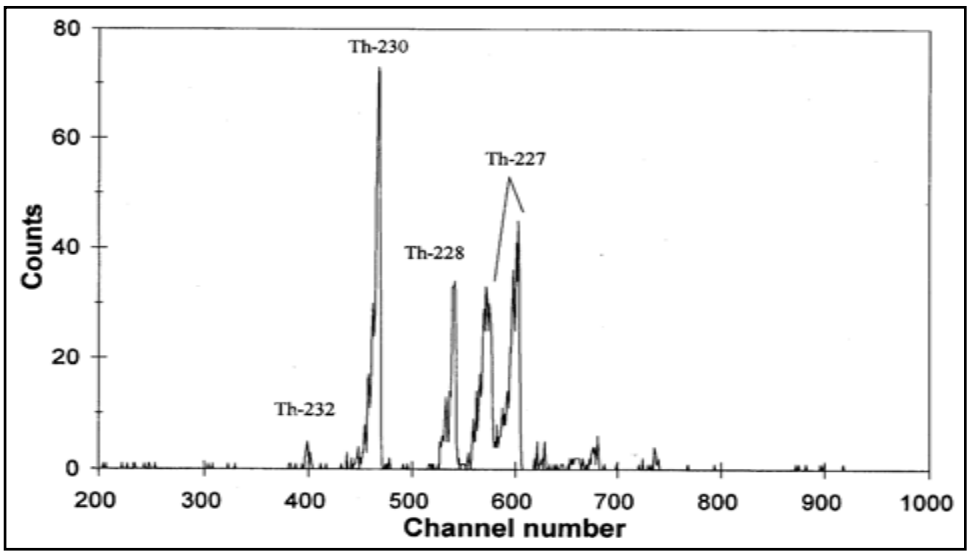


Figure 2-1: Typical alpha-particle spectrum of thorium analysis by radiochemical separation showing high ^{230}Th concentration.

Thorium in plants and food

Th is immobile in soil and less available for uptake by plants, than U. Higher concentrations of ^{230}Th and ^{228}Th than ^{232}Th may be found in foodstuffs. ^{228}Th is associated with ^{228}Ra. Ra has higher bioavailability and is often concentrated in vegetables, and therefore ^{228}Th, as decay product of ^{228}Ra, will also be present in higher concentrations than ^{232}Th. ^{230}Th is produced from ^{234}U, known to be more mobile than ^{238}U due to α-particle recoil effect, and expected to be more present in plants compared to ^{232}Th.

Thorium in humans and mammals

Inhalation is the main pathway for intake of Th. Due to its low absorption by the human gut, intake through ingestion is considered as a minor pathway (ICRP, 1996). The daily intake of Th (from drinking water and food) varies from 0.9 µg (3.5 mBq) in low background areas to 27.8 µg (113 mBq) in high monazite areas such as India (Dang *et al.*, 2000). This results in an annual dose of about 0.016 mSv from dietary intake of ^{232}Th, which is only a small fraction of the dose of 0.14 mSv.a^{-1} expected from ingestion of food (UNSCEAR, 2000).

2.1.4 Radium

Occurrence

Radium is present in uranium-bearing ores and can be released during processing of the radioactive minerals. Large quantities can accumulate in waste by-products from NORM industries (IAEA, 2014a). High concentrations may be found in well water and geothermal sites in geographical regions with naturally high concentrations of uranium and thorium in soil and rocks.

Four isotopes of radium are present in the three natural decay series (^{228}Ra, ^{226}Ra, ^{224}Ra and ^{223}Ra) – see Figure A-1 (Appendix A). When separated from its parent Th isotope, each Ra isotope produces a chain of short-lived decay products. For ^{226}Ra, the immediate decay product is ^{222}Rn, which may be readily lost from the material. If not, its short-lived products will decay with the half-life of ^{222}Rn to form ^{210}Pb. For ^{228}Ra, secular equilibrium will usually be established with the immediate daughter ^{228}Ac, while ^{228}Th will grow into equilibrium with a half-life of 1.9 a (IAEA, 2014a).

^{226}Ra has been widely studied, due to the high abundance of its parent ^{238}U in the earths' crust, high radio toxicity and its relative long half-life. Due to it high specific activity (see Table A-1, Appendix A), trace levels of ^{226}Ra can have significant activity. ^{228}Ra is even more radiotoxic than ^{226}Ra, with dose conversion factors (DCF) for ingestion of 2.8×10^{-7} and 6.7×10^{-7} Sv.Bq^{-1} for ^{226}Ra and ^{228}Ra respectively (ICRP, 1996).

As an alkaline earth metal, Ra has similar chemical properties as Ba and Ca. It exists as the divalent ion in solution, which is not easily complexed (Kirby, 1964). Ra forms insoluble carbonate and sulphate salts, whereas the nitrate, hydroxide and chloride salts are soluble in water. Ra co-precipitates with Ba- and to a lesser amount with Pb compounds, which is the principle used in many analytical techniques for chemical separation of radium. This similar chemistry also complicates many methods because lengthy procedures are required to remove other group (II) elements (see 2.13.13).

Radium in soil

^{226}Ra concentrations in soil worldwide vary from 3.7 to 126 Bq.kg^{-1} (Table A-19, Appendix A). Assuming radioactive equilibrium with ^{238}U, the estimated world average for ^{226}Ra activity in soil is 37 Bq.kg^{-1} (UNSCEAR, 2008).

Behaviour of Ra in soil is similar to other group (II) elements, with uptake influenced by factors affecting the soil exchange capacity. Radium is tightly bound to the regular exchange sites of the soil and is therefore not freely available for plant uptake. It is not easily leached. The equilibrium between ^{226}Ra or ^{228}Ra and their precursors, *i.e.* ^{230}Th and ^{232}Th, can be disturbed because of the differences in their mobility in soil.

Radium in water

Radium is present in water mainly due to the interaction of ground- or surface water with ores, rocks and soil containing Ra. ^{226}Ra concentrations in groundwater can differ significantly, as seen from the data in Table A-17 (Appendix A). High ^{226}Ra and ^{228}Ra is present in groundwater in areas close to U or Th ore bodies or in the presence of granite rock (Zhuo *et al*., 2001). Some mineral and thermal water may have high ^{226}Ra concentrations up to several Bq.L^{-1} (Bronzovic & Marovic, 2005). The concentrations in water can be reduced by co-precipitation and sorption when in contact with soil or sediments (IAEA, 2014a). Studies suggested that Ra is rapidly adsorbed from groundwater onto clays and mineral oxides. Almost all Ra in groundwater is adsorbed on particle surfaces, which affects the mobility (IAEA, 2014a).

The concentrations of the two most important radium isotopes present in water, ^{226}Ra and ^{228}Ra should be roughly equal. The concentration of ^{228}Ra depends on the concentration of thorium in the aquifer solids. Despite higher abundance of Th, geochemical factors may cause increased concentrations of U, which often results in higher concentrations of ^{226}Ra relative to ^{228}Ra in natural waters (De Oliveira *et al*, 2001). Although they are chemically similar the shorter half-life of ^{228}Ra (5.7 years) also limits its distribution in groundwater.

Ra concentrations in surface waters are generally lower than in most groundwater (Table A-17, Appendix A), but concentrations as high as 650 mBq.L^{-1} have been reported. Less data are available for ^{228}Ra, but the range seems to be similar to that for ^{226}Ra (IAEA, 2014a).

Analysis for ^{226}Ra in drinking water is routinely done in most countries, since it is considered to be one of the main sources for intake (UNSCEAR, 2000). Analysis of ^{226}Ra and ^{228}Ra are included in the new European directive for drinking water (European Union, 2013a). US regulations also require analysis of both ^{226}Ra and ^{228}Ra (2.2.7).

Radium in plants and food

Plants absorb and concentrate Ra from soil in the same way as they do calcium, which plays an important role in plant nutrition and growth. Tabulated concentrations in plants vary over a wide range (see Table A-18, Appendix A), with activity concentrations of ^{228}Ra mostly higher than that of ^{226}Ra, probably as result of higher concentrations in soil. Typically, low concentrations of ^{226}Ra are observed in plants from background areas, because of the affinity of Ra for ion exchange sites in the soil. For cereals and vegetables concentrations vary with produce type from below limit of detection to 2.2 Bq.kg^{-1}. Higher concentrations are found in vegetables with high Ca content such as beans and mushrooms. Concentrations are lower in grain and fruit than in vegetative portions (root, stems and leaves) (IAEA, 2014a). Ra is probably translocated to areas of maximum plant growth, such as leaves and root tips, and then accumulates in these plant parts.

Radium in humans and biota

Radium intake by man is primarily from dietary sources (UNSCEAR, 2000). ^{228}Ra contributes more to ingestion dose than ^{226}Ra due to a higher DCF; 0.021 and 0.008 mSv.a^{-1} respectively of the total dose of 0.14 mSv.a^{-1} from food intake (UNSCEAR, 2000).

Radium follows the metabolic path of calcium. As a “bone seeker” it lodges mainly in the skeleton. The concentrations of ^{226}Ra in bones and teeth of cattle will generally be higher than concentrations in muscle (or soft tissue) of the same source (IAEA, 2014a, p.69). Low transfer of radium to animal products has been reported, with lower transfer to milk than to beef, consistent with the UNSCEAR reference activity concentrations for ^{226}Ra of 5 and 15 Bq.kg^{-1} (FW), for milk and meat respectively (UNSCEAR, 2000).

2.1.5 Polonium and Lead

Occurrence and Properties

In appearance, polonium resembles a silvery gray dust, if you can get enough of it together to actually be able to see it. It can be produced by neutron activation of ^{209}Bi (^{209}Bi (n, γ) ^{210}Bi $\rightarrow$ ^{210}Po) (Figgins, 1961). Polonium occurs in oxidation state +4 and forms complexes in hydrochloric acid solutions, probably $PoCl_6^{2-}$ or $PoCl_4^{2-}$. It is only partially complexed in nitric acid solution. Therefore, to prevent losses due to absorption, storage of polonium in hydrochloric solution is preferred (Chen *et al*, 2001).

Lead metal is a silver-gray soft metal. The only oxidation state of importance in aqueous solution is the +2 state. Lead will be soluble in chloride solutions, when an excess of ethylene-diamine-tetra-acetic acid (EDTA) is added, due to formation of the very stable EDTA-lead complex. This complex is sufficiently stable to prevent lead sulfate from precipitating under certain conditions, which is utilized for the method for Ra separation commonly used in laboratories worldwide (see 2.13.13).

^{210}Po is an alpha emitting nuclide in the ^{238}U decay series with a half-life of 138.38 days. Because of the short half-life it has very small mass, therefore requiring the use of radiometric techniques for determination. Table A-2 and A-3 in Appendix A show the decay properties of the Pb and Po isotopes of interest for this thesis. Both ^{209}Po and ^{208}Po can be used as radiochemical yield tracers. The gammas of ^{214}Pb and ^{212}Pb are used for indirect determination of ^{226}Ra and ^{228}Ra (see Table A-2, Appendix A). ^{210}Pb is a beta emitter and emits a gamma ray at 46.5 keV.

If taken into the body by ingestion, inhalation or through wound entry, ^{210}Po represents an internal radiation hazard. It has been extensively studied over the last 45 years because of its important contribution of about 7% of the natural internal radiation dose and 29% of the average internal dose due to ingestion (UNSCEAR, 2008).

Due to the high specific activity of 1.66×10^{17} Bq.kg^{-1} (see Table A-1, Appendix A), ^{210}Po is highly radiotoxic. The high radio toxicity became notorious with the murder of the former Soviet spy Alexander Litvinenko in 2006 (Health Protection Agency, 2006), who is the first person known to have died of ^{210}Po exposure.

Polonium and Lead in the terrestrial environment

^{210}Po and ^{210}Pb is present in the atmosphere mostly due to continuous production from ^{222}Rn, which emanates from soil into the atmosphere. Radon then decays via short-lived daughters to ^{210}Pb and finally to ^{210}Po. ^{210}Pb and ^{210}Po are deposited onto the earth's surface as dry and wet deposition, resulting in uptake of ^{210}Pb and ^{210}Po in small amounts into animals and plants (Persson & Holm, 2011). Human activities such as phosphate fertilizer production and burning of fossil fuels like coal can also cause build-up of ^{210}Po and ^{210}Pb in the atmosphere.

The average activity concentration of ^{210}Pb and ^{210}Po in the atmosphere, is 0.5 mBq.m^{-3} and 0.05 mBq.m^{-3}, respectively (UNSCEAR, 2000). Annual dose from inhalation is 5.8 µSv (exclusion dose from radon), of which ^{210}Po and ^{210}Pb contributes 5.2 µSv.

Polonium and Lead in soil and sediment

^{210}Pb and ^{210}Po in soils may either be present as a product of decay of ^{238}U in the soil (supported) or from atmospheric deposition as decay products of radon (unsupported) (Hill, 1960). Usually only the top layer of soil will be contaminated from atmospheric fallout, with enrichment of ^{210}Pb with respect to ^{226}Ra in the first 10 cm, whereas equilibrium of all nuclides in the uranium series is expected in deep soil.

Activity concentrations of ^{210}Po in soils vary with soil type, with lower concentrations found in mineral- than in organic soils (Berger *et al.*, 1965). Beresford *et al.* (2008) reported concentrations ranging from 3-154 Bq.kg^{-1} in England (see Table A-19, Appendix A). Super phosphate fertilizers can also contribute to Pb and Po concentrations in soil and plants (Sethy *et al.*, 2015).

In sediment the concentration of ^{210}Po may vary depending on the efficiency of scavenging of soluble ^{210}Pb onto suspended matter and the level of organic material in the sediment. Sediment is often enriched with ^{210}Po relative to ^{210}Pb, due to higher reactivity of polonium towards particulate matter. Equilibrium between the two nuclides would be established within some months, if both remain immobile.

Polonium and lead in water

^{210}Po concentrations in water are low due to the very low solubility of polonium.

Consequently, contribution to dose from ingestion of water is usually quite small compared to intake of food. Non-regardless, in consideration of its high radio toxicity determination of its concentration in drinking water remains important. Due to the presence of granite bedrocks concentrations of ^{210}Po and ^{210}Pb in groundwater are usually higher compared to surface water.

^{210}Bi, ^{210}Po and to a minor extent ^{210}Pb are present in natural waters as hydrolyzed species (Figgins, 1961). These "surface-active" species are adsorbed onto colloidal minerals and organics and are therefore rapidly removed from the water. The highest concentration of Pb in groundwater is often found in the suspended particles (between 0.45 and 8 µm). Higher ^{226}Ra concentration compared to ^{210}Pb in published results for water seem to confirm a loss of ^{210}Pb due to precipitation or other factors (DeOliveira *et al*., 2001).

Polonium and Lead in plants and food

Both deposition of radioactive fallout and root uptake of ^{210}Pb and ^{210}Po may contribute to contamination of plants. Additionally plants may take up ^{210}Po present in certain fertilizers used in agriculture.

Since ^{210}Po and ^{210}Pb can accumulate in food, it is of great concern in radiation protection due to their radio toxicity. Global diets have been extensively sampled for the presence of these two nuclides. Reported data show a wide range (see Table A-18, Appendix A). In general: The concentrations of ^{210}Pb and ^{210}Po are high in seafood (Yamamoto *et al.*, 1994), intermediate in cereals and vegetables and relatively low in milk and meat. Concentrations are usually higher in leafy than in non-leafy vegetables as the result of atmospheric deposition (Hill, 1960; Persson & Holm, 2011).

- *Leafy vegetables:* For leafy vegetables the concentrations of ^{210}Pb and ^{210}Po are higher than for other crops. Concentrations in outer leaves are higher than in edible inner parts (Berger *et al.*, 1965).
- *Root crops:* Similar concentrations were found in crops grown in the open field or a tent (Pietrzak-Flis & Skowronska-Smolak, 1995) suggesting that the concentration in root crops is not affected by direct deposition from the atmosphere.
- *Cereals:* The edible part is mostly protected from direct deposition by chaffs.
- *Pasture:* As for leafy vegetables, ^{210}Pb and ^{210}Po in grass is mainly derived from

direct deposition on to the foliage.

Due to deposition of ^{210}Po with its grandparent ^{210}Pb on leafy vegetables, concentrations in tobacco may be quite significant. ^{210}Po is volatile at the burning temperature of a cigarette, 600-800^{o}C (Takizawa *et al.*, 1994). It binds to the surfaces of smoke particles and when inhaled can result in a dose as high as 0.29 mSv.a^{-1} (Savidou *et al*., 2006) [compared to the inhalation dose from atmospheric ^{210}Po and ^{210}Pb, which is 0.006 mSv.a^{-1} according to UNSCEAR, 2008].

Polonium in the marine environment

^{210}Po shows high accumulation in marine organisms due to atmospheric deposition of ^{210}Po in ocean water. Concentrations in species from the same region can vary, and as reported by Cherry *et al.* (1994) levels in individual fish of the same species can also vary significantly. The worldwide UNSCEAR reference value for ^{210}Po in seafood is 2 Bq.kg^{-1} with a range of 0.08 to 12 Bq.kg^{-1} (see Table A-18, Appendix A), but concentration as high as 220 Bq.kg^{-1} has been reported for some species (Carvalho, 2011). High concentrations of ^{210}Po were also reported for mussels: 227-389 Bq.kg^{-1} (Bode *et al*., 2015), 13-152 Bq.kg^{-1} (Carvalho, 2011) and 0.5-220 Bq.kg^{-1} (Yamamoto *et al*., 1994).

^{210}Po is considered as the most important contributor of dose to humans via fish and shellfish consumption (Chen *et al*, 2016; Heyraud *et al*., 1994). About 70% of the total dose due to ingestion comes from fish and shellfish (Sivakumar, 2014); therefore determination of ^{210}Po in marine organisms is very important, especially in populations whom consume large amounts of seafood.

A ratio of ^{210}Po/^{210}Pb > 1 is common in seafood, indicating high uptake of unsupported ^{210}Po (Skipperud *et al*., 2013; Yamamoto *et al*., 1994). Unsupported ^{210}Po will decay if stored for a period before consumption, which is the easiest way to reduce intake.

Polonium and Lead in humans and mammals

The major source of intake for ^{210}Po is ingestion, with a large percentage of daily Po intake coming from food (Fisenne *et al.*, 1987). Average annual dose from ^{210}Pb (0.028 mSv) and ^{210}Po (0.085 mSv) from food ingestion is 0.11 mSv, contributing about 80% of the total dose due to ingestion of 0.14 mSv (UNSCEAR, 2008). For some members of the public the dose

due to ingestion may be considerably higher due to the intake of foodstuff such as shellfish (Carvalho, 1995). Increased body burdens of ^{210}Po have been found where diets include protein-rich meat and seafood.

2.1.6 Industries and environmental media of interest for this study

As is clear from the discussion up to this point, radioactivity is ubiquitous in nature and contributes significantly to our everyday exposure. Exposure occurs either due to human activities, which disturb the natural sources of radiation making it more accessible to the environment or from an increase in the concentrations of naturally occurring radionuclides in some industries, including waste streams generated by the processes. Some of the industrial activities of interest in the thesis and which may result in enhanced concentrations of natural radionuclides in the environment are the following:

- Gold mining: Mining of uranium bearing gold ore produce tailings and can cause contamination of surface water through seepage from these tailings and waste rock dumps and release of liquid effluent and process water from mills and plants.
- Phosphate fertilizer industries: The mining and milling of phosphate ores produce large volumes of processed ore and tailings. Radionculides in the by-products, *e.g*. radium in phosphogypsum, can potentially reach streams and rivers if leached by rainwater.
- Mineral sands industry: Mining, separation and chemical processing of mineral sands rich in thorium and production of zirconia and titanium dioxide - these processes do not produce many waste products.
- Coal mining and combustion: When fossil fuels are used for electric power generation a large amount of radioactive ashes are formed as a residue from which nuclides may be leached to surface and underground water.
- Building material contains natural radioactivity causing external radiation exposure in buildings *e.g.* gypsum and fly-ash which are used as an additive in cement.

As stated in Chapter 1 the objective of this study is to investigate how radiometric techniques can be applied to assist with the evaluation of the environmental impact of these NORM industries. The occurrence of natural nuclides in the following environmental media, which are potential pathways of exposure to humans, is of interest: Water, Food, Soil, Sediment and other solids.

Sections 2.5 to 2.12 are devoted to a literature overview of the occurrence of natural radioactivity in environmental media and NORM industries worldwide and in SA.

2.1.7 Radionuclides of interest for this study

From the discussion in 2.1.2-2.1.6 it is clear that natural radionuclides are present in air, soil, water, food and the human body, and are of concern due to the fact that exposure to these natural sources may contribute to the radiation dose to humans. Table 2-2 shows the list of radionuclides in the uranium and thorium series, should be considered for dose assessment, also showing progeny assumed to be in secular equilibrium for dose calculation purposes, as is custom in most laboratories.

Table 2-2: Radionuclides of interest and secular equilibrium of progeny
Measured radionuclides for nuclide specific analysis of water indicated in green

	Radionuclide	Progeny
Uranium series	^{238}U	^{234}Th, ^{234}Pa
	^{234}U	
	^{230}Th	
	^{226}Ra	^{222}Rn, ^{218}Po,^{214}Pb,^{214}Bi,^{214}Po
	^{210}Pb	^{210}Bi
	^{210}Po	
Actinium	^{235}U	^{231}Th
	^{231}Pa	
	^{227}Ac	^{227}Th
Thorium	^{232}Th	^{228}Ra, ^{228}Ac
	^{228}Th	^{224}Ra, ^{220}Rn, ^{216}Po,^{212}Pb,^{212}Bi ,^{208}Tl, ^{212}Po

These are the nuclides for which methods for sensitive and accurate measurement in various matrices have been developed at the radio-analytical laboratory of NECSA and for which the analysis results are presented in this thesis. This list presents the nuclides prescribed by the NNR to be reported on for compliance purposes (NNR, 2013). The required sensitivity depends on the application for which the results are to be utilized, which may influence the choice of analytical technique. These requirements and limitations of various radiometric techniques used for detection of the radionuclides of concern are discussed in 2.13.

The laboratory does not perform analysis of radon. Thorium isotopes are included in the

scope of analysis due to the elevated ^{230}Th concentrations observed in some water samples from the South African mining industry (Figure 2-1). ^{231}Pa is not considered in this thesis, mainly because the importance of determination is not really recognized by the industry or the NNR. ^{227}Ac, a beta emitter is indirectly measured via alpha emitting daughters ^{227}Th and ^{223}Ra.

2.2 Regulations

In this section specific regulations applicable to the control of naturally occurring radionuclides in various industries are discussed. These include regulations for food, water, the building industry and solids from mining and NORM industries.

2.2.1 Regulatory framework

The international framework for radiation protection is well established and recognized. Organisations playing a key role are the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), the International Commission on Radiological Protection (ICRP), and the International Atomic Energy Agency (IAEA). The World Health Organization (WHO) also contributes in developing intervention levels, especially for water and food.

UNSCEAR uses scientific data to assess the effects of different levels of ionizing radiation exposure. Based on these scientific findings the ICRP publish recommendations, which are used as the basis for radiation protection of people and the environment. The IAEA compile safety standards to ensure a harmonized approach for radiation protection worldwide. The safety standards have a regulatory format but are not binding on individual countries, and are used to compile regulations at a national level.

The IAEA Basic Safety Standards (BSS) published in 1996 was a cornerstone of the IAEA safety standards for many years (IAEA, 1996). A new publication, in line with the new ICRP 2007 recommendations, was published in 2014 superseding the BSS (IAEA, 2014b). This publication aims to establish requirements (*i.e.* "shall" statements) for safety and radiation protection for all activities involving radiation exposure, including exposure to natural sources. Adoption and application of these requirements by all IAEA member states is encouraged.

The European Basic Safety Standards directive (BSS), also based on the new ICRP recommendations, was published by the European Commission to address radiation protection in the European Union (EU, 2013b). A list of specific industrial activities of concern was introduced in the new EU BSS.

2.2.2 Dose limits

The ICRP recommends that "any additional annual dose due to human activities should be kept *as low as reasonable achievable (*ALARA*)* but below the individual dose limit". A dose limit of 1 $mSv.a^{-1}$ is internationally accepted for members of the public (ICRP, 2007). This limit has been implemented in most countries worldwide. All pathways from all sources for all practices to the individual must be considered when assessing exposure with respect to dose limit.

A dose constraint for planned exposure situations is set to ensure that the annual dose limit of 1 $mSv.a^{-1}$ is not exceeded, by allowing for doses from several sources of exposure. This constraint is normally set at a fraction of the dose limit; typically 0.1- 0.3 $mSv.a^{-1}$. When the dose constraint is exceeded it does not necessarily imply non-compliance with regulatory requirements, but could indicate that follow-up actions based on the ALARA principle is required (IAEA, 2014b). Reference levels are applicable for emergency and existing exposure situations.

For workers the recommended dose limit is 100 mSv averaged over five years, not exceeding 50 mSv in any specific year (ICRP, 2007).

2.2.3 Regulations for NORM

Paragraph 3.4 of the IAEA BSS (IAEA, 2014b) states that "the requirements for planned exposure situations apply if the activity concentration of any radionuclide in the uranium or thorium decay chains is greater than 1000 $Bq.kg^{-1}$ or the activity concentration of ^{40}K is greater than 10000 $Bq.kg^{-1}$". The dose received by members of the public will generally be less than 0.3 $mSv.a^{-1}$ provided that concentrations are kept below these values. Separate standards apply for foodstuffs, drinking water, radon, residues in the environment or materials in transport. The use of commodities such as fertilizer and building materials, which contain radionuclides of natural origin, is also considered as existing exposure situations for which exemption does not apply.

Where the specified activity concentration value is exceeded, a graded approach (notification, authorization and appropriate inspections) is used by the regulatory body to determine whether control measures for radiation protection are warranted. An initial assessment of the process, materials involved and associated exposure is done, based on which the regulatory body can decide on four basic options of control:

- If the dose is consistently less than the dose limit of 1 $mSv.a^{-1}$, the material/processes can be *exempted* from regulatory control.
- Where the dose exceeds 1 $mSv.a^{-1}$, and exemption is not an option, the regulatory body may require regular assessment of the process to determine whether doses can be further reduced. A *notification* of intention to carry out the practice must be submitted to the regulatory body to keep them informed.
- To ensure that appropriate measures are taken for adequate protection of exposed individuals the regulatory body may require additional obligations. To impose these obligations they will grant authorization in the form of a *registration.*
- Stricter control measures are required when exposure to NORM is likely to exceed 6 $mSv.a^{-1}$. In this case an authorization in the form of a *licence* is issued. This form of regulation is used for operations involving substantial quantities of NORM material with very high activities.

Authorized practices have to establish radiation protection programmes with provision for dose assessment and monitoring and at a more detailed level than in the initial assessment.

The IAEA BSS recommends an activity concentration of 1000 $Bq.kg^{-1}$ for all radionuclides of natural origin (IAEA, 2014b) as exclusion (clearance) value. This was also adopted in the EU BSS. Although individual countries may apply stricter limits it is stated in EU (2013b) that "values with a higher precision *e.g.* 500 $Bq.kg^{-1}$ instead of 1000 $Bq.kg^{-1}$, could not be justified". In the opinion of the author the limit of 500 $Bq.kg^{-1}$ prescribed in SA legislation should be re-visited and harmonized with what is accepted worldwide. This will be beneficial for trade and avoid excessive regulation.

All listed NORM industries in EU (2013b) is subject to notification, including cement production and coal fired power plants. These industries are not currently regulated in SA.

2.2.4 Regulatory framework in South Africa

The South African nuclear industry is governed by the Nuclear Energy Act (Act No. 131 of 1993) and the National Nuclear Regulator Act (Act No. 47 of 1999). As statutory body the NNR is responsible for regulating mining- and mineral processing facilities involving NORM. The nationally adopted approach for protection of the public as stated in Regulation No. 388 (South African government, 2006a) are consistent with ICRP and IAEA recommendations. In terms of the regulation, no action may be authorised if there is any possibility for the radiation dose to any member of the public to exceed 1 mSv per year. A dose constraint of 0.25 mSv per year is set, allowing for a combined dose from up to four separate facilities.

Regulatory guide LG-1032 was published in 1997 (NNR, 1997), based on the then existing IAEA Basic Safety Standards (IAEA, 1996), and was recently updated. Regulatory guide RG-002 (NNR, 2013) provides guidelines on how to perform public safety assessments for NORM facilities. The NNR regulatory guide requires analysis of long-lived alpha emitters at a sensitivity level and accuracy acceptable to the NNR. The NNR is currently revising new regulations based on ICRP 103 and IAEA GSR Part 3.

NORM industries

NORM Industries have the obligation to manage radiological risk to levels that are below those stipulated in Regulation 388 (SA government, 2006). Section 21 of the National Nuclear Regulator Act (SA government, 1999) specifies that industries should apply to the NNR for authorization (certificate of exemption, certificate of registration, CoR, or nuclear installation licence) if dealing with radioactive materials. Dose limits are applicable to authorization holders.

In terms of section 2 (2.1b) of Regulation 388 the act does not apply where "the level of radioactivity concentration of each individual nuclide in materials is below 500 Bq per kilogram for naturally occurring radioactive nuclides of uranium, thorium and their progeny (excluding radon), 10 000 Bq per kilogram for ^{40}K in materials used in building construction or disposed of and 50 000 Bq per kilogram for potassium in all other materials".

The last statement is a flaw in the legislation. The maximum activity of ^{40}K in a material is ~31 000 $Bq.kg^{-1}$; *i.e.* in pure potassium metal. [Natural abundance of ^{40}K in potassium is

about 0.0117%. The specific activity of ^{40}K is $2.671x10^{5}$ $Bq.g^{-1}$. Thus, pure potassium contains ^{40}K at an activity concentration of 30.6 $Bq.g^{-1}$].

Similar to the IAEA-BSS a graded approach is followed. Below these concentrations, material/activities are not regarded as radioactive and excluded from regulatory control. When exceeding 500 $Bq.kg^{-1}$, activities are regulated to control exposure and dose to workers and the public. With dose less than 0.25 $mSv.a^{-1}$, actions can be exempted, without further consideration. Above this dose level exemption can be granted by the NNR when the radiation risk to individuals is considered to be low enough not to be of regulatory concern. This depends on the use of the material and will be considered by the NNR on a case-to-case basis. Exemption is justified through a public safety assessment.

In South Africa the principles of justification of actions, optimisation of protective measures and compliance with the dose limits and reference levels, as set by the NNR always apply. Therefore, irrespective of the criteria, exposures must always be kept ALARA.

2.2.5 Internal exposure through ingestion

Exposure as a result of intake from natural radioactivity from consumption of food and water is regarded as an existing exposure situation (ICRP, 2007). To ensure that the dose limit of 1 $mSv.a^{-1}$ is not exceeded, the ICRP and the IAEA suggest the use of reference levels for existing exposures (also referred to as guidelines levels or derived concentration limits, DCL). The use of dose constraint is only applicable to planned exposure situations.

2.2.6 Guidelines for food

The Codex General Standard for radioactivity in food (Codex Standard 193-1995) is applicable to six radionuclides, ^{241}Am, ^{239}Pu, ^{137}Cs, ^{134}Cs, ^{90}Sr and ^{131}I, expected to be present following a nuclear accident. Since natural radionuclides are present in all foodstuffs, they are excluded in the Codex guidelines because the resources required to calculate exposure are out of proportion to the health benefit achieved. However, general comment following a revision of the guidelines was that it should not be excluded "Where doses are liable to exceed 1 $mSv.a^{-1}$ from natural nuclides, it is bound to be a more serious situation than from an accident or controlled releases. In the former case the exposure is likely to stay the same level year after year; the latter case will be due to an accident, unlikely to re-occur and therefore the situation would have reverted to near normal within a year".

The IAEA has concluded that short of limiting the consumption of particular foods with higher than average activity concentrations, there is little that can be done to control public exposure from natural radionuclides in food (IAEA, 2016). The only conceivable protective actions are to prevent consumption of contaminated foodstuffs.

Since there is no specific legislation prescribing limits for natural radionuclides in food, the UNSCEAR adopted reference concentrations for natural radionuclides are often used for evaluation (Table 2-3). Typical concentrations in food vary from 0.001 to 0.1 $Bq.kg^{-1}$ resulting in an annual dose of between 0.2 and 1mSv (UNSCEAR, 2000). The exception is shellfish, in which concentrations of ^{210}Po can be as high as 2 $Bq.kg^{-1}$.

Table 2-3: UNCEAR reference values for food concentrations in $mBq.kg^{-1}$ (UNSCEAR, 2000)

Food	^{238}U	^{230}Th	^{226}Ra	^{210}Pb	^{210}Po	^{232}Th	^{228}Ra
Milk	1	0.5	5	15	15	0.3	5
Meat	2	2	15	80	60	1	10
Fish	30	10	100	200	2000	10	-
Cereal	20	10	80	50	60	3	60
Leafy vegetable	20	20	50	80	100	15	40
Root vegetable	3	0.5	30	30	40	0.5	20

South African regulations

In South Africa guidelines for food safety are implemented by the Directorate Food Control of the Department of Health. The Department recognises, as international reference, the Codex guidelines. Regulation R1931 of the Foodstuffs, Cosmetics and Disinfectants Act (Act 54 of 1972) concerns radioactivity in foodstuffs (SA government, 1990). Similar to Codex, only artificial radionuclides are specified in the Act with action levels set for ^{134}Cs, ^{137}Ca and ^{131}I.

Reference levels for concentrations of natural radionuclides in food are not specified in SA regulations. Regulatory Guide RG-002 (NNR, 2013) specifies default consumption rate values to be used for specific groups of food when performing a public dose assessment. The dose limit of 1 $mSv.a^{-1}$ applies and was used for evaluation of the food pathway in this thesis.

2.2.7 Guidelines for drinking water

Standards for drinking water quality have been in place for about fifty years - the WHO first published international standards in 1958. Since then standards have gradually become more complex as understanding of the possible contaminants that can occur in drinking water has increased. Currently, WHO guidelines are the benchmark for drinking water standards in many countries.

Radiological water quality guidelines developed globally (WHO, EPA, EU) and regionally (DWS) provide guidance for evaluation of water supplies to ensure that the total committed dose due to ingestion remains below 1 mSv per year additional to that obtained from background radiation.

WHO guidelines

WHO guidelines recommend evaluation of water at a reference dose limit (RDL) of 0.1 $mSv.a^{-1}$ (Chapter 9, WHO, 2011). Three steps as illustrated in Figure 2-2 are required for assessment of the radiological quality of the water:

- Initial screening by measurement of the gross beta (GB) and gross alpha (GA) activities. No further action is required for measured concentrations below 1 $Bq.L^{-1}$ (GB) and 0.5 $Bq.L^{-1}$ (GA).
- Concentrations of individual radionuclides are measured and compared with the guidance levels in Table 2-4, which will result in a dose of 0.1 $mSv.a^{-1}$, assuming an intake of 2 litres per day.
- Based on the individual nuclide analysis decisions can be made on further evaluation or decisions on how to reduce the dose.

Further evaluation does not necessarily require analysis of all radionuclides. The presence of ^{238}U or ^{226}Ra is usually considered first. If most of the measured activity can be contributed to these nuclides, only their concentrations are used to calculate the Total Indicative Dose (TID).

The RDL excludes the dose received from ^{3}H, ^{40}K, ^{222}Rn and radon decay products. Although ^{40}K can add significantly to the measured gross beta activity, the contribution to dose is trivial. This is because the concentration of ^{40}K is independent of intake and maintained at a

constant level in the body (homeostatic control).

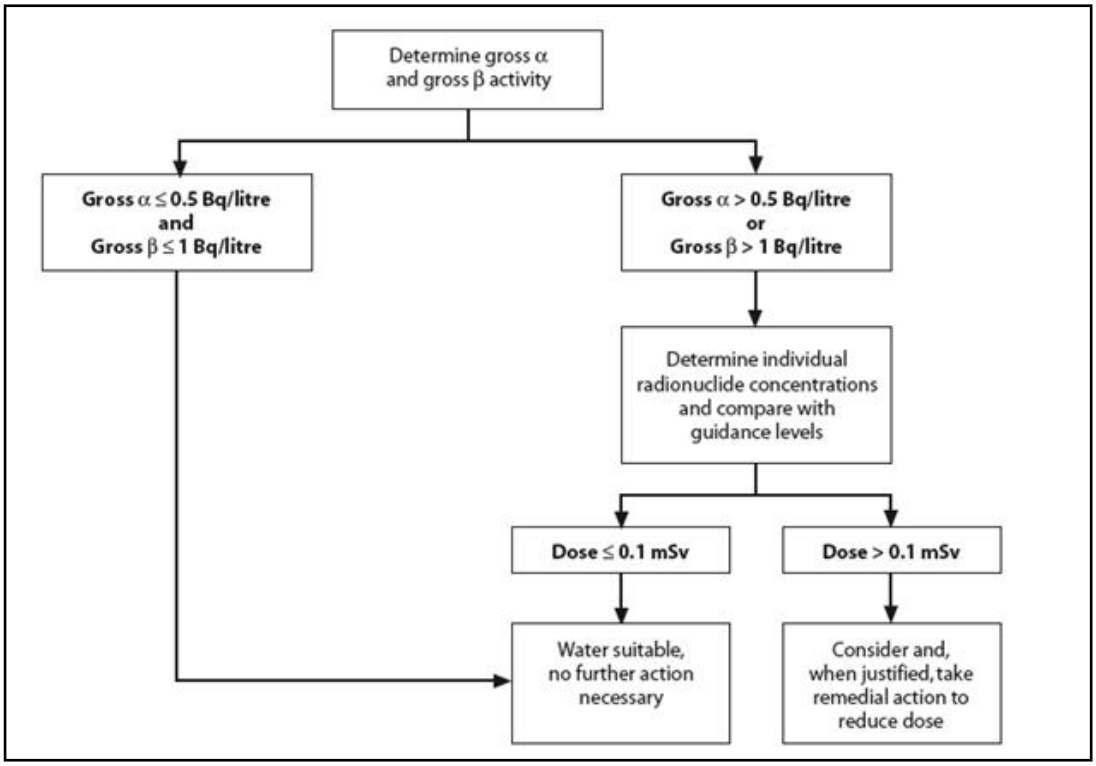


Figure 2-2: WHO assessment of radiological water quality (WHO, 2011).

Table 2-4: Radionuclide guidance levels in drinking water ($Bq.L^{-1}$) (WHO, 2011)

Nuclide	GL	Nuclide	GL	Nuclide	GL
^{226}Ra	1	^{227}Th	10	^{210}Bi	100
^{228}Ra	0.1	^{230}Th	1	^{210}Pb	0.1
^{223}Ra	1	^{228}Th	1	^{210}Po	0.1
^{235}U	1	^{232}Th	1	^{222}Rn	100
^{238}U	10	^{234}Th	100	^{231}Pa	0.1
^{234}U	10				

European Legislation

A new Council Directive was published in 2013 "laying down requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption" (EU, 2013a). Important changes in this new regulation are as follows: (1) Rn and its decay products are regulated, (2) The frequency of monitoring and screening levels for gross alpha and beta activities are stated, (3) It explains the method for calculation

of TID, (4) Specific reference levels for compliance of a TID of 0.1 mSv per year is set, (5) Requirements on detection limits of the analytical methods are given (see Table 2-5).

Table 2-5: Reference concentration values for individual nuclides in water (EU, 2013a)

Parameter	Derived activity concentration ($Bq.L^{-1}$)	LOD	Analytical method
^{238}U	3	0.02	Alpha spectrometry Liquid scintillation
^{234}U	2.8	0.02	Alpha spectrometry Liquid scintillation
^{235}U	2.9	0.02	Alpha spectrometry
^{226}Ra	0.5	0.04	Alpha spectrometry Liquid scintillation Emanation
^{228}Ra	0.2	0.02	Gamma spectrometry
^{232}Th	0.6	0.06	Alpha spectrometry
^{228}Th	1.9	0.2	Alpha spectrometry
^{234}Th	40	4	Gamma spectrometry
^{230}Th	0.7	0.06	Alpha spectrometry
^{222}Rn	100-1000	10	Gamma spectrometry Liquid scintillation Emanation
^{210}Pb	0.2	0.02	Gamma spectrometry Gross beta counting Liquid scintillation
^{210}Po	0.1	0.01	Alpha spectrometry

Guideline activity concentrations of 0.1 and 1 $Bq.L^{-1}$ for GA and GB activity respectively are used for screening (In WHO 2011 the screening level for GA was revised from 0.1 to 0.5 $Bq.L^{-1}$). Individual activity concentrations are measured if one of the guideline values is exceeded, and used to for calculation of the TID. Measurement of tritium is only required when human activity sources are present in the catchment.

Codex

In the Codex standard for bottled/packaged water (Codex Standard 227-2001) the following statement regarding radioactivity is made: "No packaged water shall contain substances or emit radioactivity in quantities that may be injurious to health. To this effect, all packaged water shall comply with the health-related requirements of the most recent Guidelines for Drinking Water Quality published by the World Health Organization". Packaged water

refers to water other than natural mineral water used for human consumption.

South African regulations

The Constitution of the Republic of South Africa (SA government, 1996a) and National Environmental Management Act (SA government, 1998a) states the right of SA citizens to have access to clean water. Chapter 14 of the National Water Act (SA government, 1998b) requires for the quality of water resources to be monitored as part of water management in South Africa. Mining companies have the obligation to supply adequate quality drinking water to all its employees (Mine Health and Safety Act, SA government, 1996b). This Act also requires that this water must be readily accessible.

South African National drinking water standard (SANS)

Fitness of water can be judged against the national drinking water standard. In the 2006 standard (SANS 241: 2006) radioactivity in water was not specifically addressed. In the latest standard (SANS 241:2015) the following is specified for radioactivity: "4.3.8. If the risk assessment indicates potential radioactivity, further testing for gross alpha and beta radioactivity shall be undertaken. If the values exceed the numerical limits specified in the WHO Guidelines, a full radionuclide analysis shall be undertaken*".* The worldwide increased interest and enforcing of legislation for the determination of radioactivity as a standard procedure had led to this requirement to be included in the latest revision of the standard.

Specifications for bottled water

The South African National Bottled Water Association (SANBWA) is the representative body for the bottled water industry in South Africa. Following legislation based on the Codex Alimentarius, bottled water industries are regulated by the Department of Health (SA government, 2006b). Regarding radioactivity the act states that: "No bottled water shall emit radioactivity in quantities that may be injurious to the health of the consumer. To this effect, all bottled/packaged water shall comply with the health-related requirements of the most recent Guidelines for Drinking Water Quality published by the World Health Organization".

A draft document specifying limits for radioactivity to be used by SANBWA members has been drawn up but has not been issued to date (SANBWA, 2012). The limits specified are similar to the latest WHO requirements (Figure 2-2).

DWS South African Water Quality Guidelines

Radiological guidelines are provided by the Department of Water and Sanitation, DWS [previously known as the Department of Water Affairs] (DWS, 1996a, 2007).

The SA water quality guidelines provide information on the requirements for water quality for different uses to ensure that the health of aquatic ecosystems are protected and maintained (DWS, 1996a). The second edition consisted of eight volumes applicable for different water use sectors, including domestic use (Volume 1). A Target Water Quality Range (TWQR) or "no-effect range" for natural radionuclides are specified for radioactivity (see Table 2-6).

Table 2-6: Target Water Quality Range ($Bq.L^{-1}$) for radioactivity in water intended for domestic use (DWS, 1996a)

Nuclide	TWQR ($Bq.L^{-1}$)
Gross alpha	0 -0.5
^{238}U	0 -0.89 (0-0.070 $mg.L^{-1}$)
^{232}Th	0 -0.228
^{226}Ra	0 -0.42
^{222}Rn	0 -11
Gross beta	0-1.38
^{228}Ra	0-0.42

The tentative guidelines of 1996 were refined in specific radiological guidelines in 2006, providing information on the approach to follow to assess the radiological quality of water in SA (DWS, 2007). It is not a mandatory standard. Although the focus is on water potentially used for drinking purposes, assessment of the radiological quality of water is relevant for all water users recognized in the National Water Act, as well as for aquatic ecosystems. It is a reasonable assumption that, if humans can drink the water safely, then most aquatic organisms will not be affected.

The guideline proposes a three tier management system as framework. To identify potential problem areas, the status of national water sources is monitored at Tier 1. Cost effective, fast screening techniques are used to assess water resources with potential radiological impact from NORM. As required by regional and local needs at Tier 2 and 3, more detailed analysis is done on water sources identified to have some radiological contamination or where human activities may have resulted in increased levels of NORM.

Class /Colour	Dose range; mSv/a	Comments and Intervention Decisions
Green - Good water quality	≤ 1	No intervention is required but further radioanalysis may be recommended depending on the human use of the water resource
Orange – water quality requires further nuclide specific analysis	> 1	Regulatory intervention is required if the water enters the pathways of human consumption.

Figure 2-3: Classification of Radiological Water Quality at Tier 1 (DWS, 2007)

As shown in Figure 2-3 two classes of water are identified at Tier 1: A green classification is considered as water of acceptable quality requiring no intervention whereas further site-specific analysis may be required for orange classification. Water is screened for gross beta and alpha activity, with contributions of ^{40}K (typically 10 $mg.L^{-1}$ in water), ^{3}H (in South Africa usually < 1 $Bq.L^{1}$) and ^{222}Rn (degassed from water therefore having limited contribution to dose), excluded. The following screening criteria apply:

— GREEN: GA < 1 and GB < 10 $Bq.L^{-1}$

— ORANGE: GA > 1 and GB > 10 $Bq.L^{-1}$

Five different classes are defined for site-specific investigations, as shown in Figure 2-4. The water quality classification scheme is based on the radiation dose received by any person consuming water from the specific source on a life-long basis. For interpretation it is assumed that blue or green water is fit for lifetime use, whereas lifetime use should be avoided for marginal water (yellow class). Red and Purple class water are seen as having unacceptable quality and not fit for use. The following protocol is proposed for monitoring of radioactivity in water:

— Simplified Screening: The dose will be less than 0.1 $mSv.a^{-1}$ resulting in BLUE classification if GA < 0.1 and GB < 1 $Bq.L^{-1}$.

— Advanced Screening: Since mining- and mineral operations in SA often results in increased concentrations of uranium and radium isotopes, the concentrations of ^{238}U and ^{226}Ra are determined. Any conclusions are validated by comparison with the uranium chemical concentration and GA activity.

— Full radionuclide analysis: A full radionuclide spectrum is performed, together with measurement of the chemical concentrations of U and K.

Class /Colour	Dose range; mSv/a	Health Effects and Typical Exposure Scenarios	Comments and Intervention Decisions
Class 0 (Blue - Ideal water quality)	≤ 0.10	There are no observable health effects. This is the dose range from ideal quality water sources. Most treated water falls in this water quality range. Additional doses that result from Human activities / actions that fall within this range are difficult or impossible to determine and/or to distinguish from variations in background doses with sufficient confidence.	Drinking water supplied at the tap should be in this category.
Class 1 (Green - Good water quality)	> 0.10 to 1	This is the typical dose range from some natural and untreated water sources (e.g. ground water / wells) as well as water sources that could be influenced by radiation and nuclear regulated actions. A dose between 0.2 to 0.8 mSv/a is the typical world-wide range of ingestion radiation dose resulting from water as well as food. A dose equal to 1 mSv/a additional to background corresponds to the regulatory public dose limit for Human activities / actions involving radioactive material.	ALARA and intervention considerations may apply.
Class 2 (Yellow - Marginal water quality)	> 1 to 10	A small increase in fatal cancer risk associated with this dose range. Only a small number of natural water sources of this quality exist, usually resulting from exceptional geological conditions. Abnormal/accident conditions at regulated nuclear and radiation facilities may result in a dose in this range when a person drinks untreated water. Intervention will most likely be required to improve the quality of water with this radioactivity concentration when present in the public domain.	Regulatory intervention is required for category TENORM impacted waters.
Class 3 (Red - Poor water quality)	> 10 to 100	Health effects are statistically detectable in very large population groups. This range represents a situation of unacceptable exposure. It is highly unlikely to find water of this poor quality in the natural environment.	Intervention is required and the time scales to be decided by the regulatory authorities on a case by case basis.
Class 4 (Purple - Unacceptable water quality)	> 100	Health effects may be clinically detectable and a significant increase in the fatal cancer risk. A dose greater than 100 mSv can only occur during a major accident at a nuclear facility. These facilities have to demonstrate that such an accident has an extremely small likelihood (a frequency of less than 10^{-4} per year).	Immediate intervention is required

Figure 2-4: Site specific classification of Radiological Water Quality (DWS, 2007)

The dose is estimated using the ^{238}U and ^{226}Ra concentrations assuming equilibrium between ^{238}U and ^{234}U (natural ratio) and between ^{226}Ra, ^{210}Pb and ^{210}Po. These assumptions are conservative compared to a calculation using all measureable nuclides in the NORM decay series. No action is required if the dose is less than the NNR dose constraint of 0.25 $mSv.a^{-1}$. If between 0.25 and 1 $mSv.a^{-1}$, the quality should be re-assessed using nuclide specific analysis, but no further action is required if less than 1 $mSv.a^{-1}$. Intervention and remedial actions may be required for water sources where the dose is more than 1 $mSv.a^{-1}$.

Specified levels for uranium in drinking water

Because of its small dose conversion factors the contribution of Uranium to the ingestion dose is very small. Regulation if mostly required due to its chemical toxicity, which determines acceptable levels of U in drinking water (UNSCEAR, 2016).

The WHO (1993) originally set a concentration of 15 µg.L^{-1} as guideline for U in water. This was changed to 30 µg.L^{-1} in 2011 (WHO, 2011), based on studies indicating no evidence of effects below this concentration. EPA regulations also set a MCL of 30 µg.L^{-1} for total uranium (Environmental Protection Agency, 2000). In the DWS Water Quality Guidelines the limit for U was set as 70 µg.L^{-1} (DWS, 1996a). The more recent limit in South Africa as per SANS 241 is 30 µg.L^{-1} (SANS, 2015).

Using the specific activities as in Table 2-1 for the natural abundance of uranium each µg of U equates to 25.3 mBq (12.4, 0.6, 12.4 mBq, 234:235:238 respectively) of activity. The weight concentration in the current WHO regulations (30 µg.L^{-1}) would relate to 0.370 Bq.L^{-1} ^{238}U and 0.740 Bq.L^{-1} total U. The reported ^{234}U/^{238}U ratios in groundwater are however commonly more than 2 (see 2.1.2). As ^{234}U contributes very little (0.006%) to the total U weight, doubling of its activity will have an insignificant weight contribution; thus it is likely that for groundwater each µg of U equates to 38 mBq (24, 0.6, 12 mBq, 234:235:238 respectively) of activity. For groundwater the WHO MCL of 30 µg.L^{-1} is therefore closer to 1.11 Bq.L^{-1} of total U.

Summary of legislation for drinking water

A summary of drinking water guidelines and limits of international and national organizations are given in Table 2-7.

Table 2-7: Summary of legislation for drinking water

Reference	Concentrations (Bq.L^{-1})					Dose mSv.a^{-1}	U µg.L^{-1}
	GA	GB	^{238}U	^{232}Th	^{226}Ra		
DWS 1996a	0.5	1.38	0.890	0.228	0.420	-	70
DWS 2007 (blue:ideal)	-	-	-	-	-	0.1	-
DWS 2007 (green:good)	1	10		-	-	1	-
SANS 2015	-	-	0.190	-	-	-	15
SANBWA 2012	0.5	1	-	-	-	1	15
NNR	-	-	-	-	-	0.25	-
WHO 2011	0.5	1	10	1	0.1	0.1	30
EPA 2000	0.56	1.85	0.38	-	0.185	-	30
EU 2013a	0.1	1	3	0.6	0.5	0.1	-
Canada 2014	0.5	1	-	-	-	0.1	20
Australia 2015	0.5	0.5	-	-	-	1	-
New Zealand 2005	0.1	0.5	-	-	-	-	20

2.2.8 Building Industry

International legislations propose reference values for the use of BM rich in natural radioactivity.

European legislation

NORM in BM in Europe has been officially regulated since 2013. Article 75 of the BSS (EU, 2013b) provides for regulation of BM form natural origin, as well as residues from NORM industries, such as slag, fly ash and phosphogypsum. The standard is similar to what has been recommended by the European Commission in 1999 (EU, 1999).

A radiation hazard, the gamma-index (I_γ) or activity concentration index (ACI) is used as screening parameter. It can be calculated using equation 2.11 (see 2.3.7) and is used to convert the activity concentration of the material (in $Bq.kg^{-1}$) into a measure of radiation dose (in mSv). The ACI relates to the incremental gamma dose in a building constructed from a specific BM (*i.e.* the dose above the dose typically received from outdoor exposure) and applies to the BM, not to its constituents.

The ACI is used as a conservative screening parameter. If ACI ≤ 1, the BM can be used without any restrictions, if not, a full dose assessment must be done to show that the reference dose level of 1 $mSv.a^{-1}$ is not exceeded. The dose criterion was selected considering current data for building material in Europe and was chosen so that the majority of normal BM on the market does not exceed the limit. Depending on the use of the material in a building, the gamma index shall not exceed values indicated in Table 2-8 (EU, 1999).

Table 2-8: Gamma index limits for building material (EU, 1999)

Dose criterion	0.3 $mSv.a^{-1}$	1 $mSv.a^{-1}$
Materials used in bulk amounts, *e.g.* concrete	$I \leq 0.5$	$I \leq 1$
Superficial and other materials with restricted use *e.g.* tiles	$I \leq 2$	$I \leq 6$

South African regulations

There are currently no regulations specific for building material in South Africa and no reference levels have been specified. SA Government notice R849 (SA government, 1994)

specifies that "any person dealing with materials that contain radioactivity should apply to the NNR for a nuclear license. If the material is to be used in the construction of buildings, the application should have been done before 31 March 1999". In terms of regulation R388 (SA government, 2006a) the act does not apply for material with a radioactivity content of less than 500 $Bq.kg^{-1}$ per individual nuclide. Solid material from various origins (including BM) is therefore currently evaluated based on this criterion.

In a conference of the South African Radiation Protection Association (SARPA) it was recommended in a presentation from the NNR that the control of BM should be investigated (Pule, 2015). Restricting the use of certain BM might have significant economical and environmental consequences locally and nationally. These consequences, together with the national levels of radioactivity in BM, should be assessed and considered when establishing building regulations.

2.2.9 Protection of the Environment

In the latest recommendations (ICRP, 2007) the Commission has specifically addressed environmental protection. The ICRP concept of reference animals and plants (RAP) correlates dose with biological effect (ICRP, 2003). A dose of 10-100 $mGy.d^{-1}$ will affect reproduction, whereas higher than 1000 $mGy.d^{-1}$ will be lethal for adult biota. The IAEA recommended dose rate limits are 10 $mGy.d^{-1}$ for aquatic animals and terrestrial plants and 1 $mGy.d^{-1}$ for terrestrial animals (IAEA, 1992). The ERICA tool uses a dose limit of 1 $mGy.d^{-1}$ for aquatic mammals and birds and 10 $mGy.d^{-1}$ for all other aquatic organisms (ERICA, 2016).

In SA the legal basis for radiological protection of the environment is as follows:

- The Constitution of South Africa (SA government, 1996a): Section 24 provides that "everyone has the right to an environment that is not harmful to their health and well-being and to have the environment protected for the benefit of present and future generations".
- The National Environmental Management Act, 1998 (SA government, 1998a): NEMA implements the environmental management policy, which undertakes to support the rights of the constitution relating to the environment. The NEMA definition of environment means surroundings within which humans exist.
- The National Nuclear Regulator Act, 1999 (SA government, 1999): Principles for

radiological protection of humans are well defined, but are yet to be established for non-human species.

2.3 Radiological Protection and Dose Evaluation

In this section the different exposure pathways and the dose calculations when considering these pathways for public exposure, as applicable for the industries considered in this thesis are discussed.

2.3.1 Radiation Protection

The regulatory framework for radiological protection was discussed in detail in 2.2. The current dose limit for exposure of members of the public from additional man-made radiation is 1 mSv per year (ICRP, 2007). There is, however, no practical way to measure the actual exposure of workers and the public (*i.e.* mSv-values) directly, except for external doses, which can be directly measured using dosimeters. Doses are calculated from the measured activity concentration of radionuclides in different samples. The process to convert these values (*i.e.* $Bq.kg^{-1}$ or $Bq.L^{-1}$) to the equivalent dose (*i.e.* mSv) is the focus of 2.3.5 to 2.3.7.

The measurements performed at RadioAnalysis as discussed in this thesis are done in support of dose assessments. The data are usually used by a Radiation Protection Specialist (RPS) in his/her capacity to evaluate the radiological impact of NORM industries on the environment, workers or the public. RA is one of the few analytical laboratories in South Africa that are capable of measuring the gross and nuclide-specific activity in different types of samples. The information is typically needed by organisations to prove that they comply with relevant safety regulations, which can be a licence issued by the NNR to a mine, or legislation that controls the import of food and agricultural products, or a building regulation on the use of contaminated residue. RadioAnalysis can convince regulatory bodies of the reliability of its results, by complying with an accepted quality standard like ISO Guide 17025:2017.

2.3.2 Dose Assessment Methodology

The term ‘dose’ is used as a general term to mean either absorbed dose (Gy) or effective dose (Sv). Absorbed dose is defined as “the amount of energy absorbed per unit mass of tissue of an organ or organism”. Effective dose is used for reporting human exposure and considers the

biological effects per unit of absorbed dose, which varies with the type of radiation and part of the body exposed (UNSCEAR, 2000).

Methodology for dose assessment

A source-pathway-receptor (SPR) approach is often used for dose assessment (see Figure 2-5). *Sources* refer to "any entity that contains radioactivity and have the potential to release the radioactivity into the environment". Source quantification requires measurement of radioactivity in potential sources of exposure to assess the potential radiation dose via all possible *exposure pathways*. An exposure pathway is the route for radioactivity to be transferred from the source to humans resulting in a radiation dose. *Receptors* refer to humans that may potentially be exposed to radiation from the sources and through the exposure pathways. The total dose is calculated considering all pathways. Radionuclide concentrations in soil, air, water and food are combined with behavioral data (*e.g*. consumption rates) to determine intake. This is converted into a dose using dose conversion factors or models.

Main routes of exposure via the *atmospheric pathway* and associated *terrestrial pathways* are:

- External exposure from activity in the atmosphere (cloud shine and immersion);
- External exposure from activity deposited on the ground (ground shine);
- Inhalation of airborne gas and radioactive particles;
- Internal exposure from ingestion of animal products and food crops produced on land contaminated through deposition of airborne radioactive dust.

Other exposure pathways *e.g*. internal exposure from ingestion of soil or inhalation of re-suspended radionuclides deposited on the ground are negligible compared with these.

Main routes of exposure via the *aquatic pathway* include:

- External exposure from radioactivity in sediments;
- Internal exposure from ingestion of contaminated water;
- Internal exposure from ingestion of radionuclides in fish;
- Internal exposure from ingestion of animal products and food crops produced on land contaminated through irrigation with contaminated water.

Other exposure pathways *e.g.* external exposure to soil contaminated through irrigation with contaminated water, external exposure when swimming (water immersion) or internal exposure from ingestion of sediment are negligible compared with those above.

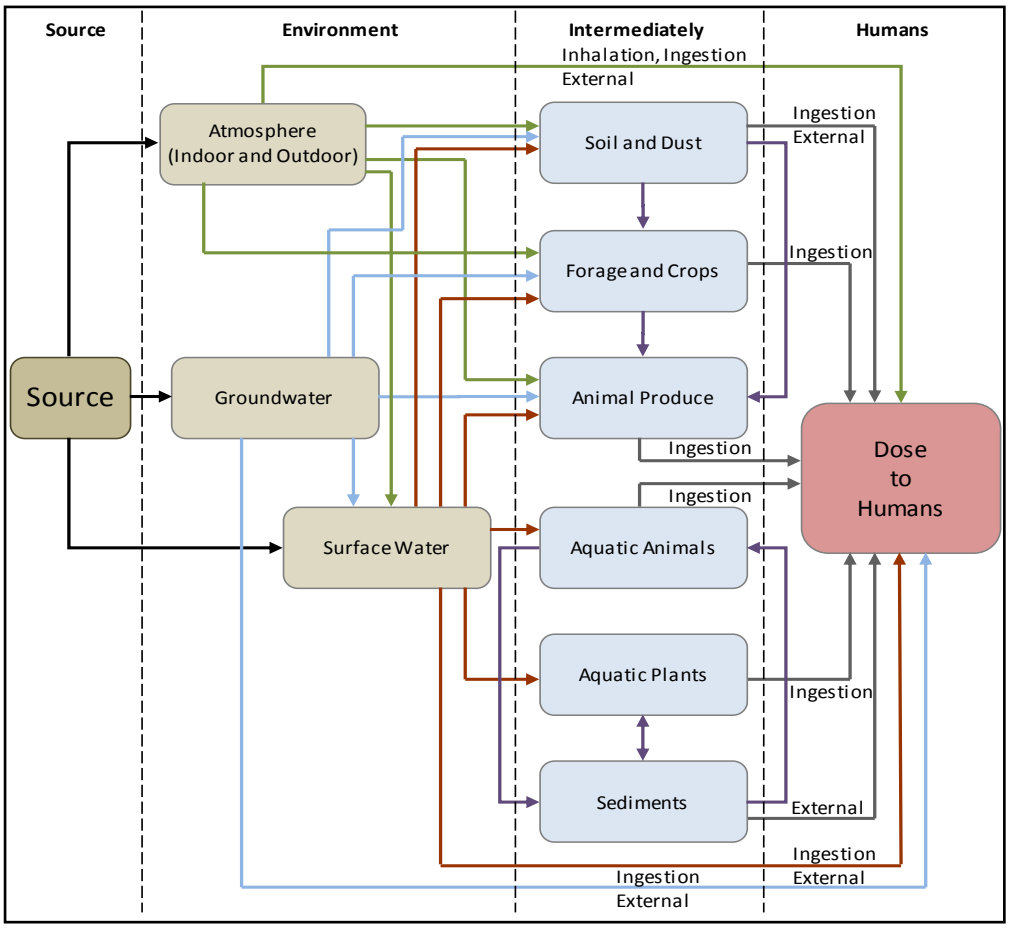


Figure 2-5: Source-pathway-receptor approach for dose assessment (IAEA, 2003a).

Secondary pathways

Source terms for secondary pathways are created by the atmospheric- and aquatic pathways (see Figure 2-6). These include: drinking of contaminated water, eating of food grown on contaminated soil (through irrigation or deposition) or eating of livestock (living in or drinking contaminated water or eating contaminated soil). Contaminants in surface water will be transferred to aquatic animals such as fish (bioaccumulation), as well as from the ingestion of contaminated sediments.

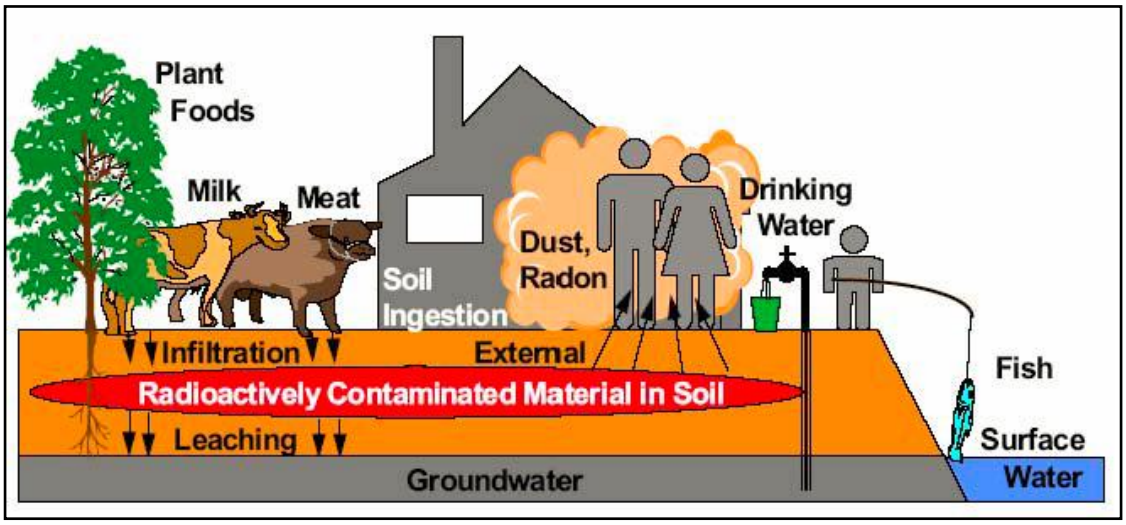


Figure 2-6: Pathways to consider for dose assessment (USDOE, 2002)

2.3.3 Atmospheric pathway

The atmospheric pathway is expected to be important only close to the dust and radon sources, with the inhalation pathway most important.

The dose from inhalation of radioactive dust particles is calulated from modelled or measured dust activity concentrations, by multiplying with appropriated dose conversion factors (DCF). Monitoring of dust emission at the source is required. Typically, water is placed in dust buckets and retrieved after a few weeks. The water is filtered through a special filter and the filters analysed for natural radionuclides. Air dispersion models are used to simulate PM10 (particulates with diameters less than 10 microns) to characterise impact through inhalation, whereas TSP (Total Suspended Particulates) is modeled to quantify the impact of dust deposition. Using the measured radionuclide concentrations, the radionuclide air concentration ($Bq.m^{-3}$, due to PM10 emissions) and dust fallout ($Bq.m^{-2}.day^{-1}$, due to TSP deposition) can be calculated.

The dose from exposure to radon is calculated from modeled indoor and outdoor radon gas concentrations. According to UNSCEAR, the highest contribution to the natural background dose is from inhalation (1.26, with range 0.2-10 $mSv.a^{-1}$) with the major contribution from radon (1.15 $mSv.a^{-1}$).

2.3.4 Aquatic pathway

Radionuclides in contaminated groundwater can be transported to the underlying aquifer. Migration to various discharge points (*e.g*. boreholes, fountain, rivers and dams) can occur through groundwater flow and various transport processes such as diffusion. Since groundwater movements may be very slow the radionuclides may take several decades to migrate to discharge points.

Contamination of surface water can occur through surface run-off, effluent releases and decanting groundwater. The rate of migration of radionuclides in surface water is influenced by factors such as annual flow rates, adsorption onto sediments and surface water/groundwater interaction (*e.g.* discharge rates). The surface water pathway may be of minor importance and restricted to the occasional occurrence of surface water run-off in case of heavy rain.

2.3.5 Dose from ingestion

According to UNSCEAR (2008), the total annual exposure resulting from ingestion is 0.29 mSv, of which 0.17 mSv is from ^{40}K and 0.12 mSv from nuclides from the U and Th series. Exposure from inhalation (excluding radon) contributes only 0.01 mSv. The human body regulates its uptake of potassium hence the dose from ^{40}K is relatively constant. Dose from other natural radionuclides may vary from 0.1 to 1 mSv depending on the type and quantity of food and drink consumed but the highest contribution is usually from ^{210}Po and ^{210}Pb (see 2.6).

For evaluation of the ingestion pathway sampling and analysis of food, water and soil is required. The dose from ingestion of radioactivity in food and water are calculated from the activity concentration of the radionuclides (in Bq.kg^{-1} or Bq.L^{-1}), the consumption rate (kg.day^{-1} or L.day^{-1}), and the dose conversion factor for the specific radionuclide.

Calculation of dose from ingestion of water

The dose from ingestion of contaminated water is calculated from measured or modeled radionuclide concentrations of water. DWS (2007) recommend calculation of a lifetime annual dose from the expression:

$D = \sum_i A_i F_i$ ……Equation 2.1

where

D lifetime annual dose from ingestion of water ($Sv.a^{-1}$)

A_i activity concentration of nuclide i ($Bq.L^{-1}$)

F_i proportionality constant for nuclide i with units of ($Sv.a^{-1}$) per ($Bq.L^{-1}$).

The proportionality constant Fi for nuclide i can be determined from:

$$F_i = \sum_x C_x \, (DCF)_{ix} W_x \quad \text{.....Equation 2.2}$$

where

C_x annual water consumption for age group x ($L.a^{-1}$)

W_x weighting factor for age group x

$(DCF)_{ix}$ dose coefficient for ingestion of water of nuclide i and age group x ($Sv.Bq^{-1}$)

The weighting factor for each age group is determined by dividing the number of years in the age group by the average life expectancy, taken to be 70 years. For example, the weighting factor for the adult age group was:

$$W_{>17} = \frac{70 - 17}{70} = 0.757$$

Calculation of dose from ingestion of food

Where measured activity concentrations in fish, crops and animal products are available the committed effective dose per age group is calculated as follows:

$$D_i(x) = \sum_p A_{ip} \, C_p(x) DCF_i(x) K_{ip} \quad \text{.....Equation 2.3}$$

where

$D_i(x)$ annual dose to an individual from age group x ($Sv.a^{-1}$)

A_{ip} activity concentration of nuclide i in product p ($Bq.kg^{-1}$) – fresh weight

$C_p(x)$ consumption rate of product p for individuals of age group x ($kg.a^{-1}$)

$DCF_i(x)$ dose coefficient for ingestion of nuclide i and age group x ($Sv.Bq^{-1}$)

K_{ip} correction factor for reduction in the concentration of radionuclide i in product p from processing.

Similar to the equation used for food, the effective dose due to ingestion from contaminated soil is calculated from measured or modeled radionuclide concentrations in soil, multiplied with appropriate dose coefficients and the annual soil consumption rate,

Dose coefficients

The dose coefficient or dose conversion factor (DCF) gives the relationship between the activity intake of a radionuclide (in Bq) and the radiation dose (in Sv) caused by this nuclide. Dose coefficients for ingestion have been published by the ICRP in publication 72 (ICRP, 1996) and was summarized in publication 119 (ICRP, 2012). The ICRP DCFs have been adopted in the International BSS (IAEA, 2014b) and the European Directive (EU, 2013b).The DCFs published in RG-002 (NNR, 2013) as obtained from ICRP publication 72 were used for dose calculations in this thesis.

DCFs are given for different age groups. The higher dose coefficients for children do not necessarily result in high doses due to the lower consumption rates. As can be seen from Table A-5 (Appendix A) nuclides with relatively high DCFs include ^{210}Pb, ^{227}Ac, ^{231}Pa, ^{210}Po, ^{228}Ra, ^{226}Ra, ^{232}Th, ^{230}Th and ^{228}Th. These are the nuclides for which methods for sensitive and accurate measurement have been developed and for which the results are discussed in this thesis.

Consumption rates

The NNR RG-002 document (NNR, 2013) prescribes generic consumption values to be used in dose calculations, as summarized in Table A-8 (Appendix A). The updated NNR values have been derived from South African national food balance sheets. For comparison the previously recommended values in LG-1032 (NNR, 1997), as well as typical literature values for consumption of food in other countries, are also shown in Table A-8 (Appendix A).

Consumption rates of meat (beef, mutton, pork) and chicken were decreased from the previous value. Cereal consumption was increased from 150 kg.a^{-1} to 250 kg.a^{-1} to be more representative of the typical African diet. No consumption rates are given for vegetables and fruit in the updated document, therefore LG-1032 values were used for vegetables. Most of the NNR values are higher than recent UNSCEAR recommended consumption rates especially those of cereal and fish. The lower value of 600 L.a^{-1} for water in the updated version is also higher than the UNSCEAR recommended value of 500 L.a^{-1} (1.4 L.d^{-1}) (UNSCEAR, 2016). The NNR values are conservative (assuming a much larger intake) when compared with the statistically compiled consumption values given by the Department

of Agriculture, Forestry and Fisheries (2016) and published data on food consumption in South Africa collected by Ronquest-Ross *et al*. (2015) – see Table A-9 (Appendix A).

Consumption rates are inherently conservative as most people do not consume water or food from one source only. It should also be clear that it is very difficult to establish a "typical" South Africa diet applicable to different potential critical groups (*e.g*. subsistence farmers, rural dwellers and modern farmers.

Dry-to-wet weight conversion factors

Results are usually reported as activity per wet weight after the analysis has been done on a dried sample. Recommended NNR values for conversion of dry to fresh weight are shown in Table A-10 (Appendix A). As remarked in the Appendix, some mistakes were observed in the data provided by the NNR, of which they should be made aware of. For comparison some literature values, as well as "true" experimental values, are shown. Since recommended literature values may contribute to inaccurate results, use of measured dry-to-wet ratios is preferred.

Calculation of dose from ingestion of crops and food animal products using soil - and water concentrations

Where concentrations of radionuclide in food products are not available, the water- or soil concentrations are used to calculate dose, using concentration ratios and transfer factors. For the case studies presented in this thesis (5.2) it was preferred to use the actual measured concentrations in food products. Equations 2.5 and 2.6 were used only in the transfer case studies in 5.3. Consumption rates of crops and food products, as well as consumption rates of fodder, water and soil by domestic animals, are given in Table A-8, water-fish and soil-crop concentration ratios in Tables A-14 and A-15 respectively and transfer coefficients in Table A-13 (see Appendix A).

The ingestion dose from eating crops like leafy or root vegetables, cereals and fruit, which were grown on contaminated soil is calculated from:

$$D_i(x) = \sum_p A_{soil}\ C_p(x) DCF_i(x) CR_{ip} \quad \text{.....Equation 2.4}$$

where

$D_i(x)$ annual dose to an individual from age group x ($Sv.a^{-1}$)

A_{soil} activity concentration of nuclide *i* in soil from deposition/irrigation (Bq.kg^{-1})

$C_p(x)$ consumption rate of product *p* for individuals of age group *x* (kg.a^{-1})

$DCF_i(x)$ dose coefficient for ingestion of nuclide *i* and age group *x* (Sv.Bq^{-1})

CR_{ip} concentration factor from soil to crop for nuclide *i* in product *p*

In this simplified formula it is assumed that the crop concentration is due to root transfer only, not taking into account deposition, dust fallout, irrigation, interception and translocation for which parameters such as the plant interception factors, irrigation rate, annual crop yield, growing period and translocation factor is required.

The ingestion dose from drinking milk and eating animal products like beef, where the animals ingest contaminated water, fodder and soils, is calculated from:

$$D_i(x) = TC_{ip} \cdot DCF_i(x) \cdot C_p(x) \cdot \left[(A_{sed} \cdot C_{sed}) + (A_{soil} \cdot C_{soil}) + \left(A_{fodder} \cdot C_{fodder}\right) + (A_{water} \cdot C_{water})\right] \quad \text{Equation 2.5}$$

where

$D_i(x)$ annual dose to an individual from age group x (Sv.a^{-1})

$DCF_i(x)$ dose coefficient for ingestion of nuclide *i* and age group *x* (Sv.Bq^{-1})

TC_{ip} transfer coefficient for the animal product (d.kg^{-1})

$C_p(x)$ consumption rate of product *p* for individuals of age group *x* (kg.a^{-1})

A_{soil} activity concentration of nuclide *i* in soil (Bq.kg^{-1})

A_{sed} activity concentration of nuclide *i* in sediment (Bq.kg^{-1})

A_{water} activity concentration of nuclide *i* in water (Bq.L^{-1})

A_{fodder} activity concentration of nuclide *i* in fodder (Bq.kg^{-1})

C_{soil} daily soil consumption rate of animal (kg.d^{-1})

C_{sed} daily sediment consumption rate of animal (kg.d^{-1})

C_{fodder} daily fodder consumption rate of animal (kg.d^{-1})

C_{water} daily water consumption rate of animal (kg.d^{-1})

When modeling radionuclide intake from animal feed, radionuclides ingested with soil attached to the vegetation must also be taken into account.

Dose from eating fish in contaminated surface water is calculated from:

$$D_i(x) = A_{water}\, C_{fish}(x) DCF_i(x) CF_{fish} \quad \text{Equation 2.6}$$

where

$D_i(x)$ annual dose to an individual from age group x ($Sv.a^{-1}$)

A_{water} activity concentration of nuclide *i* in water ($Bq.L^{-1}$)

$C_{fish}(x)$ consumption rate of fish for individuals of age group *x* ($kg.a^{-1}$)

$DCF_i(x)$ dose coefficient for ingestion of nuclide *i* and age group *x* ($Sv.Bq^{-1}$)

CF_{fish} concentration factor from water to fish for nuclide *i*.

2.3.6 Dose from external exposure

External gamma radiation is an important pathway in mining- and mineral industries, specifically where solids contain high concentrations of natural nuclides. Access by the general public to highly radioactive- or contaminated areas is usually prohibited. External exposure to the public only becomes important when living in areas containing mine ore or residues.

External exposure also occurs from soil contaminated through deposition of airborne radioactivity or through irrigation with contaminated water. The average annual background exposure from ground shine is 0.48 mSv (range 0.3-0.6 mSv worldwide) with 0.41 mSv due to indoor occupancy (radon) and only 0.07 mSv outdoors (UNSCEAR, 2008).

The gamma dose rate close to the source (in $\mu Sv.h^{-1}$) is required to predict external exposure. The dose rate can either be measured directly using a gamma detector, or calculated from the activity concentrations of the natural nuclides present in the sources. Generally consistent results are obtained by the two methods – see 2.7.1 (UNSCEAR, 2000).

External exposure from soil (ground shine)

The external dose from soil is calculated from measured or modeled radionuclide concentrations in the soil, multiplied with appropriate dose conversion factors and the exposure period:

$$D_{ext} = A_{soil} DCF_{ext} EP_{soil} \quad \text{.....Equation 2.7}$$

where

D_{ext} external dose from contaminated soil ($Sv.a^{-1}$)

A_{soil} activity concentration in soil ($Bq.kg^{-1}$)

DCF_{ext} dose coefficient for external exposure ($Sv.h^{-1}$per $Bq.kg^{-1}$)

EP_{soil} annual exposure period to soil ($h.a^{-1}$)

In the case of deposition the activity is present as a thin layer and the external dose is calculated using the DCF for surface activity concentration ($Sv.h^{-1}$ per $Bq.m^{-2}$). In case of irrigation the activity is more likely to penetrate to deeper layers of the soil and the dose is calculated from the volume DCF in $Sv.h^{-1}$ per $Bq.kg^{-1}$.

The following simplified equations were used in the thesis to calculate external dose (UNSCEAR, 2008). The external gamma dose rate (D) in $nGy.h^{-1}$ 1 m above the surface is calculated from the concentrations of ^{40}K, ^{232}Th and ^{238}U (^{226}Ra) in the solid:

$D = 0.462C_U + 0.602C_{Th} + 0.0417C_K$ ……Equation 2.8

where 0.462, 0.602, 0,0417 are the dose rate conversion factors in $nGy.h^{-1}$ per $Bq.kg^{-1}$ for ^{238}U, ^{232}Th and ^{40}K respectively (UNS, 2008).

The annual effective dose (AED) in $mSv.a^{-1}$ is calculated from the absorbed dose rate:

$AED = D \times DCF \times F \times T \times 10^{-6}$……...….Equation 2.9

where DCF = 0.74 $Sv.Gy^{-1}$ (to convert absorbed dose rate to effective dose); F is the outdoor occupancy factor of 0.2 and T is the exposure period (8760 hours per year).

UNSCEAR (2016) assumes an indoor occupancy factor of 80%; the outdoor occupancy is simply a fractional value and is 1-0.8=0.2.

Radiation hazard index

The radium equivalent activity (Ra_{eq}), also known as the NORM index, is one of the most common radiological indices used as to quantify external dose exposure. It is used to compare radioactivity of materials and is based on the estimation that 4810 $Bq.kg^{-1}$ of ^{40}K, 259 $Bq.kg^{-1}$ of ^{232}Th and 370 $Bq.kg^{-1}$ of ^{226}Ra produces the same gamma dose (Beretka & Mathew, 1985). The Ra_{eq} value is the weighed sum of the activities of the three nuclides:

$= C_{Ra} + 1.43C_{Th} + .077C_K$……..Equation 2.10

where C_{Ra}, C_{Th}, and C_K, are the activity concentrations ($Bq.kg^{-1}$) of the respective radionuclides.

With Ra_{eq} less than 370 $Bq.kg^{-1}$, the external gamma dose will be less than 1.5 $mSv.a^{-1}$. Giving the same information in a different way the external hazard index H_{ex} (also known as the Leningrad index) is defined as:

$$H_{ex} = C_{Ra}/370 + C_{Th}/259 + C_K/4810 \quad \text{Equation 2.11}$$

Dose from building material

The Leningrad index is useful to compare building material (BM). The value of the index must be less than unity for the radiation hazard to be negligible so that no restrictions are placed on utilization of a specific material. The recommended maximum levels of "radium equivalents" for building materials are summarized by Farai & Ademola (2005) as in Table 2-9.

The gamma-index (I_γ) or activity concentration index (ACI), has been defined in the European directive. It is used to convert the activity concentration of a building material in $Bq.kg^{-1}$ into a measure of radiation dose (in mSv) and can be calculated using equation 2.12

$$I_\gamma = (C_{Ra} / 300) + (C_{Th} / 200) + (C_K / 3000) \quad \text{Equation 2.12}$$

where 300, 200 and 3000 are the maximum allowable concentrations for ^{226}Ra, ^{232}Th and ^{40}K, respectively.

Table 2-9: Classification of building material according to Leningrad index

Ra_{eq}	Class	Recommendation
<370	1	Good for homes
370-740	2	Good for industries
740-2220	3	Good for roads and bridges
2220-3700	4	Good for use in foundations of non-residential buildings
>3700	5	Not to be used for construction of any type

2.3.7 Radiological safety assessment for mineral- and mining operations

Public safety assessments for NORM facilities in SA are conducted based on the guidance given in RG-002 (NNR, 2013). An initial assessment is made of the process, the materials/sources involved and the associated exposure. A source-pathway-receptor approach as shown in Figure 2-5 is used.

System description

The system description provides an overview of the operations (process) of the facilities at the NORM industry, and identifies waste or by-products generated as part of the process. A description of the site and human behaviour in the vicinity of the industry is done.

Identification of sources

All historic, current and potential future sources of radiation exposure are identified. The following activities are typical potential sources of radioactivity relevant to the *atmospheric pathway:*

- Dust from dry mining activities;
- Dust from loading and offloading of ore, product materials and tailings;
- Wind erosion of the stockpiled ore and tailings storage facilities (TSF);
- Dust emission from mineral processing activities; and
- Radon emission from product stockpiles at the processing plants, the TSF and the backfilled mining area.

Characterization of sources

Site specific data forms the basis of any radiological impact assessment. Accurate analytical data are required to support dose assessment models used to relate the sources of radioactivity to the amount of radiation to which members of the public are exposed to.

Pathways and sample analysis

For assessment of *external* exposure the dose rate can be measured using portable gamma equipment. “Hot spots” are identified and composite soil samples taken for radiochemical analysis. The dose rate can also be calculated from soil concentrations (equation 2.9). Soil concentrations can either be measured or calculated from dust deposition and irrigation, but measured concentrations are preferred.

The type and number of samples collected during a public dose assessment depend on site-specific conditions and the availability of the different media, but typically include the following:

— Groundwater collection depends on the availability of boreholes.
— Surface water is collected upstream and downstream of discharge points into the surface water body.
— Soil is collected from locations identified as "hot-spots" during the gamma survey of the site. Also from locations close to infrastructures such as processing plants, tailings storage areas or waste dumps.
— Sediments from surface water bodies.
— Crops and animal products: Depending on the availability, this could include wheat, fruits, vegetables, poultry, *etc*.
— Fish from surface water sources in the area.
— Aquatic and terrestrial organisms.
— Dust fallout and airborne dust collected at sampling locations in accordance with the indicated wind directions.

Where actual measured data are not available, empirical equations (2.3.5) are used for calculation of activity concentrations along the secondary pathways. Ground- and surface water concentrations expected from continuous leaching from tailings storage facilities can be calculated using models.

Radioactivity measurements

A full spectrum analysis is required for dose evaluation. When selecting the appropriate measurement techniques, one must ensure that achievable detection limits are low enough and suitable for the purpose.

Receptors

A typical public exposure defined from a SPR analysis is that of the agricultural community who occupy the land adjacent to a NORM facility. This exposure condition considers contributions to a total effective dose from the atmospheric pathway as well as the aquatic pathway, and is a hypothetic conservative scenario.

The agricultural community living in the area relies on water resources. They may be exposed to contaminants present in the ore, products or residues of mining operations through the *aquatic pathway* when soluble radionuclides are transferred to the local groundwater and

surface water resources with effluent water that flows from the industrial areas. Leaching of radionuclides from stockpiled ore or TSFs may also result in contamination of ground- or surface water resources. A similar effect may be expected from rain that falls on the materials and proceeds to infiltrate into the residues.

Specific information on the habits and behaviour of exposed communities is defined (*e.g.* population and age distribution, land use, *etc.).* Information about activities in the area (*e.g*. crop production, animal farming, irrigation, *etc*,) and community habits (*e.g*. food type and diet, food source, source of water and consumption rate, indoor and outdoor activities) is required. Where there is a lack of specific information, published values from RG-002 (NNR, 2013) or international literature are generally used.

2.3.8 Dose to non-human biota

Organisms may be exposed to ionizing radiation from radionuclides in the environment by both external and internal exposure. The most relevant radiation source for external radiation exposure of an organism is contamination of soil, caused by dust fallout. The following pathways should be considered (see Figure 2-7):

- External exposure from contaminated soil, sediment or water
- Contamination of fur, feathers and skin
- Inhalation of (re)suspended contaminated particles or gaseous radionuclides
- Ingestion of radionuclides
- Direct uptake from water in the case of aquatic organisms

Where actual releases to the environment occurred, radionuclide activity concentrations in environmental media and organism can be obtained by direct measurement. When not possible, the concentrations need to be estimated or modeled. The concentration ratio as defined in 2.4.3 relates the activity concentration of a radionuclide in an organism to the activity concentration in the underlying media.

Similar to human dose calculation, measured concentrations are converted to a radiological dose using a dose-rate conversion factor (DCF). DCFs (in $mGy.day^{-1}$ per $Bq.kg^{-1}$) are provided for a set of reference organisms (ICRP, 2008). Dose to non-human biota is discussed in more detail in 2.4.

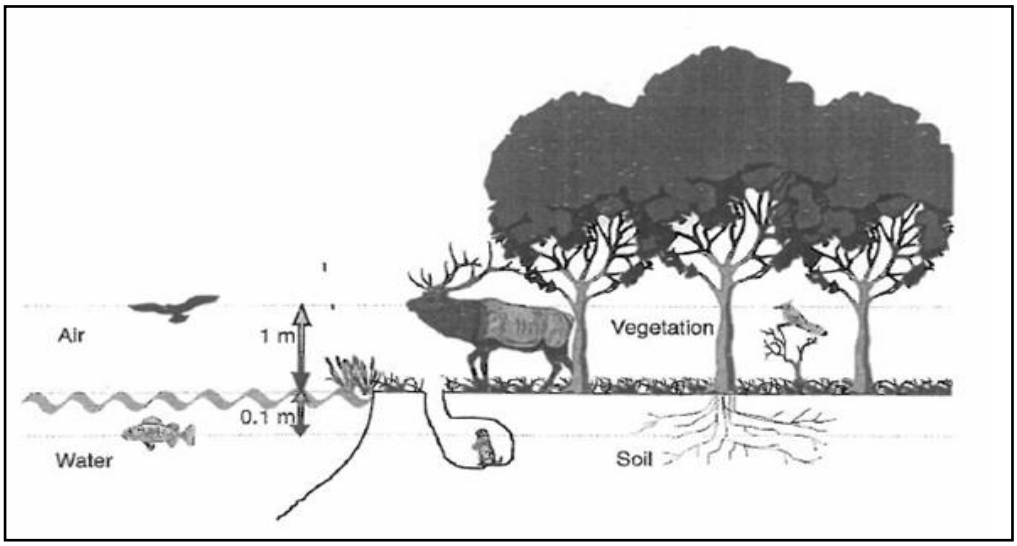


Figure 2-7: Exposure pathways for plants and animals

2.4 Protection of the environment

Non-human biota can be affected by high concentrations of radioactivity with exposure often much higher than for humans. The ICRP has created a framework for environmental radioprotection over the last decade focussing on absorbed dose to biota. Different criteria than for humans apply. A number of tools and models are available, which are being used within the regulatory framework for radiation protection in some countries.

In SA the main use of models for radiological assessment and protection of biota is anticipated to be in the NORM industries as discussed in this thesis. Environmental impact assessments conducted by these industries should demonstrate that animal and plants occurring in the area are adequately protected. The regulator in SA is yet to formulate specific national guidance for radiological protection of biota, which is important to ensure a consistent national approach. In current guidance documents it is still assumed that non-human species will be protected if humans are adequately protected.

2.4.1 Radioecology

In the research field of radioecology the aim is to understand transfer of radionuclides and the consequential exposure of humans and biota. The challenge is to apply this knowledge in models, which can be used to realistically predict the behaviour of radionuclides. Major data gaps were identified in coordinated research activities to compile concentration factors for

radioactive elements (IAEA, 2009). This scarcity of suitable data contributes to uncertainty in models.

The field of radioecology is too wide to address fully in this thesis. Of importance for the context of the thesis is how radiometric techniques can be used to address data deficiencies in the field. This includes determination of transfer factors and other parameters. Radioecology studies to determine biological effects on biota are outside the scope of the thesis.

2.4.2 ICRP system of protection

For decades radiological protection focussed on protection of humans, assuming that the environment is also adequetly protected. In the revised ICRP recommendations it was stated "that protection of man is at best an indicator of environmental protection" (ICRP, 2007). Therefore a conceptual framework, consistent with the system used for radiological protection for humans, was formulated to be used for protection of biota (ICRP, 2008, 2009b, 2014) – see Figure 2-8.

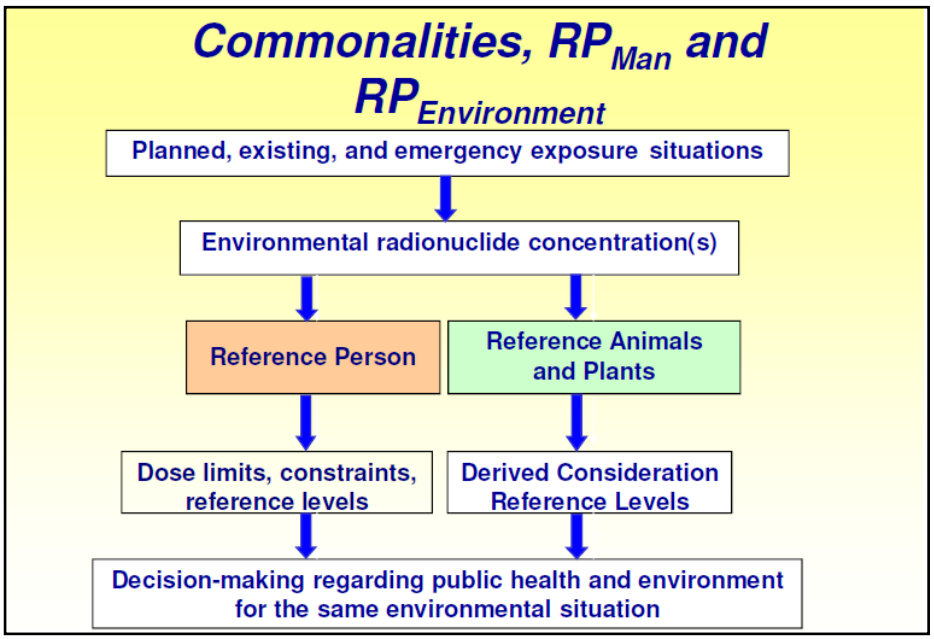


Figure 2-8: Conceptual framework for protection of both the public and the environment (ICRP, 2009b).

Reference animals and plants (RAP) are used to relate exposure to dose and dose to effect in a way similar to the system of radiological protection for humans in which a reference person is used. Reference organisms were defined as representative of all species, since it is clearly

impossible to consider all animal and plant species during dose assessments (ICRP, 2003, 2008). A RAP does not represent an actual individual or species but is a hypothetical entity with assumed basic characteristics.

Similar to human dose assessment, dose conversion factors are used to calculate the absorbed dose rate from activity concentrations. DCFs for 75 radionuclides for each RAP are available (ICRP, 2009b). DCFs of relevance for the case studies in 5.3 are summarized in Table A-11 (Appendix A).

2.4.3 Transfer factors

Transfer factors (TFs), also known as concentration ratios (CR) or bioaccumulation factors (BF) are used in dose assessment models to estimate the radioactivity concentrations in plants and animals based on the measured concentration in a source *e.g.* soil or water. Recommended transfer factors for common food products and organisms are available in several databases, such as TRS-472 (IAEA, 2010a) and the GENII computer code (Staven *et al*., 2003).

The following definitions are relevant:

Concentration factor (CF) or Concentration ratio (CR): "Describes accumulation in the plant or organism *i.e.* the ratio of the activity concentration of a radionuclide in $Bq.kg^{-1}$ fresh or dry mass in the organism to initial activity concentration of the radionuclide in water or soil". The concentration ratio is used to predict movement of radionuclides through the food chain and to non-human biota.

$$C_R = \frac{Activity\ concentration\ in\ biota\ (Bq.kg^{-1}\ fresh\ weight)}{Activity\ concentration\ in\ soil\ or\ water\ (Bq.kg^{-1}\ dry\ weight)}$$

Bioaccumulation factor (BF) for fish: Is defined as "the ratio of the radionuclide concentration in the organism (fresh weight) from all exposure pathways per concentration in water at equilibrium ($Bq.kg^{-1}$ organism per $Bq.kg^{-1}$ or $Bq.L^{-1}$ water)"

$$BF = \frac{Activity\ concentration\ in\ fish\ or\ aquatic\ organism\ (Bq.kg^{-1}\ fresh\ weight)}{Activity\ concentration\ in\ water\ (Bq.L^{-1})}$$

Transfer factor from soil to plant (TFs): "The uptake of radionuclides by plants from soil is described as the transfer factor, *i.e.* radionuclide concentration in the plant (dry weight) per radionuclide concentration in the soil in $Bq.kg^{-1}$."

$$TF = \frac{Activity\ concentration\ \ in\ plant\ (Bq.kg^{-1}\ dry\ weight)}{Activity\ concentration\ \ in\ soil\ (Bq,kg^{-1}\ dry\ weight)}$$

Transfer coefficients F_m ($d.L^{-1}$) and F_f ($d.kg^{-1}$) for milk and other animal products describes transfer from feed to animal products. F_m represents "the fraction of the radionuclide ingested daily that is secreted per litre of milk (day per litre)" and F_f, represents "the fraction of an animal's daily intake of a radionuclide that is transferred to one kg of the animal product". The transfer coefficient can be calculated from the ratio of the concentration in the animal product ($Bq.kg^{-1}$) to the activity consumed by the animal ($Bq.d^{-1}$).

$$F_m(d.L^{-1}) = \frac{Activity\ concentration\ in\ milk\ (Bq.L^{-1} fresh\ weight)}{Feed\ concentration\ (Bq.kg^{-1}) x Feed\ intake\ (kg.day^{-1})}$$

$$F_f(d.kg^{-1}) = \frac{Activity\ concentration\ in\ animal\ product\ (Bq.kg^{-1}\ fresh\ weight)}{Feed\ concentration\ (Bq.kg^{-1}) x Feed\ intake\ (kg.day^{-1})}$$

2.4.4 Terrestrial ecosystems

Naturally occurring radionuclides at NORM industrial sites can be absorbed by soil and will have different mobility depending on the soil properties. Through uptake and accumulation in edible parts of plants, these radionuclides can ultimately find their way into the human food chain contributing to internal dose (IAEA, 2010a). For better radiological assessment, it is important to understand the behaviour of natural radionuclides in soil-plant environmental systems.

Transfer of natural radionuclides to plants

Figure 2-9 shows the most important processes for transfer of radionuclides in a terrestrial ecosystem (UNSCEAR, 2016). Two major pathways are of importance for transfer to plants:

- Root uptake from water and soil.
- Interception from the atmosphere (radioactivity fallout deposition) or from re-suspended materials, and subsequent translocation to edible plant parts.

The concentration and availability of radionuclides in the soil, the soil-plant TF and the rate of deposition and translocation will influence the relative importance of these two pathways *e.g.* root uptake will be low for immobile nuclides, which are strongly sorbed to soil, in which case surface contamination from deposition becomes the more important pathway.

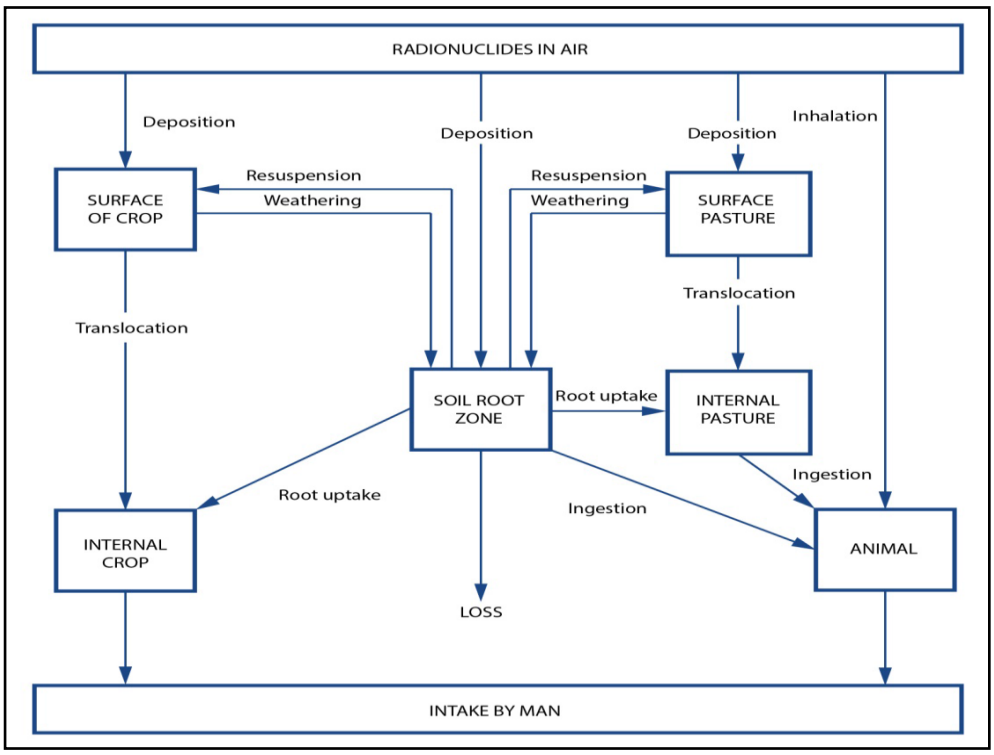


Figure 2-9: Processes for transfer of radionuclides in a terrestrial ecosystem (UNSCEAR, 2016)

Interception

The fraction of radioactivity deposited by wet or dry deposition, which are intercepted and retained by the plant, will vary depending on the plant type and stage of growth, the conditions under which the crops are cultivated and preparation before consumption. Meteorological conditions will also have an influence since deposited material can be removed from the plant surfaces by rain and wind. Absorbed radionuclides can be relocated to other parts of the plant. Final contamination of plants from direct deposition is therefore influenced by all three processes *i.e.* interception, retention and relocation.

Deposition (and interception) may significantly contribute to the activity concentration in the edible parts of pasture and leafy vegetables. For crops where the edible parts are protected by

inedible parts which are removed, *e.g.* cereals, deposition will not contribute to the activity concentrations of edible parts. Direct deposition should also not affect the radioactivity concentrations of root vegetables and tubers.

Soil-Plant transfer (Root uptake)

The radionuclide concentrations in plants can be predicted from the transfer factor, since plant concentrations are often linearly related to the soil concentration. If contributions from deposition and re-suspension of soil to the activity concentration in the edible parts are considered as insignificant, the observed CR can be regarded as soil-plant transfer only, *e.g*. in root vegetables.

Uptake and translocation of natural nuclides among different plant species vary widely, contributing to uncertainty in models. The TF for a specific plant species and radionuclide can also vary from one site to another, with season and with time after contamination. Transfer factors depend on the type of plant and part of plant concerned, the type of soil, chemical form of the radionuclide and interfering elements and environmental conditions (UNSCEAR, 2000). The bio-availability of radionuclides is directly influenced by soil reactions, especially by any factor influencing solubility (Hanlon, 1994).

Transfer of natural radionuclides to animals

Contaminated grazing land and water are a source of exposure to animals, which in turn is then a pathway to human exposure. Contamination can be via three routes: Absorption through skin, Inhalation or Ingestion of which inhalation and ingestion are regarded as the major routes of exposure. Ingestion occurs through water, contaminated feed and soil that adhere to the surface of forage/grass. Intake via water is usually a small contributor due to low intake rates. Uptake of radionuclides by animals is dependent on the animal species, mass, age and growth rate of the animal, food habits, the digestibility of the feed, *etc.*

Transfer coefficients F_m and F_f as defined in 2.4.3 has been widely adopted as the basis for quantifying transfer to both milk and meat and recommended values are incorporated in many predictive food chain models. To estimate the transfer coefficient the dietary intake rate must be quantified. For agricultural animals the intake varies according to feeding strategies (indoors or grazing). The relative proportion of grass, grains and other dietary constituents is

important in determining radionuclide intake and may vary between and within countries. Where animal practices do not involve confinement or strict feeding regimes, there is no reliable way to estimate feed intake. As an alternative, the concentration ratio of animal tissue to soil can be calculated. This can be very useful provided the intake and resulting tissue concentration is linear to the concentration of the soil. If the intake is mainly from non-soil related products such as direct deposition of fresh fallout onto forage or the ingestion of water or mineral feed supplements, the use of the soil-animal tissue CR is inappropriate.

The ingestion of soil during grazing can be an important contributor to intake of activity, particularly for radionuclides that are not taken up readily by grass. Depending on pasture conditions, soil ingestion can constitute up to 14% of the dry matter intake by cattle, but averages less than 2% over the year (Linsalata *et al*,. 1989). A commonly used value for dose assessment is 0.5 $kg.day^{-1}$; the RG-002 recommended value is 2.15 $kg.day^{-1}$ (NNR, 2013).

2.4.5 Aquatic Ecosystems

Radionuclides in the environment eventually find a way into water, resulting in a long term source in aquatic ecosystems. Uptake of radionuclides by aquatic species may occur through direct uptake from the water (and for fish through the skin or gills) or uptake from other media, including food and sediment. Parameters of importance in models used to evaluate the impact of contaminated water on aquatic species are distribution coefficients (2.7.2) and bioaccumulation factors (2.4.3).

Environmental chemistry will influence mobility and availability of the radionuclide for uptake. A radionuclide with a high K_d value is less mobile due to high adsorption to sediment, and accumulation in fish will be low. For these radionuclides a CR based on sediment rather than water better represents the correct pathway for accumulation and should be used in the model.

Bio-accumulation values vary widely with fish type, size and age of fish, feeding habits and migratory behaviour, type of water body, water chemistry, physical-chemical form of the radionuclide and absorption and re-suspension processes. The range of this potential variation for fish and other species is indicated in Table A-14 (Appendix A). Data show differences between various fish species, as well as variation within a species (IAEA, 2009). Distribution in organs may also vary; with higher concentrations found in liver and bone compared to

flesh (Skipperud *et al*., 2013; UNSCEAR, 2008).

2.4.6 Studies conducted on transfer

Many studies on transfer of natural radionuclides from soil to plants and other biota have been carried out worldwide over the last two decades (Al Masri *et al.*, 2010; Bunzl *et al.*, Kreuzer, 1979; Ewers *et al.*, 2003; Gwynn *et al.*, 2013; Howard *et al.*, 2009; Izak-Biran *et al.*, 1989; Linsalata *et al.*, 1989,1991; Persson & Holm, 2011; Staven *et al.*, 2003; VandenHove *et al.*, 2009b and Wang *et al*., 2015). The majority of these studies concern transfer to crops or plants, with only limited data on the transfer from feed to animal products. Parameters obtained from these studies are summarized in Table A-13 to A-15 in Appendix A.

Transfer factors [soil-plant concentration ratios]

IAEA TRS-472 (IAEA, 2010a) contains transfer data for a wide variety of plants and animal products, and is a useful primary reference for natural nuclides when using models for radiological assessment. Other comprehensive literature reviews of soil-plant transfer factors for U, Th, Ra, Pb and Po were compiled by Ewers *et al.*, 2003; Staven *et al.*, 2003 and VandenHove *et al.*, 2009b). Differences were common due to the impact of parameters such as climate and experimental conditions. These differences were observed even for samples of the same crops collected at the same site.

The soil-to-plant transfer factors reported by Wang *et al*. (2015) for Thorium determined by gamma spectrometry, were much higher than IAEA-TRS-472 values. In gamma spectrometry the decay daughter of ^{232}Th (^{228}Ac, ^{212}Pb, ^{208}Tl) are measured to determine ^{232}Th, assuming radioactive equilibrium of the series. However, for plant samples, a high concentration of ^{228}Ac might be present due to the uptake of ^{228}Ra from soil, resulting in falsely reported high ^{232}Th activity for plant samples and overestimated TFs. Consequently, to accurately determine the soil-to-plant TFs for Th, analytical techniques such as alpha spectrometry and NAA are recommended.

Expect for limited data presented by Bain *et al*. (1994) specific TFs for South African conditions have never been determined. The data for vegetables and fodder collected from farms in the vicinity of gold mines in SA, was within the range of values in Table A-15 (Appendix A). Unfortunately due to the non-sensitive analytical techniques used in this study, many results were below the detection limit and some of the concentration ratios,

especially those for fodder-milk are questionable.

Transfer to plants

^{210}Po in plants originates from two sources, *i.e.* ^{210}Po directly present in the atmosphere (unsupported) or decay of ^{210}Pb present in the plants (supported). Studies suggest that plant concentrations of ^{210}Pb/^{210}Po mostly originate from atmospheric deposition and that interception is significant, specifically for pasture and leafy vegetables (Berger *et al.*, 1965; Gwynn *et al.*, 2013 and Pietrzak-Flis & Skowronska-Smolak, 1995). Soil-root transfer factors for ^{210}Pb and ^{210}Po may therefore be overestimated if CRs are not corrected for atmospheric contamination. Different mobility of Po and Pb will lead to different distribution in plant parts. According to Ewers *et al.* (2003), Pb is classified as weakly mobile and Po as mobile. ^{210}Pb tends to concentrate in roots and ^{210}Po in plant stems (Al Masri *et al.*, 2010; Pietrzak-Flis & Skowronska-Smolak, 1995). Most plants are enriched in ^{210}Po relative to ^{210}Pb. Nevertheless, it is erroneously frequently assumed in dose calculations that ^{210}Po and ^{210}Pb are in radioactive equilibrium in the diet.

Studies indicate increased accumulation of Ra in plants compared to Th and U (Pulhani *et al*., 2005; Smodis *et al*., 2015; Vera Tome *et al.*, 2003) with U more available than Th (Shtangeeva, 2010). The higher soil-to-plant transfer of ^{226}Ra could partly be attributed to its similar chemical behaviour to that of Ca, which is used by plants as an essential macro element. Crop uptake was found to be more dependent on soil concentrations than water concentrations used for irrigation.

Higher concentrations of Ra and U were found in the green parts and roots of crops than in fruit (Al-Hamarneh *et al*., 2016). Generally roots serve as a natural barrier preventing transport of many trace metals, including radionuclides, to upper plant parts. In pot experiments conducted by Bain *et al*. (1994) to determine radium uptake in roots and leaves of selected vegetables (cabbage, beetroot) from irrigation they found uptake to be better in roots, concluding that root crops are more vulnerable to radium contamination than leaf crops.

Transfer to animals

Recommended values for transfer coefficients for natural radionuclides to eggs, muscle and

milk of domestic animals were published by Izak-Biran *et al*. (1989) and Howard *et al*.(2009) (Table A-13, Appendix A). Concentration ratios for fodder-milk reported by Bain *et al*. (1994) for samples collected in gold mining areas in SA were orders of magnitude higher than literature values, which may be due to sensitivity limitations of the analytical techniques used for analysis, or incorrect units used for reporting.

In comprehensive studies conducted by Linsalata *et al.* (1989, 1991) it was found that intake from direct ingestion of soil was predominant for ^{232}Th. Ingestion of phosphate mineral supplement was the major route of intake for ^{238}U and ^{230}Th and intake for ^{226}Ra was mostly from dry feed, with smaller percentages from soil ingestion. Intake of ^{210}Po occurred through ingestion of vegetation, dust and soil. Intake via surface water was negligible for all elements.

Th, U and Ra were retained mostly in the bone of the animal, with ^{226}Ra concentrations in bone much higher compared to other soft tissues. This is a direct consequence of the similar metabolic fate shared by Ra and Ca. In a recent study conducted in South Africa (Winde *et al*., 2017) high U concentrations were measured in grass and in tissue of sheep on farms in an area with elevated levels of U in groundwater. The highest concentrations were found in wool, followed by hooves, teeth and bones, whereas levels in meat and inner organs were lower. In organs, concentrations were higher in the kidney, than in liver and lungs.

2.4.7 Radiological Models

There are a number of models/software tools, which can be used to estimate exposure of biota to radioactivity. Radiological models make use of parameters derived for specific conditions to quantify transfer of nuclides *e.g*. concentration ratios. When applying models it must be kept in mind that outcomes are usually very conservative. There may be considerable variations between the prediction of various models, due to the large variation and uncertainty in the parameters used in the models. For more reliable assessments, model calculations should be complemented by measurements to verify the results.

ERICA (Environmental Risks from Ionizing Contaminants)

The ERICA integrated approach (Larson, 2008) is commonly used for environmental radiological protection. The approach is based on the concept and use of reference organisms (RO) for relating exposure to dose, and dose to effect, for different types of animals and plants in a manner compatible with the ICRP framework (Beresford *et al.*, 2008). The list of

reference organisms was selected to be typical for ecosystems within Europe. A supporting software package, the ERICA Tool (Brown *et al*., 2008) is used to estimate exposure to reference organisms. A new version of the tool was released in 2014 (Brown *et al*., 2016) containing updated transfer databases. The ERICA tool can be downloaded for free at http://www.erica-tool.com.

The software operates on three tiers – generic screening, detailed screening and site-specific analysis. Assessment at Tier 1 is conservative and does not require specialist knowledge. It is used to screen out sites with negligible radiological risk. Input media activity concentrations are compared against Environmental Media Concentration Limits (ECMLs). If the calculated risk quotient (RQ) is less than one, there is a very low probability of the dose rate to any organism to exceed the screening dose rate and the risk is considered as negligible.

Tier 2 is also a screening tier, but dose rates are explicitly calculated. More detailed input is required and the user is able to define its own organisms and edit default parameters used for calculations. Radionuclide activity concentrations in environmental media are used as input, as well as activity concentrations of the organism itself, if known. The estimated total dose rate for each reference organism is compared with the selected screening dose rate. A conservative RQ value less than one for all organisms indicates that the screening level at Tier 2 has not been exceeded. A site-specific assessment can be conducted at Tier 3 providing not only a simple yes/no answer, therefore requiring an experienced software user. Tier 3 assessment was not used in this thesis.

The assessment involves two basic calculation steps: Estimation of the activity concentration in environmental media and biota and estimation of the dose rates to biota. Parameters used for calculation of the dose rate from measured or modeled radionuclide activity concentrations in environmental media include CRs, K_d values and DCFs. The default parameter values in the model were obtained from reviews of several publications, but large variations cause uncertainties when applying the ERICA tool. It is recommended to use site-specific data in assessments where available.

If adequate measured data are unavailable, the radionuclide activity concentrations in biota are calculated from media activity concentrations (water or soil) using the CR. The definitions of CR as used in the ERICA tool is as defined in 2.4.3, where activity

concentration refers to the whole body of the biota. For the aquatic environment, distribution coefficients, as defined in 2.7.2 are used to derive activity concentrations in sediment from water concentrations and vice versa. The external and internal dose rates (in units of $\mu Gy.h^{-1}$) are calculated similar as for human dose (see 2.3.9) as the product of the activity concentration and a dose conversion factor. The estimated dose is compared to a reference screening dose rate. The default is 10 $\mu Gy.h^{-1}$, but the model allows use of a screening dose rate of 40 $\mu Gy.h^{-1}$ for terrestrial animals and aquatic mammals, reptiles, amphibians and birds or 400 $\mu Gy.h^{-1}$ for terrestrial plants and all other aquatic species. These numbers were derived from the IAEA (1992) limits.

Case studies for application of the ERICA model in this thesis are presented in 5.3.

2.5 Naturally occurring radionuclides in water

According to UNSCEAR (2000) drinking water may contribute significantly to exposure from natural radioactivity. Radioactivity in water may contribute to internal exposure via a number of pathways, as discussed in 2.3.4. Results of water samples analysed at out laboratory are used by industries for various purposes. These samples include bottled mineral water, surface water, ground water and process water from mining- and mineral industries. Selected results are presented and discussed in 5.1. Published data for radioactivity concentrations in water sources in South Africa and exposure due to ingestion of water from these sources are scarce.

2.5.1 Nuclides to consider for dose from ingestion of water

Although all nuclides in the three natural decay chains can in principle contribute to the total radiation dose from ingestion of water, the contribution from some radionuclides will be small because they are less radiotoxic (having a small DCF) and/or their parents may be present only at very low activity concentrations in water. Therefore measurement of every single nuclide is usually not necessary. The main nuclides contributing to radioactivity in water are ^{238}U, ^{234}U, ^{226}Ra, ^{228}Ra, ^{222}Rn, ^{40}K and occasionally ^{210}Pb, ^{210}Po and ^{230}Th. The highest contribution to dose is often from the radium isotopes ^{228}Ra and ^{226}Ra, and in some cases ^{210}Po and ^{210}Pb. According to literature the typical dose contributions of the radionuclides due to water are in the order: ^{210}Po> ^{228}Ra> ^{210}Pb> ^{226}Ra> ^{234}U> ^{238}U> ^{224}Ra> ^{235}U (Jia & Torri, 2007).

Concentrations of uranium isotopes in water are usually high due to its mobility, especially in areas with high radioactivity but, given their relatively low DCF, their contribution to the total dose is low. Enrichment of ^{234}U in water is common, mostly due to recoil associated with the disintegration of ^{238}U (Benedik & Jeran, 2012; Ivanovich, 1994; Rožmarić *et al*., 2012; Vasile *et al.*, 2016). Groundwater, unaffected by human activities, is therefore characterized by a $^{234}U/^{238}U$ ratio of two or greater, whereas water in contact with uranium (due to human activities) contains ^{234}U and ^{238}U in equilibrium (Skwarzec *et al*., 2001).

Thorium is more abundant than U in the earth's crust, but due to low solubility concentrations in water are low. Despite high concentrations of ^{222}Rn found in some water sources, especially well water (Vesterbacka, 2007), concentrations in tap- and bottled water are usually negligible due to its volatility and physical decay. Also, ^{222}Rn is poorly absorbed when ingested thus does not contribute to ingestion dose and can be neglected in dose calculations. Potassium is an essential mineral found in all living organisms and in all water supplies. Although ^{40}K can add significantly to the measured gross beta activity, the contribution to dose is trivial.

Measurement of gross alpha/beta activities is useful for screening to provide an indication of the radioactivity levels in the water and a conservative estimation of the potential radiological impact. However, since equilibrium cannot be assumed in water, nuclide specific analysis is highly recommended for accurate determination of individual radionuclides in water (Desideri *et al*., 2007; Forte *et al*., 2006). The approach followed for analysis of water in this study, was to perform a full nuclide specific analysis to include results for all of the major contributing nuclides listed in Table 2-2 and prescribed by the NNR (NNR, 2013).

2.5.2 Radioactivity guidance limits in water

In most developed countries, public water suppliers are required to monitor concentrations of metals and pesticides, and often also radioactivity in drinking water. Consequently many countries have established water quality standards and set concentration levels at which radioactivity must be controlled as discussed in 2.2.7.

The radiological quality of drinking water in SA should be evaluated based on international standards. This is specifically important in the bottled water industry, to enable them to export their products to the European market. However, the bottled water industry in SA is

not specifically regulated and no guidance levels for radioactivity have been set. Regulated NORM industries in SA are required to comply with a dose constraint of 0.25 $mSv.a^{-1}$ set by the NNR. A radioactive survey of water quality should be able to guarantee that no individual nuclide will contribute more than 0.025 mSv to the annual dose. As shown in 4.9.2, the analytical protocol used must have the required sensitivity to achieve this goal.

According to international standards and recommendations, water intended for drinking purposes is first analysed for gross alpha/beta activity. Gross alpha radioactivity is defined as the total radioactivity of all alpha emitters, which is mainly due to radium and uranium isotopes. When gross alpha values are exceeded it is desired to know which radionuclide in the water is responsible for the elevated radioactivity, so that an effective clean-up technology can be chosen if required (see 2.5.5). Gross beta activity in natural water is due to the long-lived isotopes ^{40}K, ^{210}Pb and ^{228}Ra.

2.5.3 Transport and dispersion of radionuclides in water

Potentially large volumes of surface water and sediment can become contaminated from effluent discharges, because dispersion of radionuclides in surface water is much faster than in the case of radionuclides leached into groundwater. The concentration in surface water can however be diluted, depending on the volume of water discharged and flow past the point of discharge.

The solubility of a specific nuclide in water will determine its mobility and rate of movement. Radionuclides released into surface water may be transferred with the water flow, or can deposit and migrate to sediments increasing the radioactivity. The K_d concept as discussed in 2.7.2, is important to assess interaction of dissolved radionuclides with solids. The mobility of some "insoluble" radionuclides, which are normally tightly bound by soil or sediment, is increased by their tendency to absorb onto small particles known as colloids, which can move with the ground- or surface water.

U is mobile under oxidizing conditions and can be transported over long distances. Under reducing conditions, U precipitates and settles down with sediments, from which it may re-mobilize when conditions change. The migration of uranium in water is an ongoing concern in environmental research, also in South Africa (Winde, 2010). Thorium is generally far less mobile than uranium and its concentration in water is usually very low (UNSCEAR, 2000). A

large fraction of thorium may be associated with colloids (Langmuir & Herman, 1980). The result is that most of the thorium will be present in suspended matter or sediment. For this reason it might be necessary to analyse both the liquid phase and filtered solids (colloids) of water samples.

Radon, being chemically inert but quite soluble in water, is very mobile in the aquatic environment. Radium has relatively low solubility and does not form any soluble complexes that enhance its dissolution. Solubility is influenced by the common ion effect; it has been widely observed that highly saline waters are enriched in Ra with concentrations as high as 20 $Bq.L^{-1}$ reported in saline groundwater (IAEA, 2014a). Th adsorbed on colloids will release dissolved species of Ra from solid matter into water via desorption ($^{230}Th \rightarrow {}^{226}Ra$; $^{232}Th \rightarrow {}^{228}Ra$; $^{228}Th \rightarrow {}^{224}Ra$; $^{227}Th \rightarrow {}^{223}Ra$).

^{210}Po is present in water in both soluble and particle-bound forms. It is mobilized in acidic water, but tends to form colloids in alkaline waters. Lead is strongly adsorbed on clays and is precipitated in contact with quartz sand and limestone.

2.5.4 Types of water of interest for the study

Mineral and bottled water

Mineral water originates from deep aquifers and often has high concentrations of natural radionuclides, especially ^{226}Ra and ^{238}U, generally exceeding typical concentrations in drinking water (Kovacs *et al.*, 2003). Consumption of mineral water has become more popular worldwide with consumption as high as 0.6 $L.day^{-1}$ in some countries and thereby the possibility of ingestion contributing to the total annual effective dose has increased. Consequently the monitoring of radionuclide concentrations in mineral water has become more important and has become standard practise in many countries. No published results on the radioactivity of bottled water in South Africa were found in the literature study.

Groundwater

The concentrations of natural radionuclides in groundwater will vary depending on the local geology, but tend to be higher than in surface water. High concentrations will be found in groundwater from areas with U and Th bearing ores (Hughes *et al*., 2005). Uranium deposits for instance, are found in granites of Namaqualand (Abiye & Leshomo, 2013) and in

association with sedimentary gold in some places in the Witwatersrand (Gauteng Department of Agricultural and rural development, GDARD 2012). Groundwater is protected from atmospheric deposition, but can be contaminated if seepage from mining residue is not properly intercepted.

The major nuclides of concern in groundwater are ^{238}U, ^{234}U, ^{226}Ra, ^{222}Rn and ^{210}Po. Concentrations of ^{210}Pb and ^{210}Po may be higher than in surface water because of the presence of high concentrations of ^{222}Rn. ^{232}Th concentration is low due to formation of insoluble $Th(OH)_4$ and high absorption of Th^{4+} on surfaces of the aquifer rock.

Surface water

The concentration of natural radionuclides in surface water is typically low compared to groundwater. Concentrations will be lower in rivers than in dams, due to dilution and flow. The chemistry of the dam will influence partition of radionuclides between water and sediment. Very low concentrations of ^{232}Th, ^{230}Th, ^{210}Pb and ^{210}Po are expected in surface water due to rapid sorption onto sediments and suspended solids. The concentration of ^{230}Th, as decay product of ^{234}U, is expected to be higher than that of ^{232}Th. High radioactivity concentrations are only observed in surface waters when impacted by industrial activities.

Mining- and mineral processing water

Water is one of the main pathways by which natural radiation may be dispersed from mining- and mineral operations into the environment. Sources of contamination include fissure water (groundwater pumped from underground mine workings), process water (used in operations for metallurgical processes, dust suppression, *etc.*), storm water run-off from contaminated areas such as waste rock dumps, tailings storage facilities and various types of retention dams and seepage from mining residue. The radiological and chemical composition of mine water varies by site and depends on the characteristics of the ore body and surrounding area.

The potential contamination of surface- and groundwater sources in South Africa as a result of gold-mining activities has been an issue of concern for many years. Mining activities has greatly altered the water quality in the Witwatersrand basin as has been reported in several studies (Coetzee *et al*., 2006; Durand, 2012; Njinga *et al*., 2016; Njinga & Tshivhase, 2017).

Public awareness of the environmental (and radiological) impact of mining has increased due to frequent press coverage.

Although much of the water used in metallurgical plants is recycled and re-used some of the water needs to be discharged. Prior to being discharged, the water may need to be treated depending on the level of natural radionuclides in the water (see 2.5.5). The requirements for water treatment depends on whether water is directly released to the environment or used for drinking purposes, since the maximum allowable pollutant concentration may vary.

2.5.5 Treatment methods

The main problem with water treatment is that the processes designed to remove radionuclides from the water concentrate those radionuclides in filters and sludge with activity concentrations ranging from 10 to 7000 $Bq.kg^{-1}$ (Fonollosa *et al*., 2015), which has implications for waste disposal. Consequently, drinking water treatment plants are included in the group of NORM industries (IAEA, 2003a).

Treatment options are tailored to the chemical characteristics of the nuclide to be removed. Radon, which is chemically inert, may be removed by physical processes such as aeration of the water. Removal processes for the chemically-reactive radionuclides of radium, thorium and uranium include flocculation, concentrated lime treatment (addition of CaO), ion-exchange or reverse osmosis. Removal efficiencies can be as high as 99%. The most efficient method for uranium removal is anion exchange (Outala *et al*., 2008).

In South Africa treatment of AMD water discharged from the gold mines is relevant (see 2.12.5). Treatment of water and studies in this regard are however not included in the scope of this thesis.

2.5.6 Typical values of radioactivity in water worldwide

Numerous studies have been done worldwide to assess the radiation dose and resulting risk to the public from drinking water. These studies provide a wide range of data summarized in Table A-17 (Appendix A). Studies include all kinds of water sources *e.g.* bottled and mineral water: (Benedik & Jeran, 2012; De Oliveria *et al.*, 2001; Desideri *et al*., 2007; Rožmarić *et al*.,2012), groundwater: (Godoy & Godoy, 2006; Kleinschmidt *et al*., 2011, Lauria *et al*., 2012; Shabana & Kinsara, 2014; Vesterbacka, 2007), tap- and surface water: (Jia & Torri,

2007; Vasile *et al*., 2016; Vesterbacka, 2007) and mine water: (Gbadago *et al*., 2011; Njinga *et al*., 2016).

From the fact that the majority of countries reported ^{238}U and/or ^{226}Ra it can be deduced that these are the two nuclides, which are most often used for screening water for its radioactivity content. Radionuclides with low solubility like ^{232}Th are generally not reported unless high concentrations are expected, as in water from monazite-rich areas (Lauria *et al*., 2012). Average ^{238}U and ^{234}U activities in most types of water are in the range of 0.001-0.20 $Bq.L^{-1}$, which corresponds to a concentration of elemental uranium from 0.1–16 $\mu g.L^{-1}$. Elevated levels were reported for groundwater from some areas, mainly attributable to U-rich geological settings.

2.5.7 Studies conducted in South Africa

Due to its chemical toxicity, several health risk assessment studies for uranium have been carried out in SA, mostly by a research group at the North-West University (Winde, 2010; 2013; Winde & Sandham, 2004; Winde *et al*., 2017). Less effort has been made to quantify concentrations of U and other natural radionuclides in water from other areas in South Africa.

Kronfeld & Vogel (1991) reported an average $^{234}U/^{238}U$ ratio of (2.03±0.42) for all the main rivers in SA (18 sampling points) with a mean U concentration of 1.42±0.94 $\mu g.L^{-1}$. The U concentration in the Olifants, Doring and Berg rivers that drain to the southwest coast was low (0.07 $\mu g.L^{-1}$). Rivers draining the Witwatersrand gold mining area (Klip, Mooiriver, Vaal) clearly showed uranium pollution from the mines characterized by high U content (2.05 to 120 $\mu g.L^{-1}$) and low activity ratios (1.05 ± 0.05).

In 1995 the DWS initiated a project to determine the level and occurrence of radioactivity in water resources at selected sites in South Africa. The screening survey focused mainly on areas where elevated levels of radioactivity were expected. Since the findings indicated possible high risk from water resources in certain areas, an intensive monitoring study was conducted by the Institute for Water Quality Studies (IWQS) of the DWS in the Mooi River catchment area, extending between Krugersdorp and Potchefstroom, in 1997 (see Figure 2-10). The aim of the study was to evaluate the radiological status of water in the catchment (DWS, 1999). For the great majority of the 41 sites monitored the radiation dose was below 0.1 $mSv.a^{-1}$ with only two sites showing elevated dose (> 0.25 $mSv.a^{-1}$ single facility dose

constraint used by the NNR), both affected by discharge of effluent mine water. The great majority of the sampling sites were also acceptable with regard to uranium chemical toxicity, with only seven sites requiring further investigation. The sites with elevated uranium concentration occurred mostly around the centre of the Mooi River catchment, and all had contributions from mine water.

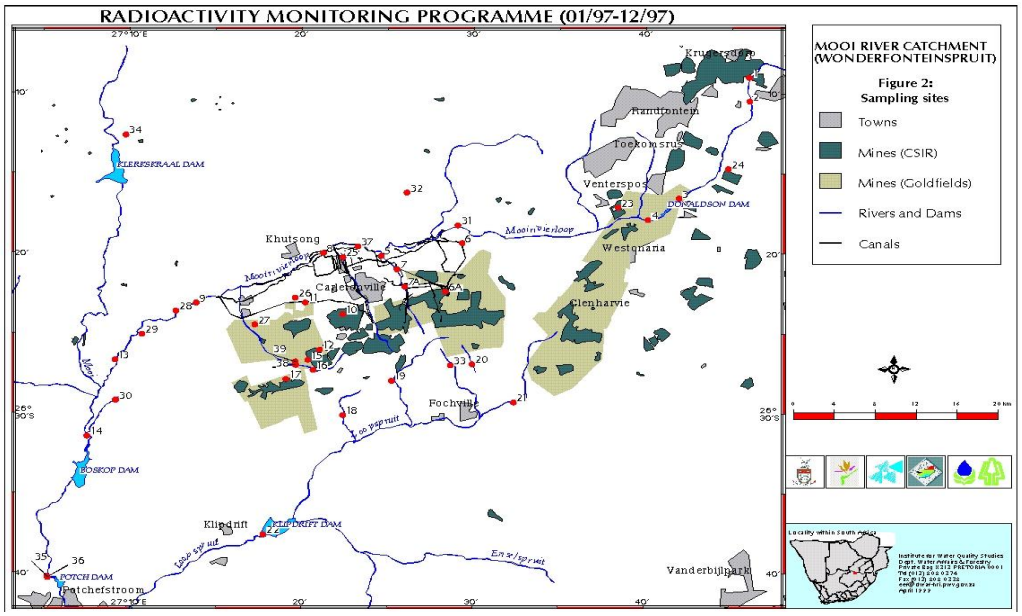


Figure 2-10: Mooi River (Wonderfonteinspruit) catchment area (DWS, 1999)

Another investigation was carried out by the DWS during 1998/9 in the Klip River catchment (DWS, 2003). The water from the majority of sampling sites in this study was of blue water quality (< 0.1 $mSv.a^{-1}$), whereas water from eight sites was classified as green (0.1 to 1.0 $mSv.a^{-1}$). Of these, two sites had a dose of > 0.25 $mSv.a^{-1}$ for the most sensitive infant age group. Possible significant U chemical toxicity concentrations were measured at three sites. An important finding from this study was that the dose at the lower end of the Klip River was not significantly different from the natural background dose value. This was important, as the Klip River flows into the Vaal System, with widespread use for drinking water purposes.

Following these case studies a guideline document was published (DWS, 2007) to provide information on the approach to follow for assessment of radiological water quality at three different tiers (see 2.2.7). A national radioactivity-monitoring programme (NRMP) was established to report on the radiological status of South Africa's water resources as part of quality monitoring requirements of the National Water Act (SA government, 1998b). Some

of the more recent data of samples analysed a part of the NRMP are presented in this thesis (see 5.1.4). The published guidelines were used for assessment of the radiological quality.

Tutu *et al*., (2009) reported high concentrations of U in surface water samples collected from a number of sites in the gold mining area (10-9820 $\mu g.L^{-1}$; ~121 $Bq.L^{-1}$, n=47) with lower concentrations in groundwater (39-162 $\mu g.L^{-1}$, n=7). The measurements were done with ICPMS. More recently Njinga *et al*. (2016) reported ^{238}U concentrations of 63.9 $Bq.L^{-1}$ in surface water close to a tailings facility in the Witwatersrand; decreasing to 1.92 $Bq.L^{-1}$ at a distance one km from the facility. The results confirmed that water draining from gold mine tailings frequently contains high concentrations of radionuclides. Concentrations of 4.46 and 9.22 $Bq.L^{-1}$ were reported for fissure (underground) and treated process water from a mine in Gauteng.

In a survey conducted by RA in which approximately 8 500 water samples were analysed (Faanhof *et al*., 1995) some areas in the Northern Cape were identified containing between 25 and 100 $\mu g.L^{-1}$ uranium (0.3 to 1.23 $Bq.L^{-1}$ of ^{238}U). High concentrations of U and elevated levels of radioactivity in some boreholes were confirmed (3-560; avg. 101 $\mu g.L^{-1}$ U) in a WRC funded study in 1998 (Toens *et al*., 1998). In a DWS follow-up study (DWS, 2005) only one of sixteen boreholes samples showed poor water quality, unacceptable for use. The water from the other boreholes that were tested was found to be ideal, good or marginal.

A masters degree study focusing on the relationship between groundwater chemistry and the occurrence of the radioactive element U impacting on groundwater reserves in Namaqualand, was conducted in 2011 (Leshomo, 2011). Samples from 57 boreholes were analysed for gross alpha/beta and uranium. The highest U concentration measured was 146 $\mu g.L^{-1}$ (1.8 $Bq.L^{-1}$ ^{238}U). U in soil samples collected 15-20 cm from the borehole varied from 402 to 22 625 $mg.kg^{-1}$ (5-280 $Bq.kg^{-1}$ ^{238}U). The reported minimum detectable activity (MDA) for the gross alpha results was 1-2 $Bq.L^{-1}$; based on which the gross alpha activity of 18 of the boreholes was reported as higher than the allowable WHO limit of 0.5 $Bq.L^{-1}$. The analytical technique used in this study seems not to have been sensitive enough for the specific purpose intended. For evaluating quality of water against WHO guidelines, an MDA in the order of 0.1 $Bq.L^{-1}$ is required (see 2.13.3).

In a more recent study Winde *et al.* (2017) again reported elevated levels of U found in groundwater in the Northern Cape. The analysis was done with ICP-MS. Some tap water

samples (2.0-106 µg.L^{-1}) exceeded the WHO limit. The concentrations in groundwater varied from 13.7-22100 (avg. 147 µg.L^{-1}), which were much higher than those reported by Toens *et al*. (1998). Similar high concentrations of U were reported in groundwater in countries, such as Finland with an abundance of uraniferous granites (Vesterbacka, 2007).

Manickum *et al*. (2014) reported on the quality of raw and potable water sources from the Umgeni catchment area, which was screened for uranium concentration and gross alpha/beta using the protocol in 4.4.1. The U concentrations ranged from <0.050 to 5.01 µg.L^{-1}, which was well below the latest WHO guideline of 30 µg.L^{-1} (WHO, 2011). The corresponding gross alpha- and beta activities of respectively 0.018-0.094 and 0.024-0.734 Bq.L^{-1} were in compliance with international WHO limits. The quality of water from this catchment was clearly not compromised by any NORM industry.

2.6 Naturally occurring radionuclides in food

Ingestion of radionuclides in foods can be an important contributor to the total dose received by an individual. Assessment of natural radionuclide concentrations in different foods is therefore important. Comprehensive studies on the concentrations of natural radionuclides in foodstuffs and the dose from intake of these radionuclides have been conducted worldwide (Choi *et al*., 2008; Fathabi *et al*., 2017; Fisenne *et al*., 1987; Rosa *et al*., 2015; Santos *et al*., 2002; Tuo *et al*., 2016.). Since about 18% of the average internal dose of the public is due to ingestion of ^{210}Po and ^{210}Pb (Clayton & Bradley, 1995) it is not surprising that the focus of the majority of published studies were on levels of ^{210}Pb and ^{210}Po in food (Arunachalami *et al*., 2014; Carvalho, 1995; Cunha *et al*., 2001; Izak-Biran *et al*., 1989; Kannan *et al*., 2001; Kim *et al*., 2017; Yamamoto *et al*., 1994).

Published data on the dietary intake of natural radionuclides in South Africa is relatively scarce. Some data on the ^{210}Po content in marine organisms (Cherry *et al*., 1994; Heyraud *et al*., 1994) and food samples (Louw *et al*., 2009) have been published. Bain *et al*. (1994) measured U and Ra in agricultural products from farms potentially affected by mine effluents. The concentration of uranium in farm grown vegetables was generally higher than those from background areas in other countries, whereas the radium values were similar. A study by Faanhof *et al.* (2007) indicated high concentrations of radionuclides in crops and low concentrations in fish samples in an area impacted by mining- and mineral industries.

NAA and gamma spectrometry was used in the study. The results presented in the case study in 5.2 are a continuance of this preliminary work.

2.6.1 Transfer of radioactivity to food

Contamination of food with radioactivity may occur from contaminated soil or water, deposition of radionuclides on plants, animals digesting contaminated plants, soil or water and phosphate-based mineral supplements. In the gold mine areas in SA it was found that radionuclides accumulate in sediment affected by mine effluent (Coetzee *et al*., 2006; NNR, 2007). These metals can be available for uptake by plants, including grass, vegetables, fruit and other agricultural products.

Radionuclides of importance are those with long half-lives that are easily taken up by crops and with high transfer rates to animal products such as meat or milk. The soil-to-plant transfer factor is a key parameter that directly affects dose assessment via the ingestion pathway, especially when models are used to estimate the activity concentrations in foodstuff. Transfer to animals and plants are discussed in 2.4. Experimental work done in this regard is presented in 5.3.

Each transfer point in the food chain normally acts to reduce the radionuclide concentration in the tissue or organ higher in the process. Findings indicate that the radionuclides found in plant tissue are often quite low compared to that in soil *e.g*. less than 1% of ^{226}Ra in soil is accumulated in the vegetables and transfer of ^{226}Ra from cattle feed to milk is only about 0.04% (Linsalata, 1994). However, certain tissues tend to accumulate selected radionuclides. This information can help with dietary choices, *e.g*. avoiding plant parts or animal tissue that accumulate radioactivity. For example, some organs do not accumulate ^{226}Ra or ^{210}Pb (e.g. kidney and muscle), while other tissues may (*e.g*. bone). Thus, humans consuming cattle muscle tissue (beef) will be exposed to lower concentrations of these radionuclides than actually ingested by the cattle simply because the radionuclides accumulate in the bone.

The irrigation of crops with contaminated water may lead to accumulation in plants to levels significantly higher than in the water with which they are irrigated. For this reason the maximum allowable concentration for uranium in water used for irrigation is 10 µg.L^{-1} (DWS, 1996b), which is lower than the upper limit for U in drinking water. In pot experiments conducted by Bain *et al*.(1994) it was however found that crop uptake was more

dependent on soil concentration than on water concentration used for irrigation. The relative importance of atmospheric deposition depends on the species *e.g.* lettuce and pasture grass are more exposed than root crops, and crops such as corn kernel where the edible part is protected from atmospheric deposition. Surface retained radionuclides will contribute to ingestion dose, if the plants are not thoroughly washed

2.6.2 Agricultural industry in South Africa

South Africa as a developing country has a vibrant economy that relies on mining, agriculture and other industries. In 2014 agriculture contributed 2.5% to the gross domestic product of the country, whereas mining contributed 8.4%. SA has only 12% of land suitable for production of rain fed crops, with only 3% of land considered as truly fertile land; 69% is suitable for grazing (DAFF, 2016). Since both industries (mining and agriculture) contributes to the economy of the country, it is important to quantify the effects of mining activities on the agricultural land. Therefore, environmental monitoring, which includes monitoring of the release of radioactivity, is done by mining industries.

Table A-9 (Appendix A) lists the main agricultural products produced in SA. For vegetables the main production is for potatoes, tomatoes, onions, green mealies, pumpkins, carrots and cabbage. The per capita consumption of the various products is also indicated in the table.

2.6.3 Typical values of radioactivity in food worldwide

Published activity concentrations of the main radionuclides of concern are summarized in Table A-18 (Appendix A). Reported data show a wide range depending on geological, agricultural and climate conditions. It is unlikely that high concentrations will be measured in food from regions with normal radioactivity soils and low atmospheric deposition, whereas food from areas in close proximity to NORM industries may have enhanced levels of radioactivity. For example Desideri *et al.* (2010) reported high ^{210}Po concentrations in mussels in the Adriatic Sea close to a stockpile of phosphogypsum compared to other areas. Higher concentrations were also reported in food from high natural background radiation areas (Arunachalam *et al.*, 2014; Fathabi *et al.*, 2017).

The difference in annual radioactivity intake worldwide is also due, at least partially, to composition of diets. UNSCEAR quotes a world-wide average annual intake of 58 Bq of ^{210}Po in the diet (UNSCEAR, 2000). This value is influenced by the high ^{210}Po concentration

in seafood and the high consumption of seafood in countries such as China and Japan.

2.7 Naturally occurring radionuclides in solids

Knowledge of radioactivity concentrations in soils and other solids are important for dose assessment, specifically to observe changes in environmental radioactivity induced by human activities. Ideally a baseline study should be done before any new industrial or mining activities is initiated in an area. Unfortunately there had been many historical mining activities worldwide and also in South Africa, which created a radioactive legacy only being dealt with now. Uranium contamination resulting from past mining activities represents a serious environmental problem at a number of sites in South Africa.

Many solid samples are analysed at our laboratory of which the results are used by industries for various purposes. These samples include soil, sediment, tailings material, rocks, scale, slag, *etc*. Some of the results are presented and discussed in 5.4. There are limited published data on radioactivity in environmental solid samples and public exposure due to the mining- and processing activities of NORM industries in South Africa.

2.7.1 Radioactivity in soil, sediment and tailings

Most minerals in the earth's crust contain small, but measurable concentrations of natural radionuclides. Generally the concentration of natural radionuclides in soil depends on the type of parent rock material; higher radioactivity levels are associated with igneous rocks such as granite and lower levels with sedimentary rocks. Many measurements of natural radioactivity in soil have been done worldwide of which results are summarized in Table A-19 (Appendix A). World average concentrations of ^{238}U and ^{232}Th in soil have been reported as 37 (16-110) and 33 (11-64) Bq.kg^{-1} respectively (UNSCEAR, 2008). The comprehensive table provided by UNSCEAR for soil worldwide however contains no values for SA soil.

There exist similarities between soil and the tailings from mining and milling of ores. Landa (2004) described tailings as "a technologically modified, soil parent material". High concentrations of radionuclides in gold mine tailings may present a hazard to the environment and to people living in the area.

The primary source for external radiation to humans is gamma radiation emitted by nuclides from the uranium and thorium series; as well as ^{40}K. The global average measured dose rate

from external sources in soil is 59 nGy.h^{-1}. The global outdoor terrestrial gamma dose rate in air 1 m from the ground calculated from the activity concentrations of ^{238}U, ^{232}Th and ^{40}K using equation 2.8 differs only slightly, with an average of 60 nGy.h^{-1} (UNSCEAR, 2000). The global annual effective external dose, calculated using equation 2.9, is 0.48 mSv (range: 0.3-0.6), with 0.07 and 0.41 mSv from outdoor- and indoor external radiation, respectively. The radium equivalent activity (in Bq.kg^{-1}), as defined in equation 2.10, is used as a common index to evaluate radiation exposure from solids.

2.7.2 Pathways and interaction of radionuclides in soil

Transfer of radioactivity from soil to animals and plants contributes to an effective dose in humans via pathways as illustrated in Figure 2-11. The mobility and behaviour of the radionuclides in the soil after deposition, will determine availability for plant uptake. After deposition, the nuclides migrate into the first cm of the soil, resulting in gamma radiation about one meter above the soil.

Radionuclides dissolved in water can be absorbed by the bottom sediments, transferring to deep sediment layers. The absorbed radionuclides can be remobilized becoming available for uptake by biota (IAEA, 2010a).

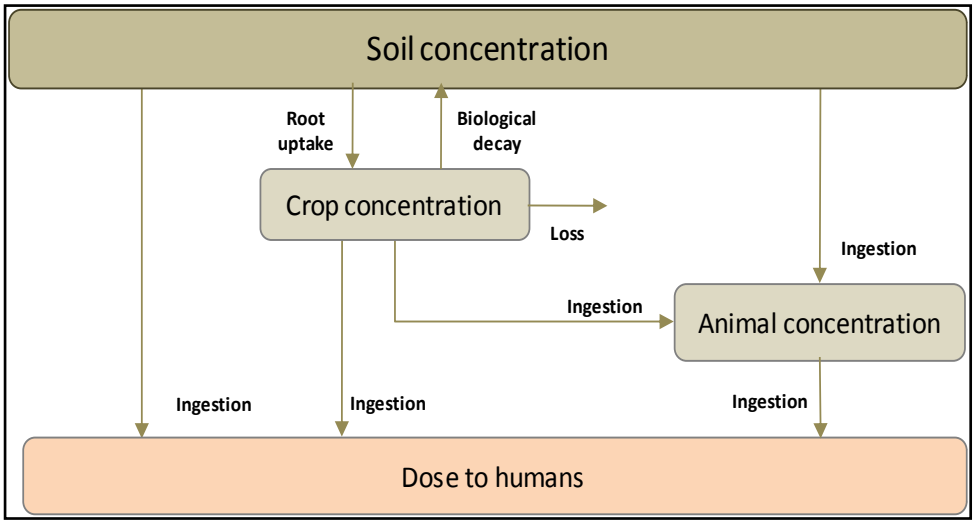


Figure 2-11: Pathways for soil

Solid-liquid distribution coefficient

The degree of sorption to the solid phase is quantified by the solid-liquid partition (or

distribution) coefficient (K_d). The K_d value is used to assess the mobility and residence time of a radionuclide in soil and is an important parameter for modeling radionuclide transport. It is defined as "the ratio of the contaminant concentration associated with the solid to the contaminant in the surrounding aqueous solution when the system is at equilibrium" (Kaplan & Serkiz, 2001). K_d in $L.kg^{-1}$ is given by:

$$K_d = \frac{contaminant\ concentration\ in\ solid\ \ (Bq.kg^{-1})}{contaminant\ concentration\ in\ water\ (Bq.L^{-1})}$$

Radionuclides that adsorb very strongly to soil have large K_d values (typically greater than 100 $L.kg^{-1}$). Radionuclides that do not adsorb to soil and migrate essentially at the same rate as the waterflow have K_d values near 0 $L.kg^{-1}$. K_d values are generally 10 fold higher for Ra, Pb and Th than for U and Po.

Theoretical partition coefficients of selected radionuclides in soil and sediment obtained from reference databases are shown in Table A-7 (Appendix A). RG-002 default values for use in South Africa seem to be based on that given in the IAEA (2010a) document. K_d values vary as function of soil geochemistry, mineralogy and organic matter content and may show a scatter of three to four magnitudes (EPA, 2004). K_d estimates are associated with large uncertainties and use of defualt values may result in significant error; therefore site-specific values are preferred for more accurate estimation of radionuclide mobility.

Methods to determine K_d values

The K_d is usually a measured parameter obtained from laboratory experiments. Methods used include the batch laboratory method, the column laboratory method, field-batch method and field modelling method (EPA, 2004). Batch tests (laboratory sorption experiments) are most commonly used and are conducted by spiking a solution with the element of interest, mixing the spiked solution with a solid for a specified period of time, separating the solution from the solid, and measuring the concentration of the spiked element remaining in solution. Different experimental conditions may contribute to the wide range of documented K_d values.

For field experiments, K_d values can be quantified from the concentration of the radionuclide in the solid phase divided by the concentration in liquid phase of the contaminated soil. This approach may lead to higher K_d values than those from a laboratory sorption test, because the radionuclide quantified in the solid phase may include radionuclides, which are not available

for exchange because it became fixed by the solid phase with time. The results presented in one of the experiments in the case study in 5.4 are an example of a field experiment where "true" equilibrium between the solid and liquid phases is expected.

Mobility of nuclides of interest in soil and sediment

Knowledge of mobility of radionuclides is important to evaluate movement of radionuclides at contaminated sites. Mobility of U and Th in soil and sediment depends on solubility and dissolution (leaching).

U occurs as uranyl (VI) in an oxidizing environment. U in this oxidation state is very mobile and can be distributed over large areas. Sorption behavior of U(VI) is influenced by pH and the concentration of dissolved carbonates. Sorption is low at pH <3 and increases with increasing pH (Vandenhove *et al.*, 2009a). In absence of large amounts of organic matter and clay, U is considered to be relatively mobile - organic matter and clay minerals provide exchange sites and increase sorption of UO_2^{2+}. Th exists as Th(IV) in an aqueous environment and its mobility is limited by formation of the insoluble hydroxide, $Th(OH)_4$. Th has a strong affinity for suspended particles and once mobile it will rapidly re-absorb to become immobile (Vandenhove *et al.*, 2009a).

Radium occurs in the environment as a divalent cation, with a high affinity for regular exchange sites. Ra is readily adsorbed to clays and mineral oxides in soils. Since Ra will co-precipitate with $BaSO_4$, carbonates and ferric hydroxides, the presence of these compounds in the soil may lead to overestimated K_d values. Lead is strongly retained and hardly ever leached significantly from soil. Sorption increases with increasing pH and the presence of amounts of clay and organic material, oxides and hydroxides. Polonium in sediment showed limited mobility under acid mine drainage conditions (pH = 1-2) compared to uranium (Barbero *et al*., 2014).

2.7.3 Leaching of soil and sediment

Leaching may be defined as "any process of net mass transfer from a solid such as soil, sediment and ore, to the leachant". Leaching studies are done to assess the release of contaminants into the environment. In general, leaching tests can be classified as: (1) tests designed to simulate release of contaminants under a specific environmental scenario (*e.g.*,

synthetic acid rain leach test), (2) sequential chemical extraction tests, or (3) tests which assess specific leaching parameters.

Sequential extraction procedures are used for speciation of heavy metal ions in soil and to determine association with different fractions: (1) water soluble extractant; (2) dilute acid: exchangeable ions (3) carbonate or organic matter fraction; (4) reducible Fe-oxide fraction and (5) mineral structure (Schultz *et al.,* 1998). The first four steps involve selective extractions, whereas the last treatment is total digestion of the remaining sample. The last fraction is not likely to contribute to the sorption/desorption fraction or to enter the mobile aqueous phase and should not be included in the K_d value.

2.7.4 Studies conducted in South Africa

Whereas some national studies had been done on radioactivity in water sources in South Africa (see 2.5.7), radioactivity in solids, soil and sediment remains largely unexplored. The data of assessments done by industry are seldom published in the public domain.

Geological formations in SA are known to contain high U concentrations with typical concentrations (own conversion to $Bq.kg^{-1}$ ^{238}U) as reported by Winde *et al.* (2017) of 62-3110 (Namaqualand metamorphic complex); 18657 (Karoo sandstones); 435-871 (Concordia west coast granite); 435-1680 (Springbok flat coal fields) and 120-37314 (Cape granites). They reported U concentrations of 6.2-65.9 $Bq.kg^{-1}$ in rock and 17.4 $Bq.kg^{-1}$ in soil in the Northern Cape, which compared to the global average of 33 $Bq.kg^{-1}$.

Bouwman & Peters (2013) reported undetectable or low U concentrations in sediment from 33 sites in the Vaal River and Orange River (average 23.6 ± 78.4 $Bq.kg^{-1}$). Only one site in the lower Vaal River catchment had a concentration of 620 $Bq.kg^{-1}$.

A study conducted by the Water Research Commission (WRC) in 2002 to investigate the presence of radionuclides in sediments in the Mooi River catchment (Wade *et al*., 2002) indicated accumulation of radionuclides in sediments downstream from gold mining activities. Using a sequential extraction procedure, uranium was found to be adsorbed to the carbonates, iron and manganese oxides and organic matter in the sediment and not in the internal structure. The bulk of the uranium was found to be mobilized by reaction with weak acid (*e.g.* acid mine drainage or acid rain). Thorium seems to remain in the inert fraction of the sediment.

Coetzee *et al.* (2006) found uranium to be of concern in sediment collected from a dam on an experimental farm situated downstream from mining activities in the WFS catchment. The average concentration of ^{238}U was 620-750 $Bq.kg^{-1}$, with a maximum of 8000 $Bq.kg^{-1}$ measured in an individual samples, compared to a local background of 12 $Bq.kg^{-1}$. The results of the speciation study were in agreement with previous studies, and found that contaminants of concern are bound to the reduced phase of the sediment. This implies that oxidising conditions (*e.g.* drying of sediment due to changes in flow regime) could remobilise these metals. Future control mechanisms should therefore ensure that reducing conditions are maintained.

In a study conducted in the WFS catchment area 10 years after the initial study, elevated concentrations of ^{238}U (563 $Bq.kg^{-1}$) were again measured in the streambed sediment of a site in the Lower-Wonderfonteinspruit (Hamman, 2012). The work was conducted on a dam on the same farm, but approximately one km downstream from the experimental group in the Coetzee study. The highest elemental concentrations were found in the clay sized fractions, which are generally available for plant uptake.

In previous work reported from this laboratory (Faanhof *et al.,* 2010) a total of 248 sediment samples from the WFS area were analysed for NORM by gamma spectrometry. The specific area was identified for investigation based on the findings of Coetzee. The measured concentrations were all high compared to world average values. The average ^{238}U activity was 934±14 $Bq.kg^{-1}$, which is almost twice the SA exemption level for natural radioactive materials of 500 $Bq.kg^{-1}$. The ^{226}Ra activity concentrations averaged 260 ± 10 $Bq.kg^{-1}$, ^{210}Pb average activity was 270 ± 20 $Bq.kg^{-1}$, ^{232}Th activity was 45.4 ± 0.9 $Bq.kg^{-1}$ and ^{40}K was 176 ± 2 $Bq.g^{-1}$. Typical background concentrations in soil from the area were as follows: ^{238}U=40, ^{226}Ra=40 and ^{232}Th=20 $Bq.kg^{-1}$ respectively (NNR, 2007).

Tutu *et al.,* (2009) reported results for radioactivity in tailings and sediment, in which U and Th was measured by both ICP-MS and gamma spectrometry (via daughter products). The large discrepancies between the results for U obtained by the two techniques proved that nuclide specific analysis should be performed whenever possible since equilibrium cannot necessarily be assumed. No discrepancies were observed for Th in the tailing samples (~140 $Bq.kg^{-1}$), indicating that the nuclides in the Th series are in radioactive equilibrium. Both Ac and Th are not very mobile and will accumulate in the tailings. The measured value in the

sediment was much lower (~1.5 $Bq.kg^{-1}$) confirming that Th does not seem to leach from tailings to accumulate in the sediment.

Njinanga & Tshivhase (2017) reported results for 45 soil samples from nine geographical sub areas in the environment of the Tudor Shaft informal settlement in Krugersdorp, which are highly affected by abandoned tailings storage facilities. The average concentrations of ^{238}U, ^{232}Th and ^{40}K in the soil, as measured with gamma spectrometry, were higher than the worldwide range (see Table A-19, Appendix A). ^{238}U and ^{232}Th activities were not measured directly but via their decay products, assuming secular equilibrium (2.13.4). Some extreme values were measured in samples collected at the top and base of the tailings dam. The gamma dose rate calculated from the concentrations of ^{238}U, ^{232}Th and ^{40}K in soil was 163 $nGy.h^{-1}$, which corresponded with the measured value of 153 $nGy.h^{-1}$ using a portable Na(I) gamma detector. This was higher than the world average measured value of 59 $nGy.h^{-1}$ (UNSCEAR, 2000). Kamunda *et al*., (2016) reported similar higher than average activity concentration of ^{238}U for soil samples from abandoned tailing dams, whereas soil samples from a background area in the North-West province had concentrations similar to the worldwide average (see Table A-19, Appendix A).

2.8 Mineral Sands industry

Mineral Sands refer to deposits in heavy minerals such as monazite, zircon, rutile and ilmenite, which were formed millions of years ago from weathering and erosion of the earth's surface. The geological processes that formed these mineral sands led to the incorporation of naturally occurring radionuclide**s** in the minerals. Radiological aspects associated with the mining of these sands and the processes by which the various heavy minerals of commercial interest are concentrated and separated are addressed in IAEA Safety Report 76 (IAEA, 2012).

2.8.1 Mining and processing of mineral sands

The key titanium bearing minerals, which are mined to produce feedstock for the production of titanium dioxide pigment, are ilmenite and rutile (Collett *et al.*, 2014). Ilmenite is usually the main product of heavy mineral sands operations accounting for 45-75% of total heavy mineral production with other heavy minerals products, zircon and rutile, each typically accounting for 2-20% (IAEA, 2012).

After the ore has been mined it is processed at a primary concentration plant to produce a mineral concentrate. The heavy sands are separated from other sands using a system of gravity separators. The primary concentrate is further processed to removed tailings and excess slime. The final Heavy Minerals Concentrate (HMC) with a heavy mineral content of at least 80-85% (IAEA, 2012) is transported to a mineral separation plant. Magnetic separation is used to separate the magnetic minerals (ilmenite and monazite) from the non-magnetic minerals (rutile and zircon). Using electrostatic separation techniques the conductors (ilmenite and rutile) are separated from the non-conductors (zircon and monazite) (IAEA, 2012). The process is illustrated in Figure 2-12.

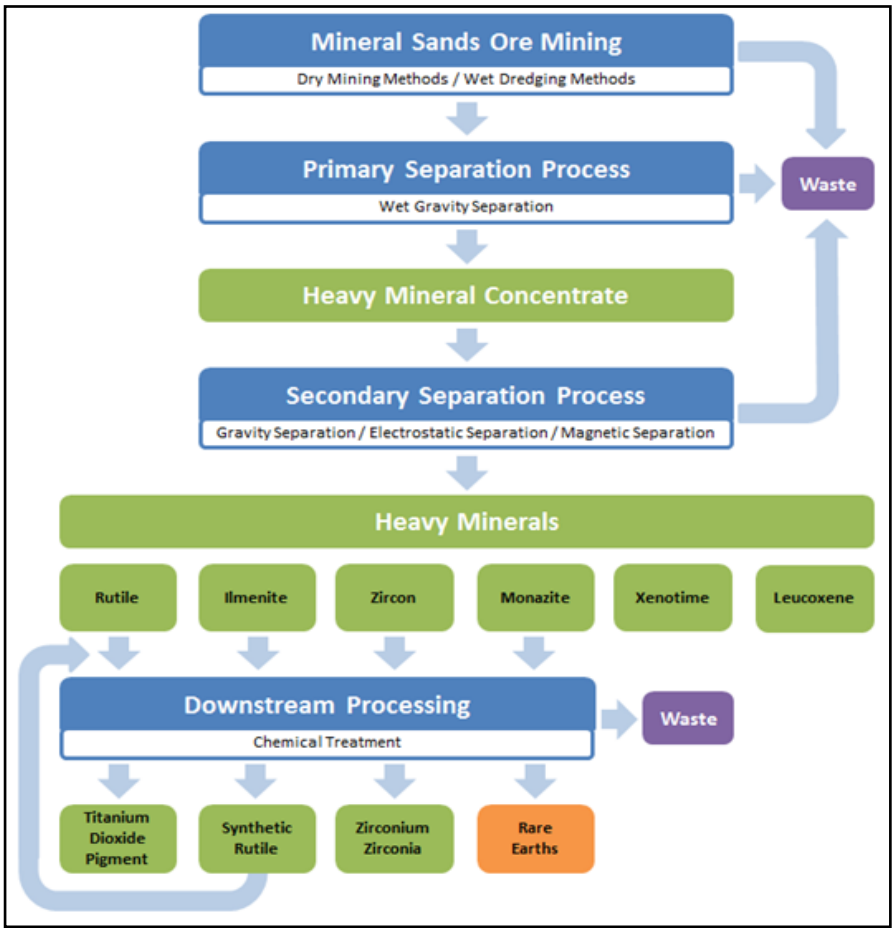


Figure 2-12: Mineral sands separation process (Collett *et al.*, 2014)

The minerals are either used as feedstock in their natural form or in an upgraded form such as synthetic rutile and titanium dioxide slag, which are produced through secondary processing of ilmenite. Upgrading of ilmenite to titanium slag by high temperature smelting is done in

South-Africa (IAEA, 2012). Monazite concentrate can be leached to obtain the rare earth elements (REEs) and also Th and U as by-products. The Th precipitate is purified and concentrated to obtain thorium nitrate, which is used in production of gas mantles and can also be used for Th-based fuels.

Residues from the mining and primary separation processes include vegetation, shells, clay, peat, topsoil and sand tailings. Residues from the secondary separation process include dust particles, clay fines, sand tailings and oversize solids. Monazite is also treated as a residue if not further processed. Residues are sent to disposal areas at the mine site, usually the mining void. Monazite, because of its relative high radioactivity content, is blended with tailings prior to disposal. The residues are covered with suitable topping material and the area is re-vegetated.

The feedstock is processed via one of two routes: the sulphate process route and the chloride process route, of which the details are not given here. The major by-products associated with the sulphate process route are gypsum, iron sulphates and sulphuric acid while those associated with the chloride process route are iron chloride, hydrochloric acid and neutralized iron oxides, hydroxides or carbonates. Some residue produced in the processes may be used as by-products, *e.g*. white gypsum is used in the building industry as a component of plasterboard and cement. Alternatively all residues from the process are disposed as waste in engineered containment facilities.

2.8.2 Natural radioactivity in mineral sands products

All materials related to the heavy mineral sand deposits contain radionuclides from the natural decay chains and are therefore considered to be NORM. The concentrations of U and Th may vary considerably from one mineral to another. Thorium is common in mineral sand deposits, whereas uranium is found at lower concentrations. The activity of the mineral can be assessed by measurement of the concentrations of the parent isotopes only, since nuclides of the U- and Th decay chains are usually in secular equilibrium. This equilibrium is disturbed by processing of ores and raw materials, which can cause the activity concentrations of the radionuclides in the different products, residue and waste streams to vary significantly. The radionuclides may become mobile and migrate to dusts, scales and other process residues, sometimes resulting in radionuclide activity concentrations higher than those in the feedstock mineral. Scales can contain concentrations as high as 400000 and

1000000 Bq.kg^{-1} ^{226}Ra and ^{228}Th respectively (UNSCEAR, 2008).

Typical radionuclide activity concentrations in mineral sands products are given in Table A-16 in Appendix A. Activity concentrations in the raw materials for rutile, ilmenite and titanium dioxide are typically less than 2000 Bq.kg^{-1}. With the exception of synthetic rutile, upgraded feedstock has lower radioactivity levels than those of the ilmenite from which they are derived. With production of synthetic rutile the majority of the thorium and uranium present in ilmenite pass through to the synthetic rutile product, and only a small proportion is removed from the process stream via the residues. The produced titanium dioxide pigments have low radioactivity concentrations, since radionuclides present in the original rutile and synthetic rutile minerals follow the solid waste stream during titanium dioxide production (IAEA, 2012).

The zircon mineral contains trace amounts of radionuclides from the ^{238}U and ^{232}Th decay series within the mineral structure. Typical concentrations of ^{238}U are 2000-4000 Bq.kg^{-1} but it may vary depending on the source (IAEA, 2006). Some zircon may contain elevated levels of thorium due to inclusion of grains of the thorium-bearing mineral monazite. Zirconia (ZrO_2) is manufactured from zircon by melting in a very high temperature furnace. The manufactured zirconia may contain higher levels of radionuclides than the parent with disturbed equilibrium (Harlow, 2017). Most of the ^{210}Pb and ^{210}Po end up in the silica fume with activity concentrations of 200 000 and 600 000 Bq.kg^{-1} reported for ^{210}Pb and ^{210}Po respectively.

2.8.3 Radiological impact of the Mineral Sands industry

Since the presence of elevated levels of radionuclides in mineral sands is well-known, protective and regulatory measures are usually in place at these industries. For regulatory purposes it is necessary to characterize and monitor radioactivity in solids from the zircon and mineral sands industry. Typical results are discussed in the case study in 5.4.5.

Occupational exposure

Occupational exposure is of specific concern in the mineral sands industry, especially where monazite-rich material is processed. Exposure to workers was found to be primarily due to external exposure to gamma radiation, and internal exposure through inhalation of long-lived alpha emitters associated with airborne dust (Collett *et al.*, 2014). Typically exposure is

reduced to 1-7 $mSv.a^{-1}$ in well managed plants (IAEA, 2012). According to UNSCEAR (2008) the maximum dose to workers in a zircon milling plant in SA was for a milling attendant (0.44 $mSv.a^{-1}$ of which 0.275 mSv was due to gamma radiation and 0.165 mSv due to dust inhalation).

External exposure to NORM can be reduced by radiological measures in the workplace such as shielding and limiting occupancy time whereas exposure to dust is likely to be controlled through general occupational, health and safety (OHS) regulations. Internal exposure from ingestion is unlikely to contribute under normal operational circumstances and can be prevented by PPE. Determination of area/individual dust inhalation dose and radon exposure is done by air sampling with subsequent gross activity analysis and radon gas measurement or calculation of radon gas exhalation.

Occupational exposure is not within the scope of the thesis, but is mentioned briefly, since the case studies in chapter five include an estimation of the dose from solids from the mineral sands industry as applicable to workers.

Calculation of exposure and dose to workers

The easiest way to monitor eternal exposure is by direct dose-rate measurements of the gamma emissions at the receptor *e.g.* workplace or individual monitoring. The dose rate can also be calculated from the measured activity concentrations in the materials using a dose coefficient. Gamma dose coefficients for exposure to bulk quantities of different types of NORM at a distance of 1 m, expressed as dose rate per unit activity concentration, are reported in IAEA safety series report 49 (IAEA, 2006) - see Table A-6 in Appendix A. Dose coefficients are given for the following chain segments, which are expected to contribute significantly to total gamma rate: $^{226}Ra \rightarrow {}^{214}Po$; $^{228}Ra \rightarrow {}^{228}Ac$ and $^{228}Th \rightarrow {}^{208}Tl$. Assuming a typical radionuclide composition for each NORM material an overall gamma dose coefficient defined as the total dose rate per unit activity concentration of the radionuclide with the highest activity concentration is also presented. When considering typical exposure for NORM industries, it is assumed that a worker spends 400 hours per year at a distance of 1 m from a large, unshielded volume of material (IAEA, 2006). Applying this to the range of dose rate values (either calculated or measured), gives an incremental effective gamma dose above background.

Using the worldwide activity concentration in IAEA safety report 76 (IAEA, 2012) and dose coefficients in Table A-6 (Appendix A), typical dose rates at 1 m from source was calculated for: Ilmenite 0.03-1.32 $\mu Sv.h^{-1}$; Rutile 0.07-0.51 $\mu Sv.h^{-1}$and synthetic rutile 0.09-1.4 $\mu Sv.h^{-1}$. This gives an incremental dose from gamma radiation in the range of 0.004 to 0.3 $mSv.a^{-1}$. The dose can of course be much higher in contact with the process material. Results for samples in a case study are presented in 5.4.4. For worker assessments in the industry gamma dose rates are usually measured with portable dose monitors.

It is important to note that external exposure to materials in which ^{40}K is the dominant radionuclide (*e.g.* fertilizers rich in potassium) can be automatically disregarded from any further consideration. The specific activity of ^{40}K, calculated from its 1.265×10^{9} year half-life, is 2.617×10^{5} $Bq.g^{-1}$ and its natural abundance is 0.0117%. The maximum possible activity concentration is 30.6 $Bq.g^{-1}$, this being the activity concentration of ^{40}K in pure potassium. Table A-6 (Appendix A) shows that the effective dose per unit activity concentration of ^{40}K ranges from 0.02 to 0.04 $mSv.a^{-1}$ per $Bq.g^{-1}$; the effective dose received is therefore always less than 1 $mSv.a^{-1}$.

Public exposure

The external dose received by a member of the public living near a mineral processing facility is generally no more than a few microsieverts per year (IAEA, 2012). There are no significant exposure pathways and doses received in the vicinity of mining operations and after refilling of the mined-out areas are likely to be lower than previous natural background levels.

Where feedstock is handled or stored members of the public may become exposed to materials containing moderately elevated levels of radioactivity. Sources include feedstock piles, which as a precautionary measure are stored in closed silos. Potential pathways include the usual (see 2.3.2) *e.g*. external gamma exposure, inhalation of dust and ingestion of contaminated water and food. Measures consistent with good environmental practice should be sufficient to ensure that no significant exposure to the public occurs. Discharge in air from production plants is strictly controlled, as is discharge of effluent. Most of the radionuclides entering the process will remain in the solid waste route, which will be disposed of in landfills. There will be no significant exposure to the public once the material is buried

provided that access is limited. Typical doses from different pathways mentioned by UNSCEAR (2008) are 0.001 $mSv.a^{-1}$ (discharge of water), 0.056 $mSv.a^{-1}$ (emissions to atmosphere) and 0.1 $mSv.a^{-1}$ (from waste facilities).

2.8.4 South African operations

South Africa is rich in mineral sands resources, which occur in some coastal areas. Nearly two thirds of the worldwide production of titanium minerals comes from just four countries: Australia, South Africa, Canada and China. More than 90% of titanium mineral production is in the form of ilmenite. In 2010 South Africa was producing 19.7% of the world total of TiO_2 (IAEA, 2012). SA accounts for 25% of the world's production of Zircon (Harlow, 2017).

Open cast mineral sands mining activities occur in South Africa. Heavy minerals are mined to produce titanium feedstock (chloride and sulphate grades), which includes ilmenite, natural rutile, titanium slag and synthetic rutile, high purity iron products and zircon. The products are used as feedstock in a wide range of applications including pigments, metals and ceramics. The industries are subject to the requirements of the NNR and have a Certificate of Registration (CoR) and radiation protection programme that meet those requirements.

The Namaqualand complex in South Africa is rich in monazite and the largest of these veins, at Steenkampskraal, has been mined intermittently since the late 1950s for thorium and REE, but has been dormant since mining ceased in 1963. A feasibility study for the mine has been done recently (Clay *et al*., 2014). Enhanced background levels of naturally occurring radioactive materials were present in the environment primarily due to contamination from prior mining operations, as well as from the natural surrounding outcrops. Radionuclide concentrations in solid material were mainly associated with monazite in materials associated with the underground mine, the historic waste rock and TSFs. Thorium activity in monazite were very high compared to other deposits in South Africa, while uranium concentrations were comparable to those at SA uranium mines.

Masok *et al.* (2016) reported radioactivity concentrations for samples collected from mineral ores at a storage facility in Richardsbay in Kwazulu-Natal. Nuclide specific analysis was performed on 30 samples collected from coal, phosphate rock, rutile, zircon and hematite stored at the facility. Concentrations for ^{232}Th were as expected in rutile and zircon, whereas ^{238}U in zircon was much lower than worldwide values (Table A-16, Appendix A).

2.9 Phosphate Industry

Phosphate rock is mined on a large scale as a source material for fertilizers and other phosphorus containing products, such as phosphoric acid and gypsum (UNSCEAR, 2008). Phosphate reserves are geographically concentrated, and are largely under the control of countries such as Morocco, China and the US with South Africa having about 2.3% of the world reserves and producing 2.3 million tonnes per year (IAEA, 2013). Europe and India are totally dependent on imports. South Africa exports about 16% of its supply of phosphate rock (www.foskor.co.za).

2.9.1 Radioactivity in phosphate ores, fertilizers and by-products

The potential problem of high concentrations of NORM in the phosphate mining and fertilizer production industry has been recognized for more than twenty years (Wymer, 2007). Due to their chemical affinities U and Th associate with minerals such as phosphate rock which therefore contains radioactivity above the average observed for the earth's crust and soil. The radionuclide concentrations of the different products depend on the geological characteristics of the phosphate ore as well as the extraction process used for phosphate mining and production. Several papers have been published in countries concerning the radiological characterization of the raw material, products and by-products of the phosphate industry. Typical concentrations are summarized in Table A-22 in Appendix A.

Phosphate ore

There are two main sources of phosphate-bearing ore, both containing NORMs and defined by origin. The most common source is phosphate of sedimentary origin (phosphorites), with as little as 4% being from igneous origin (apatite). Sedimentary material has higher concentrations of the ^{238}U decay series, whereas concentrations of ^{232}Th series radionuclides are generally not significantly elevated above soil background values. The radionuclide content of the ore is generally less than 3000 Bq.kg^{-1} (IAEA, 2006); with typical concentration of ^{238}U series in sedimentary phosphate deposit of 200-1500 Bq.kg^{-1}. In igneous phosphate ores, the concentrations of both the ^{238}U and the ^{232}Th series radionuclides are elevated (to about 100-200 and 100-400 Bq.kg^{-1}, respectively) but with lower concentrations of the ^{238}U decay series, compared to sedimentary ores (IAEA, 2013). Concentrations in phosphate rocks are similar to those in ores. The concentrations in tailings

are also generally similar to those in the ore from which they are derived. In ores and rocks of both sedimentary and igneous origin the ^{238}U and ^{232}Th decay chains are generally in equilibrium.

Phosphoric acid

Phosphoric acid, the raw material for production of phosphate fertilizers, is obtained in a wet process by reaction of the phosphate rock with sulphuric acid. During this process a by-product, known as phosphogypsum, is produced. This process disrupts the radioactive equilibrium within phosphate rock and the radionuclides are partitioned into various phases according to their solubility. Usually most of the U (90-95%) migrates to the phosphoric acid. Since ^{238}U and ^{234}U exist in the same chemical form, they remain in equilibrium during the digestion process. ^{238}U concentrations in phosphoric acid vary over a wide range from 140-2600 $Bq.kg^{-1}$ (IAEA, 2013).

Thorium also appears in the phosphoric acid, whereas more than 80% of the Ra, Pb and Po originally present in the phosphate rock migrates to the phosphogypsum (IAEA, 2014a). There are conflicting findings on the migration of Pb and Th during the acid digestion with some reports indicating migration to the phosphoric acid, depending on the process conditions and the characteristics of the phosphate rock (IAEA, 2013).

Fertilizers

The phosphoric acid is the starting material for different fertilizers, *e.g.* single super phosphate (SSP), triple superphosphate and mono-ammonium phosphate (MAP) and di-ammonium phosphate (DAP). In the process of fertilizer production the equilibrium is further disturbed and the radionuclide concentrations of the phosphoric acid are reflected in the various fertilizer products derived from it. The resulting fertilizer, are enriched in U (up to 150% relative to the ore, but depleted in Ra (UNSCEAR, 2008). The reported concentrations of ^{238}U in ammonium phosphate fertilizers (MAP, DAP) produced in different countries generally are in the range 300-3000 $Bq.kg^{-1}$; the concentration of ^{226}Ra is much lower in the range of 10-100 $Bq.kg^{-1}$. The presence of low levels of ^{232}Th in MAP and DAP is also indicated.

Phosphogypsum

Approximately five tons of phosphogypsum ($CaSO_4.2H_2O$) are generated for each ton of phosphoric acid (Gezer *et al*., 2012). The waste is moved to storage areas, or so-called gypsum stacks (Figure 2-13). ^{226}Ra, being chemically similar to Ca, is usually the main source of activity of the phosphogypsum (PG) with concentrations in the range of 200-3000 $Bq.kg^{-1}$ for material derived from sedimentary phosphate ore. The ^{226}Ra concentrations in PG derived from igneous ore are lower, ranging from 10-700 $Bq.kg^{-1}$. When the rock contains large quantities of ^{232}Th the PG will also have significant ^{228}Ra concentrations. The activity concentrations of ^{238}U are mostly below 100 $Bq.kg^{-1}$.



Figure 2-13: Phosphogypsum stockpile

PG is used in building materials and agriculture, although commercial use has been restricted in some countries because of concerns about its radioactivity content even though such concerns do not always have a proper scientific foundation. PG is used to replace natural gypsum, which is used by the cement industry as a set retarder for Portland cement (see 2.10.2). PG plasterboard is reported to have ^{226}Ra activity concentrations ranging from insignificant levels, as found in natural gypsum, up to 700 $Bq.kg^{-1}$ (IAEA, 2006).

Even though PG has a wide range of uses, production far exceeds demand, resulting in two alternative management approaches for surplus PG: (1) Stockpiling in large, above ground

containment structures known as stacks allowing the material to be used at a later time; and (2) Discharging to water bodies, thus permanently disposing of the material.

2.9.2 Environmental impact of the phosphate industry

Progressive changes in environmental regulation, notably within the European Union, have largely brought the discharge of PG to water bodies to an end, causing considerably more PG to be stored on land. Phosphate fertilizer is now mostly produced in and imported from Africa and the Middle East, transferring the waste disposal problem back to the ore-producing countries where direct discharge is still an important source of radioactivity to the environment (IAEA, 2014a). In SA it was still practise to discharge PG to the sea as dilute slurry in 2013 (IAEA, 2013). In principle, given appropriate conditions in the receiving water body the environmental impact of disposal can be negligible, but discharges need to be regulated to ensure acceptable levels of risk to humans and to the environment.

The use of phosphogypsum as a soil amendment may affect the levels of NORM in water, sediment, soil and crops and has been studied extensively. Papastefanou *et al*., (2006) reported ^{226}Ra concentrations in soil cultivated with PG from 50 to 479 Bq.kg^{-1}, which was significantly higher than in soil unaffected by mining, 35-55 Bq.kg^{-1}. Concentrations of ^{226}Ra and ^{210}Pb in food grown on mined phosphate lands were statistically higher than the concentrations of these nuclides in foods from background areas. However, an upper estimate of the likely incremental increase in annual ingestion dose was only 0.027 mSv (IAEA, 2013).

Several studies of the environmental impact of the phosphate industry have been published. Vandenhove *et al*., (2015) performed a preliminary environmental risk assessment of environmental contamination resulting from the activities of five phosphate fertiliser plants (located in Belgium, Spain, Syria, Egypt, and Brazil). The ERICA Tool was used to predict radiation dose rates and associated risk to the selected reference organisms using the ERICA default parameter setting. Some of the ecosystems were found to be potentially at risk with ^{226}Ra or ^{210}Po generally the highest contributors to the dose.

2.9.3 Radiological impact of the phosphate industry

According to the IAEA BSS the requirements for planned exposure situations apply if the activity concentration of any radionuclide in the uranium or thorium decay chains is greater

than 1000 $Bq.kg^{-1}$ (IAEA, 2014b). The phosphate industry is identified as being among those industrial activities that are likely to be subject to the requirements for planned exposure situations. The main areas of possible radiological concern in the phosphate industry are the following:

Occupational exposure occurs mainly from gamma radiation due to accumulation of mineral concentrates or residues. Radium bearing scales and sediments are formed inside the process equipment in the plants. The radionuclide concentrations in these materials vary from values similar to those in the original rock up to 1000 times greater (IAEA, 2006). Dose rates are generally highest near process tanks, piping, filters and large material stockpiles. Exposure to external gamma radiation and/or to inhaled dust might need to be considered during maintenance and decommissioning of plants. Assessments of occupational exposure suggested that workers receive doses of less than 1 $mSv.a^{-1}$ (IAEA, 2013). There is little potential for members of the public to receive significant external exposures from phosphoric acid production facilities. The activity concentrations in bulk materials are moderate and exposure to gamma radiation outside the site boundary can be expected to be negligible.

Some phosphate rock is converted in high temperature furnaces to elemental phosphorus, which is used for the production of high purity phosphoric acid. The residual solids in the furnace, also known as slag, contain ^{226}Ra concentrations ranging from 750 to 1100 $Bq.kg^{-1}$. Use of this slag as construction material may contribute to dose to the public (UNSCEAR, 2008). During the process, ^{210}Pb becomes concentrated in the precipitator dust by up to a thousand times (IAEA, 2006). The exposure of workers to this dust, as well as the disposal of any waste material, needs to be controlled.

Process water used in various stages of the production process is recycled by sending it to a large pond on the phosphogypsum stack for cooling and for settling or re-dissolution of solids before being returned to the process. Normal environmental protection requirements will ensure that no contaminated water is released to the environment, so there is little potential for public exposure via contamination of surface water bodies. Phosphate fertilizer can possess traces of nuclides, which might cause increased concentrations in watersheds of predominantly agriculturally used land. Exposures may vary widely from place to place depending upon the application rate of fertilizers and local environmental conditions. Doses are likely to be insignificant.

The processing of phosphoric rocks may generate gaseous and particulate emissions containing ^{238}U and ^{226}Ra. When discharged to the environment this may result in radiation exposure of the public (UNSCEAR, 2008). However, this dust tends to become rapidly deposited in the vicinity of the source and is unlikely to be transported to nearby residential areas. According to UNSCEAR (2008) the resulting dose from release of ^{222}Rn to the atmosphere is 0.13 $mSv.a^{-1}$ (external) and 0.002 $mSv.a^{-1}$ (air) for phosphorous and 0.02 $mSv.a^{-1}$ (external) and < 0.0004 $mSv.a^{-1}$ (air) from fertilizer production.

Production of phosphoric acid generates large quantities of PG, which are usually stockpiled in the immediate environment of the plants. Long-term storage and maintenance of PG in huge PG piles (also called stacks) can pose serious economic, environmental and radiological problems. Radon emanation and particulate air emissions from the pile, leaching of radionuclides from PG into groundwater and effluent discharges to surface bodies may result in contamination of the surrounding environment. Measures are taken during the construction and operation of PG stacks to keep the environmental impact of PG stacks within acceptable bounds. Nevertheless, leaching of the radionuclides from PG stacks by rain-or drainage water and distribution to the environment remains a concern. For examples, enhanced levels of ^{210}Po in some areas in the Adriatic sea due to erosion of the PG stockpiles along the coast, which resulted in seepage of radionuclides into a lagoon, was reported (Desideri *et al.*, 2010).

2.9.4 The phosphate industry in South Africa

As in other countries, phosphate fertilizer is essential to agriculture in South Africa. A phosphoric acid production facility has been in operation in the Lowveld region of South Africa since the 1960s. The process of producing phosphoric acid involves the digestion of fluoro-apatite ore with sulphuric acid. Products produced include phosphate-based granular fertilisers such as MAP, DAP and SSP, as well as phosphoric acid (P_2O_5). The two phosphate fertilizer producers in South Africa both hold CoRs with the NNR and therefore have to comply with set conditions and regulatory requirements.

Only limited peer-reviewed publications on radioactivity concentrations in products from the phosphate industry in South Africa was found. Van der Westhuizen (2007) reported lower concentrations of the ^{238}U decay series, but higher ^{232}Th concentrations in the igneous material found in the Phalaborwa complex in South Africa, compared to levels found in most sedimentary products. Concentrations in phosphate rock from the area was reported as

$^{238}U=^{226}Ra=^{210}Pb$ (140 $Bq.kg^{-1}$) and $^{232}Th=^{228}Ra=^{228}Th$ (550 $Bq.kg^{-1}$). Similar activity concentrations in rock phosphate were reported by Masok *et al*. (2016). Concentrations in phosphate tailings were lower with similar concentrations for the U- and Th series nuclides (260-350 $Bq.kg^{-1}$). From a safety assessment conducted at the phosphate mine the dose to members of the public was found to be less than 0.25 $mSv.a^{-1}$, with a maximum of 0.189 $mSv.a^{-1}$, thus in compliance with SA legislation, which implies that the industry can be exempted from regulatory control (Van der Westhuizen, 2007).

Msila *et al*. (2016) evaluated the suitability of PG from the Lowveld region of South Africa for use as building material. The activity concentration of the natural radionuclides in all of the 19 analysed PG samples were below the 500 $Bq.kg^{-1}$ limit set for regulation in SA. The radionuclides of the natural series were found not to be in secular equilibrium. The values obtained for the external and activity concentration indices were 2.12±0.59 and 2.65±0.76 respectively. The calculated radium equivalent Ra_{eq} was 513±76 $Bq.kg^{-1}$.

Bezuidenhout (2015) used in-situ gamma ray spectrometry to map and investigate the concentrations of naturally occurring radionuclides at a closed phosphate mine on the West Coast of South Africa. The measurements showed fairly high concentrations with medians of 320 $Bq.kg^{-1}$ for ^{226}Ra, 64 $Bq.kg^{-1}$ for ^{232}Th and 390 $Bq.kg^{-1}$ for ^{40}K. The highest concentrations were however confined to specific areas of the mine, such as the tailings dams, the refinement plant and parts of the excavations. The average estimated effective dose rates of all the areas were found to be 0.078 $mSv.a^{-1}$ with a maximum of 0.45 $mSv.a^{-1}$ found within the area that used to be the processing plant of the mine.

2.10 Building Industry

The building industry requires large quantities of low-cost raw material; therefore there has been increasing interest in using industrial waste products generated in NORM industries as substitutes for natural products in Building Material (BM). Concern has risen, however, over the potential content of radiological and other contaminants in the recycled materials. Caused by enrichment processes industrial by-products often contain higher radioactivity than other (natural) BM. The use of the industrial by-products as BM should therefore be evaluated. Therefore the reuse of NORM residues in BM has been as topic of research for many years.

As early as 1979, a report on exposure to radiation from natural radioactivity in BM was published (OECD, 1979) in which an attempt was made to quantify exposure to radioactivity from BM. The growing attention to these aspects has led authorities in especially European countries to develop specific regulations to guarantee the health of the public. Article 75 of the EU BSS released in 2013, specifically addresses NORM in BM (EU, 2013b). Criteria for the use of BM in construction have been defined so that the increase in dose with respect to natural background may not exceed 1 $mSv.a^{-1}$ (see 2.2.8).

In order to assess the possible radiological risk to human health due to living in buildings, it is required to measure the radioactivity concentrations in the BMs. The most commonly used method is gamma spectrometry, which exploits high energy resolution and high counting efficiency to perform qualitative and quantitative analysis (see 2.14.4).

In South Africa difficulties may arise in townships built in and around mining areas. There may be outcrops of uraniferous rock in the locality or elevated soil concentrations at some distance from tailings deposits. These will result in a risk of excessive radiation exposure if these materials are inadvertently used for building purposes or even if housing is located on such ground. No specific regulations for BM currently exist in SA.

2.10.1 Radioactivity in building material

Building materials (BM) can show elevated concentrations of natural radionuclides. This can be of natural origin, when the radiation is already contained in the raw material (*e.g*. natural stone), or it can be due to the addition of industrial products (*e.g*. zircon sand), intermediates or by-products (*e.g*. coal ash, phosphogypsum and furnace slag) to the raw building material. Natural material and waste products used in BM include the following: Aggregate, cement, clay, concrete, feldspar (minerals used in ceramic industry), fly-ash, gypsum, lime and limestone, mud bricks, phosphogypsum, sand (bricks and concrete), slag wood and zircon sand.

Bricks: Are made of lime and clay or sand-lime. Red mud bricks have fairly high radioactivity but do not pose a problem in their application as paving (Beretka & Matthew, 1985).

Cement: Cement is commonly used in construction of buildings both in urban and rural areas in South Africa. Due to its high production rate and wide use by the population, the radiation

originating from it deserves special attention as the work in this thesis seeks to achieve. During cement production different additive agents, such as gypsum and fly-ash, are added to the clinker. Radioactivity of the cement may be increased through the inclusion of these additives.

Concrete: Commonly used for building construction and prepared by mixing cement, sand and water. The radioactivity content will vary depending on the origin of the sand, cement and water.

Fly-ash: Is a by-product of coal combustion obtained from coal-fired power stations. This fine powder is normally disposed as waste but can be used as a replacement of sand and cement in pre-mixed concrete, clay bricks and for the filling of underground cavities. The finer fractions are used as a cement extender. The natural radioactivity of fly-ash is often one order of magnitude higher than the activity concentrations of other cement components that are in their natural form. Fly-ash has been found to have higher concentrations of radionuclides than the coal itself since the elements carrying the natural radioactivity are enriched (Xinwei, 2005). A trend of increasing activity towards smaller sizes has also been reported (Beretka & Matthew, 1985). Their work indicated that levels in fly ash and phosphogypsum could be reduced by the simple process of sieving the material and discarding the fines.

Granite: The use of granites as BM has become very popular in recent years. Granites are coarse-grained igneous rocks consisting of quartz, alkali feldspars and mica, and often contain high activity concentrations connected with the presence of potassium as a major element in the composition of K-feldspars and minerals such as monazite and zircon present in granite rocks. Concentrations of ^{40}K can be as high as 1200 $Bq.kg^{-1}$ (UNSCEAR, 2008).

Limestone: Lime (CaO) and limestone ($CaCO_3$) are important compounds of Ca. Lime are a white solid material that can be produced from limestone by the process of decomposition at 1000-1100^{o}C. Limestone is the main raw material for the manufacture of Portland cement (about 60-65% of CaO). Natural radioactivity concentrations are low.

Natural gypsum: Sedimentary rock extracted from mines or underground quarries. It is typically used in the manufacture of plasterboard and in Portland cement and generally has low radionuclide content.

Phosphogypsum: By-product gypsum generated during the manufacture of phosphoric acid for fertilizer (see 2.9.1). It can be used for making plaster-board and has potential for use as a retarder in Portland cement. It may have enhanced levels of radioactivity, specifically ^{226}Ra, which may be one or two orders of magnitude higher than natural gypsum, depending on the origin and the chemical treatment of the raw material. No practical technology appears to be in use for removing the ^{226}Ra, although as mentioned above, some studies indicated that the concentration can be reduced by fractionating the waste according to particle size (Beretka & Matthew, 1985). Utilization of PG in countries with large reserves of gypsum is not high, but it is often used in countries without much natural gypsum. The use of PG in BM has been restricted in some countries.

Silica Fume: Silica fume is the condensed vapour by-product of industrial smelting processes and is used as a cement extender. It may contain high radioactivity concentrations.

Slag: Blast-furnace slag is a by-product of the iron-making process. It is used mainly as an aggregate in concrete as well as an additive in cement. The radioactivity concentrations in the slag depend on the ore type, the origin of the raw material and the metallurgic processes.

Zircon sand: Used in the ceramic and refractory materials industry particularly for glazing tiles. Usually have high levels of radioactivity (~1000 $Bq.kg^{-1}$), which can result in a dose of 0.019-0.113 $mSv.a^{-1}$ depending on the Zr content (UNSCEAR, 2008).

Tiles: May have significant radionuclide content, due to the inclusion of zircon sand in the tile glaze.

Wood and insulation materials: Commonly used as BM and are unlikely to have a high radionuclide content.

2.10.2 Production of Cement

The main raw materials used in the manufacture of Portland cement are limestone, clay, shale and silica sand. These materials are blended in specific proportions and fired at high temperatures to form cement clinker. Clinker is cooled and ground with approximately 3-5% gypsum to produce the finished product locally referred to as CEM I (see Figure 2-14). CEM 1 consists mainly of calcium oxide (60%), silica (22%), alumina (3.8%) and iron oxide (4.2%) present in the raw material obtained from limestone quarries. Some magnesium oxide

is also present but varies with the origin of the raw material.

The CEM 1 material is inter-milled or mixed with relatively small amounts of mineral materials called "cement additives or extenders" such as blast furnace slag, fly-ash and condensed silica fume. The minor constituents do not exceed 5% by mass related to the sum of all main and minor constituents. Used in varying proportions, these additives, which are of natural or industrial origin, give the cement specific properties such as reduced permeability, greater resistance to sulphates and aggressive environments, improved workability, or higher-quality finishes. Portland type I cement contains less than 3% fly ash and Type II has 20% fly ash (Concrete institute, 2013).

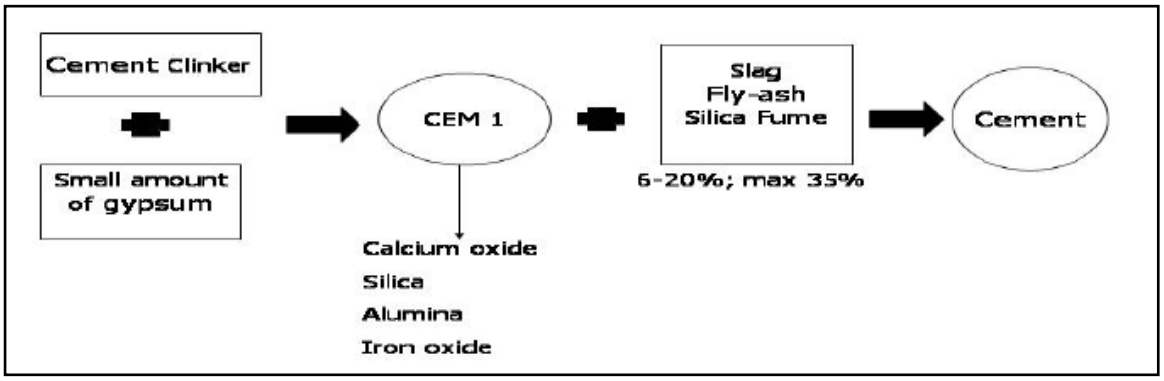


Figure 2-14: Production of cement

2.10.3 Radiological concern in the building industry

Portland cement is a gray powder with a diameter ranging from 0.05 to 5 µm, which is within the range of sizes of respirable dust. Cement as a BM may be a source of large amounts of dust polluting the air with ^{226}Ra. The ^{222}Rn gas emanated from the ^{226}Ra may constitute a radiation hazard to both people working directly with the cement materials and inhabitants of dwellings constructed with cement. According to UNSCEAR (2008) the cement industry releases about 157 and 78 GBq per annum of ^{222}Rn and ^{210}Po to the atmosphere respectively, resulting in a fairly insignificant effective dose of 0.005 mSv.a^{-1} via the external radiation pathway and less than 0.004 mSv.a^{-1} via inhalation.

The natural radioactivity of BM is usually determined from the ^{232}Th, ^{226}Ra and ^{40}K concentrations. These nuclides are predominant in almost all raw and produced materials widely used in the building industry. The radioactive equilibrium could be disturbed in

materials that have undergone chemical treatment *e.g.* ^{226}Ra dominates in phosphogypsum, ^{232}Th in red mud bricks and ^{40}K in aggregates, clay bricks and concrete.

The dominating exposure pathways due to elevated activities of these nuclides in BM are exposure by external irradiation and exposure by inhalation of radon and its progeny and subsequent irradiation of the lung tissue. An individual living in an apartment block made of concrete with average concentrations (40 Bq.kg^{-1}, 20 Bq.kg^{-1} and 400 Bq.kg^{-1} for Ra, Th and K respectively) typically receives an annual dose of about 0.25 mSv due to external exposure (EU, 1999). In Europe the application of a gamma index (I) to control natural radionuclides in BM are proposed (EU, 2013b). The EC guidance states a value of *I=1* for bulk material and a value of *I=6* for other material of restricted use. If this is fulfilled, the external exposure for a 7000 hour stay in a house (standard room geometry) remains below 1 mSv.a^{-1}; and the exposure by inhalation of radon is of minor significance (see 2.2.8).

Because radon is an inert gas it can move freely through porous media such as BM, although usually only a small fraction of that produced in the material reaches the surface and enters the indoor air. The fraction of ^{222}Rn that can diffuse through the BM is known as the emanation coefficient. Typical excess indoor radon concentrations due to building materials is about 10-20 Bq.m^{-3}, but in some areas it can be as high as 1000 Bq.m^{-3} (EU, 1999). A reference level of 300 Bq.m^{-3} is set in the new EU-BSS (EU, 2013b).

Radon concentrations in indoor air are dependent on changes in the emanation rate from soil, which in turn is determined by atmospheric pressure, temperature and wind speed. Changes in ventilation conditions, due to the opening of windows and doors, will affect the concentration levels. In addition, climatic changes can result in seasonal variations. In countries with good weather such as in South Africa, which favours ventilation and where people do not spend so much time indoors, the effect of radon may not be as bad as in European countries with colder climates. However the densely populated region on the Witwatersrand is surrounded by waste from the goldmines, which contains enhanced concentrations of ^{222}Rn from the uranium originally present in the ore. This may increase radon exposure to people in dwellings in the area. Determination of radon concentrations and exposure due to inhalation are not addressed in this thesis, since it is outside the scope of work routinely performed at our laboratory.

2.10.4 Typical values of radioactivity in BM worldwide

Due to radiological concern there has been renewed interest in the study of radioactivity in BM during the last decades and several studies had been conducted worldwide (Arabi *et al.*, 2015; Beretka & Mathew, 1995; Farai & Ademola, 2005; Hassan *et al.*, 2010; Kpeglo *et al.*, 2011; Ndontchueng *et al.*, 2013; Pantelic *et al.*, 2015; Pavlidou *et al.*, 2006; Ravisankar *et al.*, 2012; Righi & Bruzzi, 2006; Viruthagari & Ponnarais, 2011; Xinwei, 2005). From the results presented in Table A-20 (Appendix A) it is clear that natural materials and those derived from industrial wastes and by-products may have high levels of radioactivity, and that it may vary significantly for different countries.

It is worth noting that activity concentration values of the ^{238}U decay series in BM are generally published as ^{226}Ra concentrations. The majority of the reported results were determined by gamma spectrometric measurement of the three radionuclides: ^{40}K, ^{226}Ra and ^{232}Th. Dulanska *et al.*, (2016) used a radiochemical method, which enabled efficient radium separation from different type of BM with recoveries of up to 96 %. The ^{226}Ra activities determined by gamma spectrometry were in good agreement with the alpha spectrometry results.

Trevisi *et al.* (2012) set up a database of activity concentrations measurements of natural radionuclides in BM. It contains results for about 10 000 samples of bulk materials (bricks, concrete, cement, natural- and phosphogypsum) and superficial material used in the construction industry in Europe. Averages are shown in Table A-20 in Appendix A. Using the gamma index criterion for European countries the majority of samples exceeded $I_\gamma = 0.5$ value (dose of 0.3 mSv.a^{-1}). It was therefore decided in the EU that it will be more realistic to apply $I_\gamma = 1$ value (dose 1 mSv.a^{-1}). Only a small percentage of the data exceeded this value (5% of bricks and concrete). The data for gypsum confirmed that this material has no radiation protection significance. As regards PG, it is known to contain high levels of ^{226}Ra; 98% of phosphogypsum samples exceeded $I_\gamma > 0.5$ and 84% $I_\gamma > 1$; which implies that the use of this BM should be restricted and is not to be used as a bulk material.

2.10.5 Studies conducted in South Africa

A nation-wide survey of indoor radon exposure in South Africa (Leuschner *et al.*, 1989) reported an average radon concentration of 40 Bq.m^{-3} for a sample of 100 houses, with higher

concentrations found in houses with wooden floors. According to this survey it was decided to measure the radon levels in homes in areas with mine waste or natural granites, known to have high U levels. However no evidence of any further studies could be found in literature. The indoor radon concentrations of houses built on the slopes of the Paarl Mountains, which boast granite outcrops, were measured by means of electret ion chambers (Lindsay *et al*, 2008). It was found that the average radon concentration in houses on the west (granite) side of the town (132±11 $Bq.m^{-3}$) was about three times higher than those on the east side (37±3 $Bq.m^{-3}$). The mean activity concentration of soil samples on the west side was also 3-4 times higher than those on the east (see Table A-19, Appendix A).

Except for these studies on radon exposure, no other published work on the radioactivity of BM in South Africa could be found. No national investigations have been conducted. Cement is an important construction material for houses and buildings in South Africa. However, information of the radioactivity concentrations of ^{232}Th, ^{226}Ra and ^{40}K, in cement products and its raw materials in South Africa, is not available in literature.

2.11 Coal Industry

Fossil fuels such as coal and lignite play an important role in electric power generation, also in South Africa, which is considered as the sixth largest coal producing country in the world (UNSCEAR, 2016). Coal contains natural radionuclides, which are released to the atmosphere in the process of combustion. The amount of radioactivity around a power plant depends on several factors such as the ash content of the coal, the electrostatic filter efficiency and meteorological conditions. Depending on the emission control system of the chimney, a small proportion of the ash, called the fly ash, are released into the atmosphere. The natural radionuclides in fly ash may be enriched compared with their content in coal or surface soil. The ashes are sometimes disposed of, but also utilized in other applications such as the building industry. It is important to have knowledge of the radiological characteristics of the produced ashes, to determine the radiological impact thereof.

Eisenbud & Petro (1964) first pointed out that the radiation dose from the use of fossil fuel for power generation could add significantly to the dose due to natural radiation. According to UNSCEAR (2016) in its evaluation of human exposure to ionizing radiation from electricity generation, the coal cycle gives a higher collective dose per unit electricity in normal operations than the nuclear cycle. Many studies have been undertaken by scientists

worldwide on the radiological characterization of coal and coal ash and their environmental impact (Akkurt *et al*, 2009; Baxter, 1993; Jankovic *et al*., 2011; Mishra, 2004; Pandit, Sahu & Puranik, 2011; Parial *et al*., 2016). Limited published data for natural radioactivity of samples from the coal industry in South Africa could be found.

2.11.1 Coal-fired power plants

The conversion of coal into electricity results in the generation of solid coal combustion by-products including bottom ash, boiler slag, and fly ash of which fly ash is the principal component (Figure 2-15).

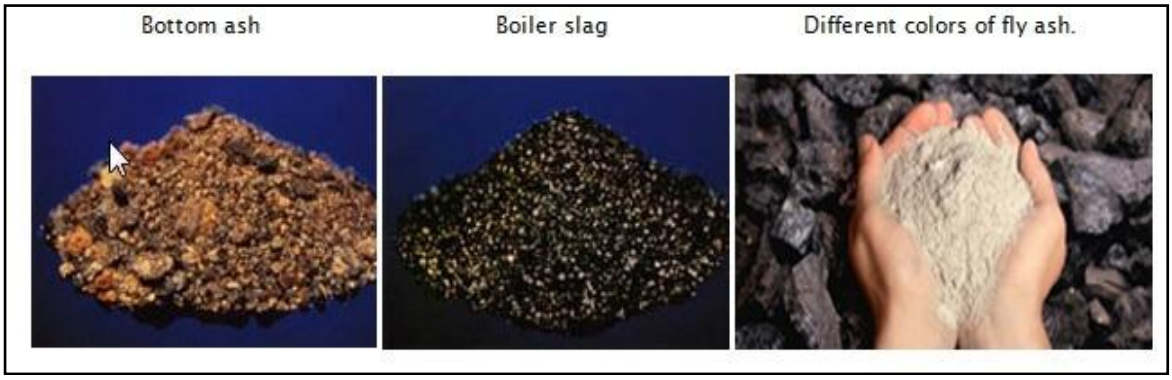


Figure 2-15: Coal combustion by-products

Coal is mined from a quarry and transported to power stations. In a typical pulverized fuel coal-fired power plant (CPP), the coal is ground to a particle size of between 5 and 400 µm in diameter. The pulverized coal is blown into the boiler by air through furnace burners. Combustion takes place in the centre of the boiler at temperatures from 1300 to 1700 ^{o}C and the combustion products are discharged into the atmosphere through smoke stacks (World Coal Association WCA, 2013) – Figure 2-16.

After the combustion process, the leftover coarse material is discarded at the bottom of the furnace known as bottom ash or slag and stockpiled in waste dumps. The leftover finer material, commonly known as pulverized fly ash (PFA), is carried by the exhaust gas stream to the stacks. Typically, 10% of ash is precipitated as bottom-ash or slag and 90% as fly ash. Emission from the stacks to the atmosphere is controlled by emission control devices such as mechanical filters and electrostatic precipitators (ESP). Depending on the efficiency of the emission control devices, most of the PFA is collected, while the rest is released to the atmosphere. Old-type power plants have an ash retention efficiency of about 90% with 10%

discharged to the atmosphere, and modern type CPPs (Eskom CPPs) retain 99.9% with only 0.1% discharged. The collected ash is taken to ash heaps or dams for disposal, and some of the ash is recycled or sold. The disposal of the huge amount of ash introduces serious environmental problems and may be a significant source of radiological exposure.

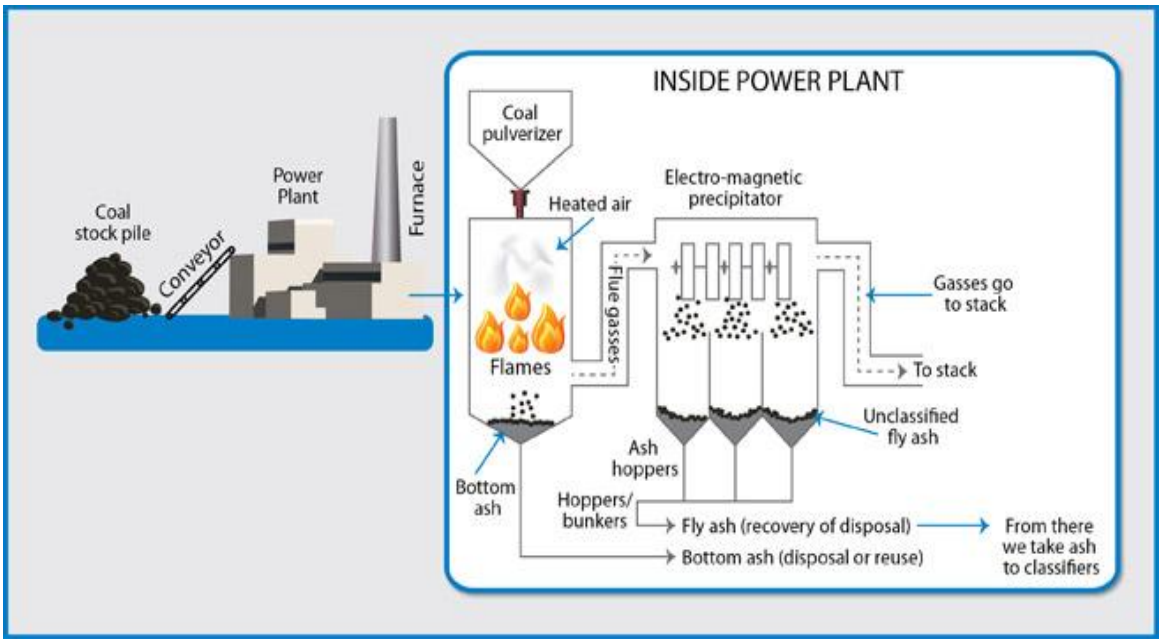


Figure 2-16: Schematic of a Pulverized fuel power station (WCA, 2013)

2.11.2 Natural radioactivity in coal and coal fly ash

Assessment of the radiation exposure from CPPs depends on the concentration of radioactive elements in coal and in the fly ash which remains after combustion. The organic matter from which coal is formed contains a significant fraction of clay minerals, which is the source of ^{232}Th, ^{40}K and silica-associated uranium. Th is generally present in the inorganic matrix and U is found in both the mineral- and organic fractions of the coal (Parial *et al*., 2016). On average, the activity concentrations of ^{40}K, ^{238}U and ^{232}Th in coal are 50, 20 and 20 Bq.kg^{-1} respectively and the decay products are in radioactive equilibrium with their precursors (UNSCEAR, 2008).

The radioactive equilibrium is disturbed during coal combustion. Most natural radionuclides are released from the original coal matrix and are distributed between the gas phase and solid combustion products. Bottom ash is enriched in inert elements, whereas fly ash enrich preferentially in volatile elements. Slag shows a slight depletion in most radionuclides,

except for ^{210}Pb and ^{210}Po, which are significantly depleted, because of its volatility during combustion. The less volatile elements such as U, Th and the majority of the decay products are present in the mineral constituents and are almost entirely retained in the solid combustion waste. Th and Ra are essentially refractory elements and remain with the ^{40}K in the bottom ash. Most of the U associated with the clay, remains with the bottom ash (Parial *et al*., 2016). The U that is dispersed in the mineral fraction of the coal as uraninite becomes volatile as the UO_3 species and is released with fly ash through the stacks to the environment.

Fly ash is separated from the heavier bottom ash or slag. The concentrations of radionuclides in the ash tend to be significantly higher than in the coal, but do not generally exceed 1000 Bq.kg^{-1}. The smaller particles, having a higher surface-to-mass ratio, are enriched in the volatile nuclides, particularly ^{210}Pb and ^{210}Po, therefore escaping ash has a higher concentration than the larger particle fly ash captured in the filters (Sahu *et al*., 2014). In a recent study by Chuangao *et al*. (2017) it was shown that ^{210}Po was mainly captured by the ESP (> 50%), with little left in the bottom ash, and a small fraction directly discharged into the environment through the stacks. ^{210}Pb and ^{210}Po can also accumulate on the inner surfaces of the burner kettles where concentrations > 100000 Bq.kg^{-1} for ^{210}Pb had been reported (IAEA, 2006).

2.11.3 World averages of radioactivity in coal and fly ash

Coal can be highly variable in radionuclide concentration depending on the coal basin and the quality of the coal. Table A-24 (Appendix A) provides a summary of the range of concentrations for coal and coal fly ash. Higher ash content coal will usually have higher activity concentrations. The activities of the natural radionuclides in coal are as a world average a bit lower than the average for those in the earth's crust (UNSCEAR, 2000). Bituminuous coal (hard coal) is the most abundant form of coal with a moisture content of 7-13 % and ash content of 10-49%. This type of coal is exported from SA to other countries (Duliu *et al.*, 2005). For low-quality coal, such as lignite, ^{226}Ra concentrations up to two orders of magnitude higher were reported in the literature (Karangelos *et al.*, 2004).

Literature values for fly ash also show a considerable range. The world average concentrations of radionuclides in escaping fly ash are estimated to be 265, 200 and 240 Bq.kg^{-1} for ^{40}K, ^{238}U and ^{226}Ra, respectively (UNSCEAR, 2008). The natural radioactivity in the fly ash waste product is concentrated by volatilization and sorption processes relative to

the original coal. This is more commonly associated with lead and polonium isotopes (metallic boiling points 1749 ^{o}C and 962 ^{o}C respectively). The average activity concentration of ^{210}Pb and ^{210}Po in coal are 20 and 20, whereas in fly ash it is 930 and 1700 Bq.kg^{-1} respectively (Baxter, 1993). In most of the studies reported in literature it is not clear whether the fly ash analysed was samples from the fraction released to the atmosphere (filters) or collected from precipitators, although it is assumed that it is mostly the latter. It is highly likely that the distribution of particle sizes would be different for these two sample types and, as has already been mentioned, the activity concentrations vary with particle size.

The most common method to determine the radioactivity of coal and fly ash is gamma ray spectroscopy. When using gamma spectrometry one must be careful because secular equilibrium with parent radionuclides cannot always be assumed. Use of alternative methods, such as alpha spectrometry after digestion and radiochemical separation, is not common (Mola *et al*., 2013). Accuracy may vary as found in an inter-comparison study conducted by eight laboratories in the Nordic countries (Ericson, 1985), due to difficulty of extracting the activity from the ash.

From literature data the following general conclusions can be made:

- The radioactivity of coal is comparable with that of other environmental material.
- Radionuclides of the Th and U series in coal are in equilibrium.
- Coal ashes are more radioactive than the average material in the earth's crust.
- Natural radioactivity in the fly ash is concentrated relative to the original coal, typically by a factor 5-10 (UNSCEAR, 2016).

2.11.4 Radiological and environmental impact of coal fired power plants

For a full radiological assessment of the coal industry and impact on the public all exposure pathways have to be considered. Dose to the public arise primarily through inhalation of radioactivity during the passage of the cloud containing fly ash from the stacks and through ingestion of food, after deposition on crops and pasture. Additional pathways may be external radiation from the plume and from particulates deposited on the ground (see Figure 2-6). More soluble nuclides such as ^{238}U can leach from the surface of the ash piles into groundwater. Pathways of lesser concern are emission of gamma radiation from the coal dumps and radon emanation from the coal waste, which contains ^{226}Ra which will contribute

to the ^{210}Pb and ^{210}Po concentrations in the atmosphere. The associated individual doses are small compared with doses due to inhalation of radon and its progeny at levels that occur naturally in homes (UNSCEAR, 2016).

UNSCEAR estimated that for an individual living approximately 1 km from a coal-fired power plant producing 1 GW year of electric energy annually, the resulting annual effective dose would be about 0.001 mSv for a modern plant and about 0.02 mSv for an old plant (UNSCEAR, 2016). Higher doses were reported by other authors: Jankovic *et al.* (2011) reported a range of 0.058 to 0.18 mSv annual dose from ash samples from five investigated CPPs and Pandit *et al.* (2011) reported an estimated external dose of 0.68 mSv.a^{-1}. These higher doses may be due to higher NORM content of the coal (*e.g.* lignite) and also from poor fly ash removal efficiency of the filtering system.

From literature studies it can be concluded that the maximum dose to an individual living in close proximity to a modern CPP will be equivalent to a minor increase above the radiation from the natural environment. Components of radiation that impact on the world population are illustrated in Figure 1-1. Natural sources account for the majority (>70%) of radiation. On this plot, the average population dose attributed to coal burning is much less than one percent of the total dose.

Radiological and environmental impact of fly ash

Air-borne ash containing high levels of natural radionuclides may be dispersed over a wide area and fall to the ground by means of dry deposition and precipitation, contributing to radiation dose exposure. This may lead to elevated levels in soil, which can be taken up in plants. The transfer of radionuclides from ash into growing plants is of interest when evaluating the ingestion pathway for ash released from the stack and the radiological implications of using ash as a substitute fertilizer. Some studies confirmed higher activity concentrations of ^{210}Po and ^{210}Pb in the vicinity of CPPs compared to control areas due to the emission of flue gases and fly ash. Sert *et al.* (2011) found activity concentrations from 124-1125 and 94-724 Bq.kg^{-1} for ^{210}Po and ^{210}Pb in moss and lichen samples used as bio-monitors around CPPs. Ericson (1985) found that addition of peat ash did not have any measurable effect on the crop grown in the peat soil.

There are conflicting views in literature whether use of fly ash could represent a significant

risk to human health. With a few exceptions, consensus among the scientific community is that the activity concentrations in the final building products are usually too low to be of regulatory concern. In a study conducted by the Nordic countries the radiological impact from the use of fly ash in BM was found to be minimal (Ericson, 1985). Turhan *et al*. (2011) found Portland cement samples containing up to 25% PFA to comply with international regulations. Since there is some concern that there is potential to have exposures above $1mSv.a^{-1}$ in buildings with concrete containing a high percentage of fly ash the gamma index is used to identify whether the dose criterion is met (see 2.2.8).

Although a percentage of fly ash is being utilized constructively, there is still a significant amount that is disposed of in ash dumps. Once the land has been utilized for the disposal of fly ash, it is close to impossible to rehabilitate the soil in order to make it suitable for crop production. Another challenge is the potential leaching of radionuclides from the dumped fly ash into surrounding soil or ground water and accumulation throughout the food chain (UNSCEAR, 2008).

2.11.5 The coal industry in South Africa

South African reliance on coal as a source of power dates back to 1870, when it was first used in a Kimberley diamond mine. Currently coal is a vital part of energy production in South Africa, providing more than 72% of the electricity (Eskom, 2014a). In 2015 the net maximum capacity of coal fired power by Eskom was 35721 MW (Eskom, 2015a). This implies a major environmental footprint. All of Eskom's current CPPs, as well as Medupi, and the future Kusile power plant, are pulverized fuel plants. The latter two power stations will be supercritical CPPs, which means they are more efficient being able to produce more electricity with less coal. They will have fabric filter plants to reduce ash emissions (Eskom, 2015b).

South Africa produces an average of 224 million tons of marketable coal annually and it has an estimated 32 billion tonnes of coal reserves (Eskom, 2014a). According to Eskom's 2014 report, SA coal is of low quality with ash content of about 20-30%. Therefore if all radionuclides remain in the ash, the activity concentration in the ash would be approximately five times that of the original coal. Eskom's CPPs consume approximately 109 million tons of coal per annum, producing 25 million tons of ash (Eskom, 2014b). The large volumes of coal ash generated are largely disposed of at waste dumps close to the power stations, the

maintenance of which has become a severe economic and environmental concern of Eskom. Re-use of ash in other applications, reduces the volumes of this waste only marginally. Approximately 1.2 million tons (or 3% of all ash produced by Eskom) is sold annually mostly for use as an additive in cement. The production of fly ash greatly outweighs the volumes required by the building industry.

Utilization of coal fly ash in SA

Fly ash constitutes more than 90% of the solid waste from a CPP. The chemical characteristics of fly ash vary widely and are influenced by the coal combustion process. It is generally greyish in color and consists of inorganic, in-combustible matter present in the coal that has been fused during combustion into a glassy, amorphous structure. The particle size normally ranges from 0.5 to 200 μm. The finer more reactive fraction collected from the electrostatic precipitators have exceptional pozzolanic characteristics that enhance the strenghth of cement. Civil engineers also "engineer" the properties of concrete by using higher ratios of fly ash to provide better compaction. The Lesotho Highlands water project used up to 40% fly ash. In the late 1980s an ash industry was established in South Africa when a decision was made to introduce fly ash blended cements. Blended cement containing between 15 and 35% fly ash was introduced throughout the country and are currently marketed by cement producers under various brand names (Concrete institute, 2013).

Although incorporation of fly ash into BM is unlikely to contravene legislation (UNSCEAR, 2008), the activity concentration in the final product should be measured or assessed reliably from the activities of the component materials, if there is reason to suspect that it contains enhanced levels of radionuclides (see 2.10.3).

Activity concentration in coal and fly ash from South Africa

Even though SA is listed as one of the top-10 producing countries of coal by UNSCEAR (2016), the table of averages of radionuclide concentrations found in coal worldwide in the UNSCEAR document does not have values for South African coal. The results presented in 5.6 for coal and ash samples analysed over the last five years can contribute to this data, but is by no means an attempt to evaluate the radiological impact of CPPs in South Africa.

Although not analysed in South Africa the results reported by Font *et al.* (1993) are for SA

coal used as fuel in a thermal power plant in Spain. The ^{238}U concentration in the fly ash (150 $Bq.kg^{-1}$) was lower than the typical average value of 200 $Bq.kg^{-1}$, whereas the ^{226}Ra concentration (250 $Bq.kg^{-1}$) was similar to the world average of 240 $Bq.kg^{-1}$. Since the carbon content of the SA coal is much higher than that of lignite used in Spain, it produces smaller amounts of solid residues on burning. This makes it a more appealing choice in terms of environmental impact. Results reported by Zeeavart *et al.,* (2006) and Duliu *et al.* (2005) included coal from South Africa. The values were within the normal range observed globally for good quality coal (UNSCEAR, 2008). Much higher concentrations were reported by Lloyd (2002) in his review of the environmental impact of coal mining. The concentration of U in the coal waste dumps was reported as 300-600 ppm (3730-7460 $Bq.kg^{-1}$ ^{238}U). Mainganye (2012) also reported similar very high concentrations for fly ashes from power stations in SA with Th concentrations between 384 and 493 ppm (1558-2000 $Bq.kg^{-1}$ ^{232}Th).

2.12 Gold Mining Industry

Mining has been identified as one of the potential sources of exposure to NORM (UNS, 2008). In South Africa natural radioactivity is associated with gold/uranium mining and processing.

2.12.1 The gold mining industry in South Africa

Following the discovery of gold resources in South Africa in 1886, the mining industry has played a central role in the country's economic, political, and social environment and gold remains one of the main mineral commodities mined in South Africa today. There are five mining basins in South Africa, collectively called the Witwatersrand basin, which can be considered the largest gold and uranium mining basin in the world (Naiker *et al*., 2003) – see Figure 2-17.

Uranium is a natural constituent of the earth's crust with an average global concentration in soils and rocks of 2–4 $mg.kg^{-1}$ (UNSCEAR, 2000). The ore bodies of the Witwatersrand basin contain elevated U levels commonly ranging from 100 to 300 $mg.kg^{-1}$. In South Africa U is mainly produced as a by-product of gold (Winde & Sandham, 2004). Because U was not extracted as a by-product of gold-mining prior to the 1950s, the bulk of U from the mined reefs is now present as a residue on the surface in so-called 'slimes dams' or Tailings Storage Facilities (TSFs) exposing it to a chemically much more aggressive environment (Coetzee *et*

al., 2006). According to published figures in 2012, a total of about 52 kilo tonnes of gold has been extracted, with 430 kilo tonnes of low-grade uranium still present in the mine residue (GDARD, 2012).

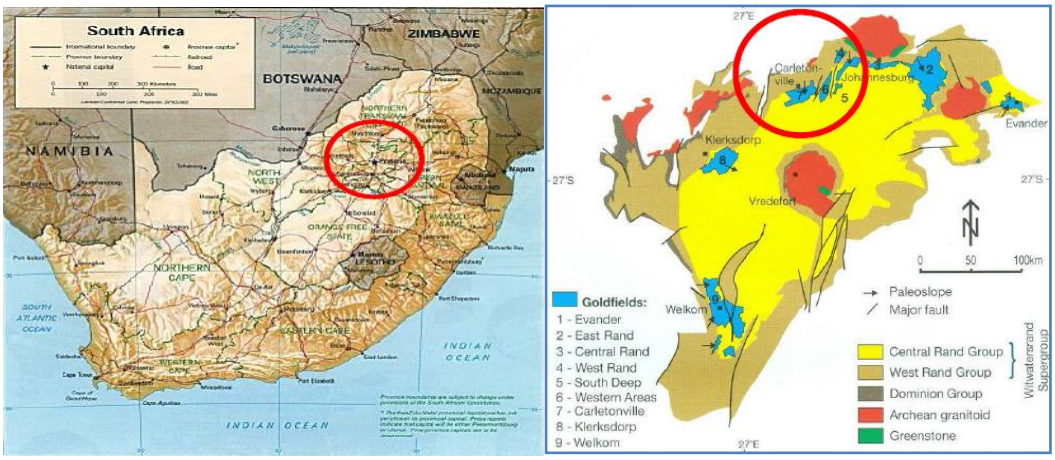


Figure 2-17: Gold mine area in South Africa (Albrecht, 2010)

2.12.2 Radiological and environmental impact of gold mining in South Africa

In the last three decades there has been a great deal of interest in mining-related U pollution in South Africa, especially in the WonderfonteinSpruit Catchment Area (WCA). A number of studies have been published; some with limited circulation (Coetzee *et al.*, 2002, 2006; Wade *et al*., 2002; Winde, 2006a,b, 2010; Winde *et al*., 2017). Most of these studies found evidence of heavy-metal and radionuclide pollution downstream of mining activities. Results of these studies are discussed in more detail in 2.5.7 (water) and 2.7.4 (solids).

Mine effluent contains uranium and daughter nuclides. From an operational perspective, active mining companies in SA usually pump contaminated underground water to the surface. Once pumped to the surface, a component of the water is treated internally to be re-used as process water and the remainder is treated according to DWA effluent-discharge policies prior to release, usually by neutralization. Mine water can be of environmental concern, even a long time after the mining operations have ceased. Once radionuclides enter the environment they can be adsorbed onto the streambed sediment. Cattle wandering into streams to drink can stir up the sediment, resulting in ingestion of the radionuclides contained in the sediment, as well as mobilization or transport into surface water. Radioactivity in soil

in the region can have an impact on vegetation surrounding the water bodies, which in turn poses a threat to the farming industry adjacent to mining areas.

The Far West Rand in Gauteng is densely populated because of the presence of gold mines and soil that has agricultural value. Informal residential settlements are established on or adjacent to TSFs scattered around towns and cities in the SA goldfields, which may result in exposure of residents to direct external gamma radiation, inhalation of radon gas and ingestion of radionuclides. To limit the risk due to external gamma radiation the Chamber of Mines allows no human settlement within a 500 m buffer zone around a TSF, but this guideline is often ignored (see Figure 2-18). There are currently little publicly available data on radioactivity in airborne dust and radon in the vicinity of TSFs. However, it can be expected that the most hazardous areas will be those in close proximity to mine residue deposits.



Figure 2-18: Google map showing houses build in close proximity to a TSF (Albrecht, 2010)

Gold deposits of the Witwatersrand basin occur in association with pyrite (FeS_2). Pyrite, which may constitute up to 3% of the gold bearing reefs, and other sulphates remain stable underground, but produce iron hydroxide and sulphuric acid when exposed to water and oxygen - the major cause of acid mine drainage (AMD). Waste rock piles containing pyrite can constitute an important source of pollution to the environment. Rainwater falling on the dumps oxidises the pyrite, forming sulphuric acid, which percolates through the dump, dissolving heavy metals (including natural radionuclides), and emerges from the base of the dump to join the local groundwater as a pollution plume. This polluted water ultimately emerges on surface in the streams draining the areas around the waste piles as AMD (Winde

& Van der Walt, 2004). While the quality of effluent released via point discharges can be controlled to a certain extent, *e.g.* by diverting effluents into return water dams, the same is not true for seepage from sources such as TSFs and waste rock dumps.

Occupational exposure to mine workers in underground gold mines in SA occurs mainly through radon. An average exposure of 7 $mSv.a^{-1}$ was reported in 2000 with 3700 of about 125000 workers receiving a dose of more than 20 $mSv.a^{-1}$; 71% of dose was due to inhalation of radon gas, 25% to external exposure and the remaining 4% to dust inhalation (UNSCEAR, 2008).

2.12.3 TSF legacy

Although not classified as U-tailings, gold mining deposits in South Africa, in fact, contain about the same or even higher U-concentrations than many 'genuine' U-tailings in other countries where mainly low-grade U-ore was mined. Average U_3O_8-concentrations in tailings of 46 mines in the Witwatersrand basin ranged from 10 to 343 $mg.kg^{-1}$, with a mass-weighted average U concentration for all tailings of about 100 $mg.kg^{-1}$ (Winde & Sandham, 2004).



Figure 2-19: Tailings Storage Facility

Airborne radiometric mapping revealed high gamma activities from TSFs (Coetzee *et al*., 2006). These TSFs are mostly unlined and many are not vegetated, providing a source of dust, as well as soil and water pollution – see Figure 2-20. Due to the small particles of the tailings, particulate matter can be transported over relatively long distances to agricultural

land in the surrounding areas. In SA, many TSFs and un-rehabilitated footprints of re-mined tailings dams are unfenced and thus used for recreation, and for livestock grazing. Typical exposure pathways as discussed in 2.3.2 are shown in Figure 2-20: Inhalation of dust or particulate matters from the dump, direct contact with soil from the dump, deposition of dust on leaves of vegetables and plants, ingestion of crops grown on contaminated soil, consumption of meat/milk from cows grazing on contaminated land, drinking contaminated water and consumption of fish from contaminated water.

Past technologies were not able to recover 100% of the gold, resulting in varying amount of gold still contained in historical TSFs. Due to recent technological advances, gold can now be recovered economically by re-mining these facilities. The plan is for the reclamation area to be rehabilitated and cleaned, preferably to farming land status. However, radiometric surveys over reprocessed mine residue deposit footprints have, in some cases, still shown elevated levels of residual radioactivity in the soils and it must be accepted that some areas will never be suitable for unrestricted development (Liefferink, 2009).

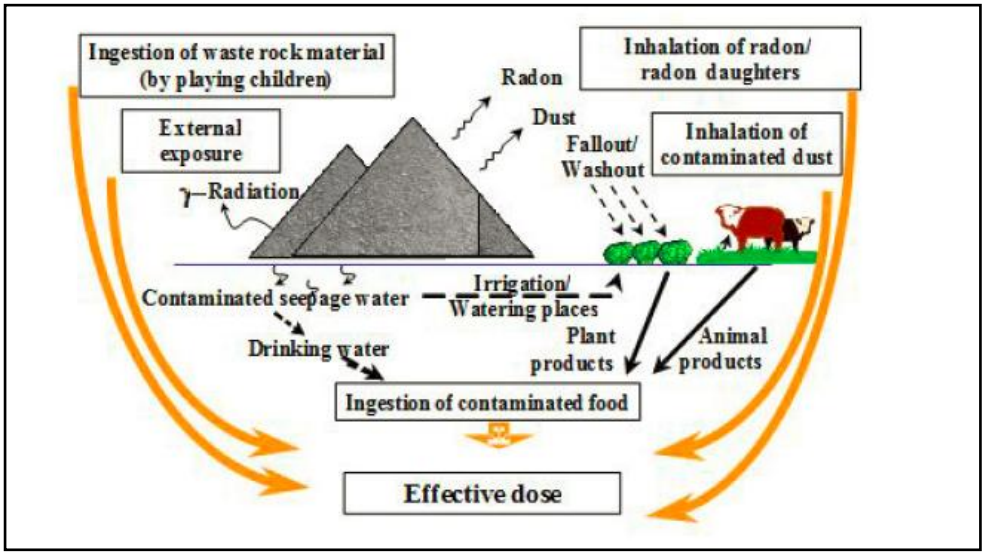


Figure 2-20: Exposure pathways at a tailings storage facility

2.12.4 Wonderfonteinspruit

The Wonderfonteinspruit Catchment Area (WCA) forms part of the Witwatersrand basin. The Wonderfonteinspruit (WFS) originates to the south of Krugersdorp in the Gauteng Province and flows in a south-easterly direction to join up with the Mooi River upstream of

Boskop dam, near Potchefstroom in the Northwest province of South Africa. A map of the catchment can be seen in Figure 2-10 (DWS, 1999).

The WCA has been exposed to pollution for more than a century and serious concerns have been raised about heavy metal pollution and radioactivity in the WFS (Coetzee *et al*., 2006). Although much of the pollution has been caused by historic mining activities and most of the mines in the Upper Wonderfonteinspruit areas have been closed, the area is dominated by TSFs and waste rock dumps, which are potentially significant contributors to pollution, as discussed in the previous paragraph.

The widespread uranium pollution present in the WCA has provided unique research opportunities and has been the topic of numerous studies and reports. Uranium has been identified as the major element of concern in surface- and groundwater contamination linked to mining activities in the WCA (Coetzee *et al*., 2002, 2006a, b; Wade *et al*., 2002; Winde, 2006 a,b, 2010). Results from the different studies suggest that the degree of pollution in the area varies. U concentrations at many sites were found to fluctuate by several orders of magnitude.



Figure 2-21: Wonderfonteinspruit

A comprehensive survey by the DWS found that the water quality of the majority of sites monitored in the catchment was either ideal or acceptable for lifetime use and only two sites of the 41 sites had significant elevation of radiation dose (DWS, 1999). Both these sites involved the discharge of mine water that had been pumped to the surface and showed large

variations over the study period. Concentrations decreased downstream of the sources, indicating removal of the dissolved fraction by interaction with sediments.

Owing to a range of chemical and physical processes, which remove dissolved uranium from the water phase, contamination is not confined to water but also affects sediments in dams, wetlands and floodplains. High concentrations of U were measured in sediments in some areas (2.7.4). This indicates that immobilisation is a dominating process, turning sediments into sinks for uranium. This binding is maintained by the generally reducing conditions within the sediment bodies. Research has shown that absorbed radionuclides may be remobilized by environmental processes such as the discharge of acid mine drainage and the drying out of sediments due to a reduction in water flow (Wade *et al.*, 2002). The sediment bodies cannot necessarily be relied upon to always protect downstream water users in future (Coetzee & Van Tonder, 2006).

A study conducted by the NNR in 2007 has confirmed the presence of radioactive contamination in the WCA and identified several sites in the WFS catchment with significant radiological risk. The results indicated that the dose due to consumption of produce grown in the area was of regulatory concern (NNR, 2007). Elevated U-concentrations reported for some of these products (vegetables) fuelled further headlines in the press on imminent health risks. The report recommended further measurements and studies. Only limited results in response to these suggested studies were found in the literature study. In a masters degree study the transfer and accumulation of toxic and trace elements in soil, grass and cattle in the WCA was investigated. Transfer of radionuclides was not included in the study, except for U for which elemental analysis was performed using ICPMS (Hamman, 2012).

2.12.5 Acid Mine Drainage and contamination of water

The formation and uncontrolled release of AMD is unequivocally the single most important impact of gold mining activities in South Africa on the environment and many studies have been conducted in the main gold-mining basins to determine the nature of the water ingress and the resulting AMD problems (Coetzee *et al*., 2010; Durand, 2012; Johnson & Hallberg, 2005; McCarthy, 2011; Naiker *et al*., 2003). In the Witwatersrand basin AMD water pumped from the mine voids, had a major impact on the water resources in the area. Uranium concentrations of 20-858 $\mu g.L^{-1}$, up to 30 times higher than the WHO limit for drinking water of 30 $\mu g.L^{-1}$, were measured in water from various sampling points from the western, central

and eastern basins (DWS, 2013).

AMD is a well-understood process and arises primarily when a sulphate bearing mineral such as pyrite, associated with sedimentary rock, comes into contact with oxygenated water (McCarthy, 2011). The reaction results in the formation of sulphuric acid, which during rainy weather, is carried away with the water streams, which in turn results in detrimental effects to the environment and downstream water sources. Although the process, termed pyrite oxidation, occurs naturally, it is enhanced when water moves through and over the surfaces of acid bearing rock having been exposed because of mining activities disturbing the underlying geology. AMD is generally characterized by one or more of the following: low pH, high Total Dissolved Solids (TDS), high sulphates and elevated levels of toxic heavy metals, as well as naturally occurring radionuclides (McCarthy, 2011).



Figure 2-22: Acid mine drainage

Since gold mining began on the reef in 1886, the effect in the water table has been dramatic. To extract the maximum amount of gold, the industry employed elaborate pumping systems to draw groundwater from the sunken shafts thereby creating a continuous mine void extending from the East Rand to the West Rand. It caused much of the groundwater to be exposed to pyrite resulting in groundwater of poor quality with elevated concentrations of heavy metals in the Johannesburg area (Naicker *et al.*, 2003). As mining was discontinued, the recovering water table (acid mine water) began to decant to the surface in the Western basin via seepage from a previously unknown Black Reef excavation, generally referred to as the Black Reef incline (BRI) (Coetzee & Van Tonder, 2008).

To remedy the problem of decant of AMD in the Western basin, a water treatment plant was installed to collect, contain and treat water from the void. The treated water was clear with a

neutral pH and relatively low Uranium concentrations (less than 0.070 $mg.L^{-1}$), but had a very high sulphate concentration (about 1500 $mg.L^{-1}$) non-compliant with SANS 241 requirements (SANS, 2015). In 2010 the government issued a press release outlining a model to deal with the AMD challenge that is affecting the Western, Central and Eastern basins impacting on the Vaal- and Crocodile River systems (DWS, 2010). Uncontrolled decant in the Western Basin has stopped since commencement of the short term intervention of increased pumping rates and an upgrade to the neutralization plant. Reports indicate a major improvement in the water quality in the Tweelopie Spruit, as well as, an improvement in groundwater quality (DWS, 2013).

The water emanating from flooded mine voids in the Witwatersrand is not the only source of AMD that requires management. The tailings and waste rock generated by mining are significant sources of AMD owing to their interactions with rainwater and surface streams (Winde *et al*., 2004). For control of AMD and management of risk the focus should be on minimization of the generation of AMD at mine sites. AMD can best be controlled by controlling water entry into the site of acid formation, by diversion of surface water away from the residue storage areas, flood prevention of open cast pits and underground mines, prevention of hydrological seepage into the affected areas and controlled placement of acid-generating waste.

Even if the above measures are implemented, AMD will still be produced and require treatment to a quality that is fit for a predetermined use, or for discharge to surface streams. Recommended water treatment options include neutralization by adding high density sludge, desalination by reverse osmosis and ion exchange for removal of uranium. The disposal or use of residues from waste treatment such as sludge and brine may pose a serious environmental challenge (Coetzee *et al*., 2010).

2.13 Review of analytical techniques

Analytical techniques with the required sensitivity and accuracy are required for quantification of the naturally occurring radionuclides. The selected instrument (or method) depends on the results needed and the nuclides present and should be "*fit for purpose*". This section provides an overview of radio-analytical (or radiometric) techniques and their application for the analysis of radionuclides of interest in this thesis. Implementation of specific methods is discussed in Chapter 4.

2.13.1 Radiometric techniques

Radiometric techniques are based on the detection of emissions from alpha or beta particles, or gamma rays. The decay rate (A, number of decays per second) of the radionuclide of interest is measured (Equation 2.13). Detectors, which can be used for the measurement of these emissions, include gas-flow proportional counters, scintillation detectors (NaI and Liquid ScintillationCounting) and semi-conductor detectors (germanium (Ge) for the detection of γ-photons, and silicon (Si) for α-particles.) Semi-conductors detectors are usually used when spectrometric information is needed, due to relatively good counting efficiency and superior energy resolution.

2.13.2 Analytical considerations with radiometric counting

Activity, activity concentration and radioactive decay

The radioactivity of a nuclide (A) (*i.e.* the number of atoms that decayed during a period of one second) can be expressed as (L'Annunziata, 2003):

Activity (A) = $-dN/dt = \lambda N$

= $[\ln 2 / t_{1/2}]^* N$ …… ……..... Equation 2.13

Including decay:

= $[\ln 2 / t_{1/2}]^* N_0.\exp(-\lambda t)$

= $[\ln 2 / t_{1/2}]^* N_0.\exp(-0.693^*T/ t_{1/2})]$……....Equation 2.14

where

A	activity of the sample (Bq)
N	number of atoms at time t
N_0	number of atoms at the beginning
$e^{-\lambda t}$	decay factor
$t_{1/2}$	half-life of the nuclide (s)
T	decay period (s)

Following the sample analysis process, the activity concentration for each radionuclide (at time t_1) is calculated based on the following equation, and expressed in $Bq.kg^{-1}$ or $Bq.L^{-1}$

$$A = \frac{N}{t} = \frac{G-B}{t.Y.R.\varepsilon.\mathrm{m}}$$……...….Equation 2.15

where

A	activity of the sample (Bq)
N	nett (*i.e.* background corrected) number of counts
t	counting period (seconds)
G	gross number of counts observed in time interval "t"
B	background counts during the same period
Y	the yield of particles for the decay process, as a fraction (= 1 for gross counts)
R	chemical recovery (= 1 if no separation)
m	mass of sample counted (or volume)
ε	counting efficiency, or fraction of the particles that reach the entrance window of the system defined for a certain type of radiation.

Conversion of mass concentration to activity concentration

The reporting unit for activity is in Becquerel (disintegrations per second). The reporting unit for results obtained by non-radiometric techniques such as ICP-MS and KPA is mass concentration units, usually $\mu g.L^{-1}$. This can be easily converted to activity concentration units in $Bq.L^{-1}$ using the specific activities calculated with Equation 2.16:

$$\text{Activity (A)} = \lambda N$$

$$= [\ln 2 / t_{1/2}]^* [N_A .m/ MM] \quad \text{.....Equation 2.16}$$

where

N_A Avogadro's constant 6.023×10^{23} (atoms/mole)

MM Atomic mass of nuclide (grams/mole)

Specific activities for the nuclides of interest were calculated and are listed in Table A-1 (Appendix A).

Counting efficiency and efficiency calibration

Counting efficiency is the relation between the activity of the nuclide in the count sample and the area of the corresponding peak in the pulse height spectrum, *i.e.* fraction of the particles reaching the entrance window (L'Annunziata, 2003). The counting efficiency is determined by measuring the peak area expressed as a count rate (N) of a calibration sample with known activity (A), and then calculate the efficiency (= ε) using Equation 2.15.

Attenuation

All α- and β-particles are subject to absorption in material surrounding the atom that is decaying. The energy loss of α-particles in the material is referred to as attenuation of the radiation (L'Annunziata, 2003). The approach is usually to use samples that are so thin that self-absorption can be ignored. When counting samples that are relatively thick, the effect of the material itself cannot be ignored, which force the analyst to make corrections for attenuation.

Energy calibration and resolution

Energy calibration relates the observed peak location in the pulse height spectrum (in channels) to the energy of the corresponding photon (in keV). It is good laboratory practice to run a weekly calibration check on every spectrometer in use. The information collected for that purpose, will give an indication of the magnitude of energy drift.

Energy resolution refers to the ability of the detector to resolve peaks that are close to each other in the pulse height spectrum. The full width at half the maximum height (*i.e.* FWHM value) of a peak in the pulse height spectrum is used as a quantitative indication of the expected resolution of a detector (Longworth *et al*., 1998).

Chemical yield or recovery

Since losses will occur with sample preparation and chemical separation the use of yield tracers is required (Longworth *et al*., 1998). A known quantity of a radioactive isotope of the same (or similar) element to the field sample is added to the sample before the separation process is started, and then the activity recovered in the count sample is measured. The most appropriate tracer to use is an isotope of the same element not present in the sample. The added isotope should not add peaks to an already complex spectrum.

Background radiation

A detector cannot distinguish between radiation coming from the sample that is being counted and that coming from the environment. The experimental reading has to be corrected for this to obtain the true counting rate of the sample only. To improve the sensitivity of the detector, the background contribution must be reduced as far as possible.

Method blank

The background count gives information on contamination of counting equipment. For radiochemical procedures it is standard practice to prepare and analyse a "blank" sample to obtain a method blank value. This is then subtracted from the activity values that were measured for the field samples. The blank sample is prepared exactly as the field samples, except is does not contain sample material. Blank corrections add to the error of measurement, and reduce the precision of the method (L'Annunziata, 2003).

Counting statistics

The standard deviation is typically calculated as the square root of the number of counts detected from a particular sample and not from replicate analysis (L'Annunziata, 2003).

Analytical sensitivity (Limit of detection, LOD)

The limit of detection (LOD), *i.e.* the smallest value for N in Equation 2.15 that is significantly above the background, is determined by the instrument background and the counting period of both the sample and background. In radiochemistry the detection limit is commonly calculated using the Currie formula (Currie, 1968). The detection limit (sample and background counted for the same period) for a 95 % confidence interval is given by:

$$LOD = 2.71 + 4.65 * \sqrt{B} \quad \text{Equation 2.17}$$

where

LOD limit of detection (counts)

B background count rate

In Equation 2.17 it is assumed that both the sample and background are counted for the same period. If different count periods of t_G and t_B are used for sample and background respectively, a revised version of Equation 2.17 is applied to calculate the detection limit:

$$LOD = 2.71 + 3.29 * \sqrt{B \,.\, (1 + \frac{t_G}{t_B})} \quad \text{Equation 2.18}$$

The number of counts calculated from Equation 2.17 or 2.18 represents an equivalent amount of activity known as the minimum detectable activity (MDA) in Bq, and is calculated using the same approach as in Equation 2.16

$$MDA = \frac{LOD}{\varepsilon.t} = \frac{2.71+4.65.\sqrt{B.t}}{t.Y.R.\varepsilon.\mathrm{m}}$$ ……..….Equation 2.19

The MDA is defined as the "*smallest activity concentration that is certain to be detected with a certified degree of confidence*" (Longworth *et al*., 1998).

Factors that influence the LOD include background count rate, sensitivity of the detector and, particularly, the length of time a sample and background are counted. A longer count period is generally preferred because it results in the accumulation of more pulses, better counting statistics and higher precision. But there is a practical limit on the length of time that is available for counting. To achieve adequate detection limits, large sample sizes or pre-concentration procedures are often required. Because of these variables, LODs between laboratories, employing the same or similar chemical separation procedures, will vary. Detection limits for some of the radiometric techniques, as obtained from literature, are summarized in Table A-4 in Appendix A.

2.13.3 Gross alpha/beta techniques

Gross alpha/beta measurement is widely used to screen environmental samples for the presence of radioactivity (Longworth *et al.*, 1998). Basically, two techniques exist for the simultaneous quantification of alpha and beta emitting nuclides in the same sample: gas flow proportional counting and liquid scintillation counting.

One must distinguish between the terms "gross alpha activity" and "total alpha activity", which are often incorrectly used as interchangeably terms. Gross alpha refers to where a measurement is done using an instrument that cannot distinguish between particles of different energies, so it is basically a screening technique. Total alpha activity refers to a summation of alpha emitters, which are all individually analysed using tracers and chemical separation, in the sample.

Liquid scintillation counting (LSC)

Liquid Scintillation counting with alpha/beta discrimination is a relatively fast and simple method and has been popular since the 1950s (L'Annunziata, 2003). It is ideal for high-throughput gross alpha/beta screening of water, filters and swipes. Some of the attractive features of LSC are its near 100% counting efficiency for alphas and reduced sample preparation for most samples (especially liquids). Disadvantages are the use of LSC

cocktails, even though they are environmentally friendly and the relative high background compared to gas-flow proportional counters. For betas the background is 10-20 cpm and for alphas 1-3 cpm, with low-background instruments having alpha backgrounds of 0.1-1.0 cpm (Smit, 2000).

LSC cannot distinguish between individual alpha and beta nuclides. The energy resolution (FWHM=750 keV) is poor compared to spectrometric techniques, but better than gas proportional counters. Latest instruments are equipped with electronics, which can discriminate alpha pulses from beta pulses based on the duration of the light pulses they produce in the liquid scintillator (L'Annunziata, 2003). Calibration of the instrument is required to establish an adequate value for the pulse shape discriminator parameter. Under optimum conditions misclassification of alpha and beta signals due to spillover is below 0.5% ((Zapata-Garcia *et al*., 2012).

Gas flow proportional counting (GFPC)

Gas flow proportional counting (GFPC) is most often used as a standard screening technique for gross activity determination. For simultaneous determination of both alpha- and beta activity an instrument with a discriminator is required to distinguish between alpha and beta emitters. The instrument measures "gross" activity and cannot be used to identify specific nuclides.

The technique requires a uniform thickness, homogeneous layer of residue material as counting source to prevent self attenuation of alpha emitters and mid-range energy beta emitters. Attenuation of α particles are pronounced when the layer is thicker than about 0.2 $mg.cm^{-2}$; or even sooner for materials with a higher atomic number (Smit, 1999a). In cases where finite sample thickness is unavoidable, the alpha counts have to be adjusted to correct for self-absorption. This is typically done by doing a self-absorption calibration to determine the change in counting efficiency and spill-over as a function of the sample thickness (expressed as total mass of sample).

The calibration process requires two samples (a pure alpha and a pure beta emitter) for which the activity values (and uncertainty on them) are certified. The beta efficiency is often determined with a source prepared from ^{90}Sr (energy 0.546 MeV) in secular equilibrium with its daughter ^{90}Y (energy 2.281 MeV). Beta efficiency is a function of the beta-decay energy,

which means there is no single beta counting efficiency to use for the calculation of the gross beta activity. Alpha efficiency is normally determined with ^{241}Am with alpha energy 5.479 MeV. Alpha counting efficiency is fairly constant over the range of 4-6 MeV. Typical counting efficiencies are 30% for alphas and 40% for betas (Smit, 1999a).

The main advantages of this technique are the relatively low costs and simplicity (Longworth *et al*, 1998). Low backgrounds can be obtained and the misclassification of alpha from betas is low 1-3%. Typical background count rate is 0.7-0.8 cpm for beta and 0.05-0.5 cpm for alpha (Smit, 1999a). The LOD is typically 1-2 orders of magnitude higher than for α-spectrometry. Self-absorption reduces efficiency, which results in a higher LOD.

Gross alpha/beta determination of water samples

Most guidelines for drinking water quality suggest gross alpha/beta screening as the first step of the radiological characterization of the water (see 2.2.7). Recommended methods such as EPA method 900.0 (EPA, 1980) and STM 7110B (Eaton *et al*.,1999), use GFPC and consist of two steps: evaporation of the water to dryness and measurement of the residue deposited on a planchet. The amount of liquid that can be evaporated is limited since the presence of even milligram quantities of material will greatly affect the counting efficiency for alpha emitters. Other disadvantages include the time needed to evaporate the water samples, difficulty in preparation of homogenous surfaces and limited numbers of samples that can be prepared for counting simultaneously.

The gross beta measurement includes a contribution from ^{40}K, a beta emitter that occurs naturally in a fixed ratio to stable potassium. The contribution of ^{40}K to the beta activity should be subtracted following determination of total potassium, using the factor of 27.6 Bq of beta activity per gram of total potassium (WHO, 2008).

LSC with alpha/beta discrimination capability is often the method of choice when high throughput screening for the presence of alpha activity is required due to the drawbacks of the above-mentioned standard methods. MDA's of 0.01 and 0.07 $Bq.L^{-1}$ for gross alpha en beta respectively can be achieved with a 100 ml water sample and counting for 16 hours (Forte *et al.*, 2015).

2.13.4 Gamma spectrometry

Many α and β decay nuclides also emit gamma rays and can therefore be determined by gamma spectrometry (ISO 18589-3:2015). High purity germanium detectors (HPGe) detectors are most widely used for analysis of environmental samples, due to their excellent resolution compared to NaI detectors. NaI detectors are significantly less expensive than germanium detectors but most likely cannot provide specific radionuclide identification (L'Annunziata, 2003). Energy resolution at 661 keV is typical about 50 keV for NaI and 1.5 keV for HPGe detectors (Smit, 1998). Low-energy photons (*i.e.*, x-rays and gamma rays below 50 keV) can be measured using specially designed detectors with an entrance window made from a very light metal or carbon composite, typically beryllium (low energy gamma spectrometry).

Gamma spectrometry is a useful non-destructive method and permits simultaneous determination of many radionuclides in a bulk sample, without the need for complex and time-consuming radiochemistry (Semkow *et al.*, 2002). The samples can be measured as they arrive at the laboratory, or it can be dried, ground to a uniform particle size, and mixed to provide a more homogeneous sample if required. Samples of any matrix can be analyzed as long as the detector is calibrated for the sample geometry and density and radionuclide gamma energy.

The technique is limited by the weak emission probabilities of many potential useful emission lines, the relative poor efficiency of HPGe detectors over a wide range of energy, the difficult task of precisely calibrating the detectors and the need to evaluate self-absorption effects (L'Annunziata, 2003). HPGe detectors must be kept at low temperatures, typically 77 K, by using liquid nitrogen to maintain good resolution (Longworth *et al.*, 1998). Counting efficiency for HPGe detectors is low (< 10% absolute efficiency) and the background count rate is high (> 10 counts per hour). The detection limit depends on the counting time, crystal diameter and the geometry use, but is typically higher than 0.050 Bq, which is a few orders of magnitude higher than alpha spectrometry (Hou & Roos, 2008). More recently large volume germanium crystals have become available, which significantly increases the counting efficiency to 100-150%.

Energy calibration is done by counting a standard containing a number of nuclides (or a nuclide emitting a large number of different energy photons, *e.g.* ^{152}Eu) covering the desired

energy range for the instrument (Longworth *et al.*, 1998). The stronger peaks in the spectrum are assigned to the known nuclide lines, the location (channel) of each peak determined accurately, and the photon energy plotted against channel number. The counting efficiency of a gamma spectrometer is defined as the fraction of the photons of a particular energy emitted by a source that contributes to the corresponding full-energy peak observed in the pulse height spectrum. The same standard is used for efficiency calibration.

Data reduction is the critical step in gamma spectrometry. There is often several hundred individual gamma ray energies detected within a single sample. Data processing software is usually used to identify the peaks and associate them with the proper energy (keV), using the energy calibration (L'Annunziata, 2003). The peak area values (counts) are corrected for the efficiency of the detector (by using the efficiency calibration for the counting geometry), to provide results in terms of concentrations with the associated uncertainty.

Gamma determination of naturally occurring radionuclides

The main gamma energies of the alpha- and beta- emitting nuclides in the natural decay chains are shown in Table A-2 in Appendix A (NUDAT, 2017). Some radionuclides in the series cannot be determined by gamma spectrometry directly, but only via measuring of their daughter nuclides (*e.g.* ^{238}U, ^{228}Ra, ^{232}Th). In these cases it must be ensured that there is equilibrium between the parent nuclide and the daughter nuclides to be measured.

Uranium-238 series

Direct gamma determination of ^{238}U is difficult. The gamma rays at energies 49.55 and 113.5 keV has extremely low emission probabilities of about 0.064% and 0.0102%.

Assuming secular equilibrium, measurement of ^{238}U is sometimes done using the 63.3 keV (3.7%) peak of ^{234}Th. The 63.3 keV line has interference from a peak at 63.8 keV (0.263%) from ^{232}Th. Corrections can be done assuming equilibrium between ^{232}Th and ^{228}Th, but will cause uncertainty in the results. Self-absorption of these low energy gamma rays in the sample matrix is also significant. The use of the double line energies of ^{234}Th at 92.4 and 92.8 (2.13% + 2.10%) is also not recommended to quantify ^{238}U, due to the weak intesnsity of the low energy emissions. The lines of ^{234m}Pa at 766.4 keV (0.317%) and 1001.03 (0.842%) are more suitable due to their higher energies, although they have low emission

probabilities and sum coincidences have to be considered.

Reported results for ^{238}U measured by gamma spectrometry are most often obtained by measurement of ^{226}Ra via the ^{214}Pb (295.2 keV, 19.3%; and 351.93 keV, 35.6%) and ^{214}Bi (609.36 keV, 45.5% and 1102.3 keV, 15.1%), therefore assuming equilibrium of the uranium/radium chain. Unfortunately many authors report the results failing to mention that equilibrium of the uranium-238 series nuclides have been assumed in these measurements (Ebaid *et al.*, 2000; Oyedele, 2006).

Direct measurement of ^{234}U at 53.2 keV (0.12%) is also potentially cumbersome due to the possible interference of the 53.2 keV (1.08%) line of ^{214}Pb, with 10-times higher intensity than ^{234}U at 53.2keV. Equilibrium with ^{238}U in the series is usually assumed for ^{234}U.

While ^{226}Ra does emit a gamma ray at 186.2 keV line, it is not very useful for analytical gamma spectrometry because of its low intensity (3.64%) and interference from the much more intense line of natural ^{235}U at 185.7 keV (57.5%). The energy resolution of HPGe detectors is generally insufficient to separate the two peaks. Corrections can be made if uranium has been measured by an alternative technique, but it will only be correct if the assumption that the natural equilibrium has not been disturbed is true. The second (more popular) option is to determine the ^{214}Pb and ^{214}Bi progeny of ^{226}Ra, assuming negligible radon emanation from the sample, which can be more or less achieved by sealing the sample in air-tight containers for an appropriate time interval of typically 2-3 weeks prior to the measurement.

Low-energy gamma spectrometry is used for quantification of low-energy emitters such as ^{210}Pb (46.55; 4.25% keV), which is not within the energy range of the high-energy detectors, which are often calibrated from 200-1500 keV (Smit, 1998).

Uranium-235 series

^{235}U is determined using its own intensive line at 185.7 keV (57.5%). The contribution from ^{226}Ra (186.2 keV), which interferes in this area must be corrected for. The measured ^{235}U activity can be used to calculate ^{238}U assuming the ratio of $^{238}U/^{235}U$ to be constant for soils and rocks at 21.7.

^{227}Ac has no high intensity gammas. Determination via the 235.96 keV line of ^{227}Th is preferred.

Thorium-232 series

For ^{232}Th the only exploitable line at 63.8 keV has very weak intensity (0.26%), a direct measurement is not possible. ^{232}Th is usually measured via ^{228}Ac assuming equilibrium of the thorium series ^{232}Th→^{228}Ra (^{228}Ac) →^{228}Th (^{212}Pb, ^{208Tl}).

^{228}Ra is determined from its daughter ^{228}Ac (911, 2; 25.8% keV), which is in equilibrium due to its short half-life of 6.13 hours. ^{228}Th can be determined through its short lived daughter ^{224}Ra (which is in secular equilibrium within 22 days) measured on ^{212}Pb (238.63; 43.6% keV), ^{212}Bi (727.3 keV; 6.67%) and ^{208}Tl (583.19; 84.5% keV). If the derived concentrations for ^{224}Ra, ^{212}Pb and ^{208}Th do not differ from ^{228}Ac, they can also be used for evaluation of the ^{228}Ra concentration.

In publications referring to ^{232}Th as determined by gamma spectrometry, it is likely that these authors used the gammas from the thorium series progeny assuming radioactive equilibrium, as shown here. Although this approach is probably acceptable for geological samples, assumption of equilibrium is not always true in environmental samples because of the presence of ^{228}Ra (5.75 yr) in the decay chain between ^{228}Th and ^{228}Ac, which can cause disequilibrium due to its higher solubility and more efficient uptake by plants compared to thorium. The activity of ^{228}Ra (measured on the 911 keV line of ^{228}Ac) can provide some information on the state of equilibrium of the ^{232}Th series.

Potassium-40

^{40}K is included in the isotopic mixture of natural potassium with an isotopic mixture of 0.0119% and is determined by gamma spectrometry using its 1470.83 keV line.

In summary: Using gamma spectrometry natural nuclides in solids of importance for this study can therefore be measured as follows:

Uranium-238 series:

^{238}U via ^{234}Th (low energy gamma) and ^{234m}Pa (but NAA is preferred);

^{226}Ra via ^{214}Bi and ^{214}Pb

^{210}Pb (low energy gamma)

Uranium-235 series:

^{235}U,

^{227}Ac via ^{223}Ra, ^{219}Rn and ^{227}Th

Thorium-232 series:

^{228}Ra via ^{228}Ac

^{228}Th via ^{212}Pb and ^{208}Tl

Some difficulties will be experienced with measurement of the following nuclides of interest in the thesis:

- ^{230}Th at 67.7 keV will potentially have poor sensitivity due to the low yield of its energy (0.38%) and accordingly may show meaningless results in dose calculations. For solids equilibrium with ^{226}Ra is therefore assumed.
- ^{231}Pa cannot be quantified with gamma spectrometry due to lack of an appropriate gamma emission. However, one may possibly assume equilibrium with its daughter ^{227}Ac taking the age of the sample into consideration.
- ^{227}Ac has to be estimated from both its daughters ^{227}Th and ^{223}Ra, which both suffer from interferences from other nuclides.

2.13.5 Instrumental Neutron Activation Analysis (INAA)

Instrumental Neutron Activation Analysis is a method for elemental analysis, based on activation of a stable nuclide to an unstable nuclide by exposure of the sample to a high flux of neutrons (Longworth *et al.*, 1988). This reaction is known as the (n,ϒ) reaction. The emitted gamma rays of the radioactive (or activated) components are detected by high resolution gamma spectrometry as discussed in 2.13.4. The spectra obtained with INAA, usually contain many lines, which increase the probability of having peaks that overlap. Sample should be counted long enough to obtain reliable counting statistics for the full-energy peaks used for measuring activity values.

The major advantage of NAA is its extreme sensitivity for some elements. Sensitivity varies from 10^{-3} to 10^{-10} grams per gram of sample with and accuracy of about 2-10% of the reported value (Smit, 2001). The high sensitivity of the method, however also makes it vulnerable to contamination. Water, radioactive material and compounds which can be easily

activated are not suitable for NAA, since there is a risk to irradiate the material, which may have a potential impact on the safety of the reactor or pose a contamination or radiation hazard to personnel.

NAA is used for routine determination of U and Th in solid samples. It has been used for analysis of foodstuffs in a study where foodstuffs grown in a catchment area influenced by mining and mineral processing industries were analysed (Faanhof *et al.*, 2007). NAA is a complex and expensive analytical method, and is usually applied only where its unique advantages are important enough to justify the high costs.

2.13.6 Alpha spectrometry

Alpha spectrometry is based on the direct measurement of alpha particles generated by alpha emitting nuclides. The energies of the alpha emitters of the three naturally occurring series are shown in Table A-3 in Appendix A. Detectors for alpha spectrometry are semi-conductor detectors using high purity silicon as detector material (see 2.13.1).

The efficiency of a solid state detector in the range of 2.5-8 MeV is typically 20-30% and depends on the geometry (Longworth *et al.*, 1998). Background is typically less than 5 counts per day; the corresponding detection limit is less than 0.1 mBq for a counting efficiency of 30% (Smit, 1999b). Increase in the background of a detector is caused by recoil and mechanical transfer of radioactivity from a count sample to the detector or the geometry rig.

Typical energy resolution is in the order of 15-30 keV for detectors under ideal counting conditions and with a commercially prepared source (Canberra, 2006). Despite this good resolution, the relatively small difference in energy between some α-emitters makes it difficult to spectrometrically separate all peaks for example, ^{234}U and ^{230}Th (Figure 2-23) and chemical separation is usually required (L'Annunziata, 2003). Even after separation, spectral overlap is common, and some form of de-convolution may be necessary.

For good resolution a thin source is required, which is usually prepared by either electro-deposition on stainless steel disks or co-precipitation (L'Annunziata, 2003). An energy resolution of better than 25 keV typically indicates a good quality prepared source. Electro-deposition provides, perhaps, the best resolution with typical FWHM of 20-40 keV and is used for preparation of calibration sources and nuclides with difficult to resolve peaks (L'Annunziata, 2003). The greatest disadvantage is that it is time consuming, requiring one

or more hours per sample. Since a platinum anode is used, it is also costly for most laboratories. Yields better than 90% are obtained for U and Th (Hallstadius, 1984).

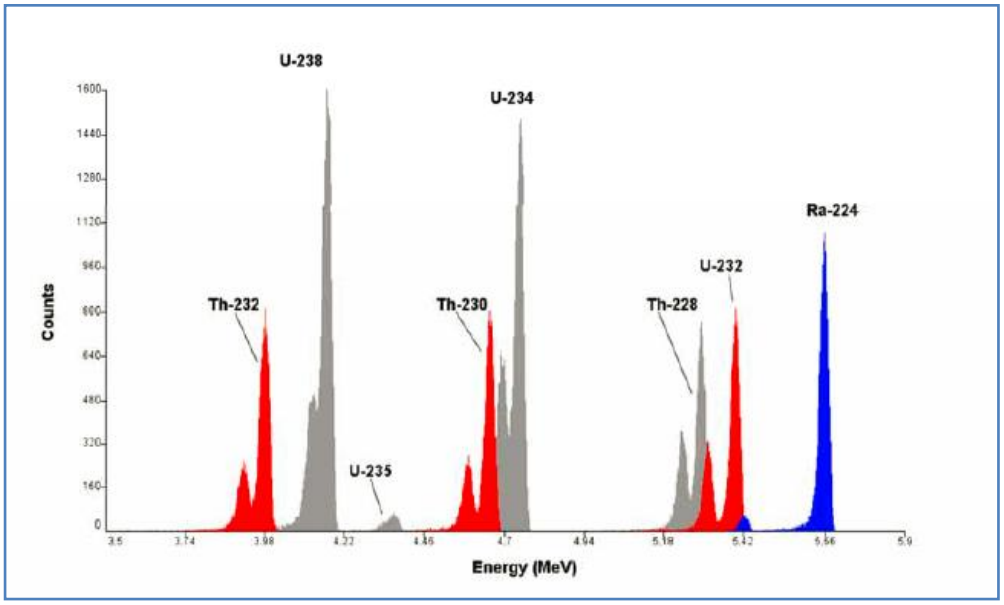


Figure 2-23: Overlap of interfering peaks of U and Th Isotopes

Micro-precipitated sources using microgram amounts of rare-earth element carrier (50-100µg) can provide excellent spectral resolution, while having the advantage of rapid sample throughput. The method is widely used (Eichrom, 2014d; Sill, 1987a). Atypical FWHM is 50-60 keV, which is nearly as good as electro-deposition. For good resolution the sample size must be limited to 100 µg of the element being determined, which will ensure a sample thickness of less than 0.025 $mg.cm^{-2}$ (Sill, 1987a).

Polonium sources are usually prepared by direct deposition of silver and nickel discs as discussed in section 2.13.12. This technique has high recovery and strongly discriminates against all other alpha emitters found in environmental samples. For Radium, $BaSO_4$ co-precipitation is often preferred (Benedik, 2016; Lozano, Fernandez & Gomez, 1997; Sill, 1987b). The procedure provides very good recovery and sources of good quality, with a resolution of 50-60 keV (IAEA, 2010b).

In gamma spectrometry, the most fundamental concern in obtaining quality results is the proper calibration of the detector and electronics. Although that is equally important in alpha spectrometry, the most important factors in obtaining quality results are proper sample

preparation (see 2.13.8), reproducible radiochemical separation (see 2.13.9), and mounting techniques that produce thin, uniform samples. More than any other factor, the chemistry dictates the quality of the result.

2.13.7 Kinetic Phosphorescence Analysis (KPA)

KPA is based on measurement of the phosphorescence of uranyl ions taken at selected time intervals. After excitation of the sample by laser, the natural logarithm of the light emitted by the sample will decay linearly with time from its starting value, which is when the population of excited analyte molecules was at a maximum. The intensity of light emitted from the excited uranium molecules at any time is directly related to the concentration of the analyte.

KPA is very specific for determination of U. It measures trace U(VI) present in solution as uranyl ion UO_2^{2+}. U(IV) is insoluble and does not phosphorescence and has to be oxidized to U(VI) in acid before the sample is analysed. Analysis of one sample typically requires one minute, once the sample is prepared.

Interferences are common causing either absorption or quenching (Sowder *et al*., 1998). In samples such as drinking water, interferences are not a problem, and no sample preparation is required. However, natural water may contain a significant amount of salts, requiring pre-treatment. Most of the interferences can be reduced by one of the following: filtering of the sample to let particles settle out, dilution (if U concentration is high enough), evaporating to dryness or wet-ashing with a nitric acid / hydrogen peroxide mixture (used for urines, biological samples, soil and vegetation).

2.13.8 Sample preparation for radiometric analysis

Using radiometric techniques for the analyses of environmental samples, typical problems are not associated with the efficiency of the instrumental method but rather with the sample preparation method. Most environmental samples require some treatment before counting. Internal tracer nuclides are typically added early in the pre-treatment phase.

After filtering and acidification of water samples pre-concentration of a large volume of water is required as preparation for radiochemical separations and to lower LODs. This can be done by evaporation, ion exchange or various co-precipitation techniques (Longworth *et al.*, 1998). This “scavenging” serves as a preliminary purification steps, as many common

elements are left behind in the process.

For solid samples pre-treatment may involve crushing and grinding, sieving, drying, drying and combustion to remove organic matter. Dry and/or wet ashing is used to remove organic constituents (MARLAP, 2004,12.1). If not analysed by direct methods, solid samples usually require decomposition and dissolution. Bock (1979) defines "dissolution" as the dissolving of solids or substance with or without chemical reaction, whereas "decomposition" refers to the "opening-out" at higher temperatures. Extended treatment with acids, fusion or microwave digestion may be required for total dissolution. Variable and incomplete dissolution is one of the major causes of inaccurate results. Therefore, non-destructive, direct radiometric techniques are usually preferred for the analysis of solid samples at our laboratory.

Radionuclides may be present in two fractions: Easily leached superficially absorbed fraction and highly insoluble inside mineral grains. The purpose of analysis and final use of the data should be considered in the choice of dissolution procedure. Leaching procedures are quicker and simpler and relies on the solubility of the nuclide of interest and may be sufficient in some cases (Longworth *et al.*, 1998).

2.13.9 Radiochemical separation procedures

Radiochemical separation is required when it is not possible to determine the activity of a radionuclide of interest by direct radiometric techniques. Desirable characteristics of radiochemical methods are (1) to obtain high yields and low LOD, (2) clean separations with no interferences and (3) "as soon as possible". Most types of samples, *e.g.* water, soil, food, require some type of treatment before they can be counted by alpha spectrometry. The three basic chemical procedures that alpha samples must undergo before counting are:

- Sample pre-treatment to concentrate the analyte from the bulk sample: Leaching or dissolution of solids; pre-concentration of liquids into a smaller volume for increased sensitivity (see 2.13.8).
- Chemical separation/extraction and purification to separate the nuclide of interest from other interfering natural radionuclides and stable elements. This may involve co-precipitation, liquid-liquid extraction, ion exchange, extraction chromatography, or some combination of these (see 2.13.10 to 2.13.13).
- Source preparation to prepare the sample for counting; sample mounting (see 2.13.6).

Extraction chromatography (EXC)

There have been significant advances in radiochemistry, with the development of commercially available extraction chromatography resins, of which the characteristics are well described in literature (Horwitz *et al.*, 1992b, 1993, 1995). Many papers of application using these resins have been published in the last 25 years, however, the optimal conditions for separation for specific applications in the radioanalytical laboratory at NECSA still had to be investigated (as discussed in Chapter 4).

Extraction chromatography (EXC) combines the selectivity of liquid-liquid extraction with the ease of operation of column chromatography. The resins are manufactured by Eichrom and consist of an inert support impregnated with an extractant, which is specific for various elements. No single resin is capable of separation of all nuclides of interest and tandem arrangements are usually necessary. Acid dependencies of the resins can be found on the manufacturer's website at www.eichrom.com. Separation using column EXC is simpler than ion exchange, less waste is produced and it has higher accuracy and precision. Potentially hazardous reagents (used for solvent extraction) are eliminated. EXC is considered as more expensive than classical methods due to the high resin costs. Nevertheless, only a few laboratories worldwide still use more classical "older" separation methods. Several types of extraction chromatography resins are utilized in the work discussed in the thesis.

UTEVA resin (Uranium and Tetravalent Actinides) is selective for U (VI). It consists of diamyl-amylphosphonate sorbed onto an inert polymeric support called Amberlite XRAD-7. U and tetravalent actinides are strongly sorbed onto the column in HNO_3: the higher the nitrate concentration, the better the uptake of actinides. U sorption by the resin is most effective at high (>1 M) acid concentrations (capacity factor, $k' > 100$). Sorbed U can be readily eluted using dilute acid ($k' < 1$). Recoveries for U are better than 95% (Horwitz *et al*., 1992b). Behaviour of Th roughly parallels that of U, but retention of U(VI) is stronger than for Th(IV) at all, except lower, concentrations of HNO_3. The good selectivity of UTEVA for U over Th makes U separation simpler. The large difference in k' for U and Th in the range of 4-6 M HCl allows for the selective elution of Th from the resin after both U and Th have been loaded with U remaining on the resin. UTEVA resin is sufficiently stable for re-use, since loss of extractant is negligible. According to Horwitz *et al.* (1992b), the UTEVA resin only exhibits a small decrease in column capacity after washing with nearly 1000 free

column volumes, FCV (1 FCV = 1.3 ml) of 2 M HNO_3.

TEVA resin (TEtraVAlent actinides) is selective for Th (IV). It consists of quaternary ammonium salt (Aliquat-336) sorbed on an inert polymeric substrate. In HNO_3 concentrations ≥ 0.5 M sorption of tetravalent actinides exceeds that of other actinides. The k' value for Th(IV) is an order of magnitude greater than for U(VI). Commonly encountered cations are essentially not retained and elutes in the first ten FCVs. No traces of Th are found in the first 30 FCVs. Low retention of Th on TEVA is found in all concentrations of HCl due to formation of a relatively weak-neutral $ThCl_4.8H_2O$ complex in HCl (Horwitz *et al.*, 1995). Th is readily removed from the column with a small volume of HCl, typically 4 M HCl.

TRU resin (TRansUranium) is selective for actinides (II, IV, VI). It consists of a combination of CMPO (octylphenyl-N,N-di-isobutyl carbamoyle phosphine oxide) diluted in tri-n-butyl phosphate (TBP) on an inert substrate. TRU retains all but pentavalent actinides in HNO_3. Actinides are sorbed at high (> 1 M) HNO_3. Tetra- and hexavalent actinides are also retained from dilute HNO_3. Non-actinide ions such as Po and Bi are not retained. Fe and Ca, which is used as a co-precipitant for actinides, are also not retained. K' for a given actinide is 100-1000 times higher on TRU, than on UTEVA. Because of the strong retention it cannot be eluted by lowering the nitric acid concentration and a different acid has to be used (Horwitz *et al.*, 1993). Th(IV) and U(VI) show very high affinity for HCl concentrations higher than 3 M. K' for Th decreases from > 10^4 to ~1 in HCl when reducing the concentration from 8 M to 1 M. U can been stripped by 1 M HF, H_3PO_4 or $HClO_4$. Since column material is stable, TRU resin can be re-used, if cross contamination can be prevented.

SrSPEC resin is selective for Pb and is used for the separation of Pb and Po. The extractant used is a crown-ether (4,4'(5')-di-t-butylcyclohexano-18-crown-6) diluted in octanol (Horwitz *et al.*, 1992a).

In the following sections (2.13.10-2.13.13) a theoretical overview of available radiometric techniques for determination of the nuclides of interest in this thesis are given. Hundreds of different methodologies have been published for specific applications. The analytical method to be used depends on the LOD and precision required. The focus will be on radiochemical separation techniques, which are the speciality field of the author of this thesis.

2.13.10 Radiometric techniques for determination of ^{210}Pb and ^{210}Po

There are widespread information in literature concerning the measurement of ^{210}Pb and ^{210}Po in different kinds of samples. Because of the lack of radioactive equilibrium in most environmental samples, individual analysis of both ^{210}Pb and ^{210}Po are desirable for realistic dose assessments. ^{210}Pb is a short-lived beta emitter (22.3 years) and decays by emitting soft β-particles of energy 20.0 keV (81%) and 61 keV (19%) accompanied by 46.5 keV gamma rays (4.25%) to ^{210}Bi (5 days) and then to ^{210}Po as shown in Figure A-1 (Appendix A).

Determination of ^{210}Pb

There are four principle radiometric techniques for determination of ^{210}Pb:

Direct counting of the low energy gamma (46.5 keV) by gamma spectrometry: Gamma spectrometry is generally used solely for solid samples. The main advantage is that no sample preparation and chemical separation is required. Due to the relatively poor efficiency and high background count rate in the lower energy region, the LOD is high. The method is therefore not practical to be used for environmental water samples, since very large volumes are required. Typical reported LODs are 0.4 Bq (Clayton & Bradley, 1995) and 0.662 Bq (Kulzer *et al*., 1996).

Separation of the daughter ^{210}Bi and beta counting of the high energy beta (1.17 MeV). Bi is separated from the matrix and counted.

Separation of ^{210}Pb and beta counting of the ingrowing daughter ^{210}Bi after equilibrium has been established: Pb is separated from the matrix and other radionuclides. The separated Pb is kept for a month for in-growth of ^{210}Bi and then counted using GFPC. The LOD is about 0.003-0.030 Bq (Kulzer *et al*., 1996). ^{210}Pb can also be counted directly after separation with an LSC, which allows discrimination of α and β pulses.

Separation of progeny ^{210}Po and alpha counting (5.32 MeV)*:* ^{210}Po is removed from the solution. The sample is kept for at least four months after the first analysis to allow for in-growth of ^{210}Po from ^{210}Pb. The newly generated ^{210}Po is then again separated and measured by alpha spectrometry. Bateman equations are applied to calculate the activity concentrations. This method is the most sensitive for indirect determination of ^{210}Pb (Kulzer *et al*., 1996). Due to low background counts and high counting efficiency, LODs of 0.0001–0.001 Bq can

be obtained. A main disadvantage is the need to wait for radioactive equilibrium to be established.

Where ^{210}Pb is determined by measurement of its progenies it is necessary to know the degree of equilibrium that exists between the progeny and its parent. For ^{210}Po a period of more than four months is required to reach 50 % and 18 months to reach 88 % ingrowth. For ^{210}Bi, with half-life 5.01 days, 98 % of equilibrium is reached in 30 days. Changes of relative activities for ^{210}Pb, ^{210}Bi and ^{210}Po in time are presented in Figure 2-24.

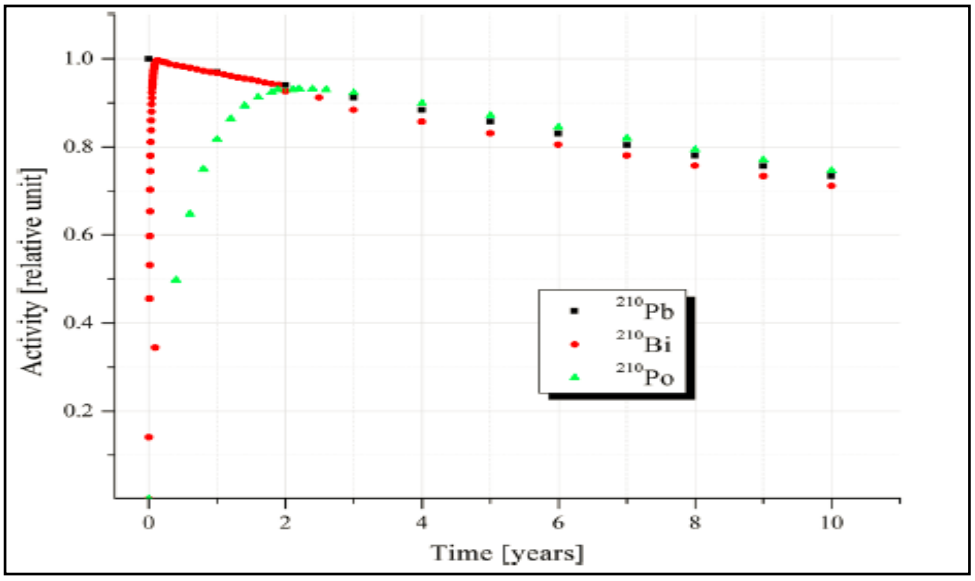


Figure 2-24: Changes of relative activities for ^{210}Pb, ^{210}Bi and ^{210}Po in time in an isolated system (Seslak *et al.*, 2016)

The three nuclides in the series can be chemically separated using different methods include solvent extraction, precipitation, ion exchange, extraction chromatography and auto deposition of Po on metal discs. Of these, autodeposition and extraction chromatography are most often used.

Determination of ^{210}Pb using extraction chromatography resin

The extraction chromatography resin SrSpec was developed in 1991 for separation of Sr, but also has extremely high sensitivity for Pb (Horwitz *et al.*, 1992a). Pb and Po are selectively separated on SrSpec, and other natural radionuclides do not interfere. The use of SrSpec has increased in the 2000's and has been widely used for simultaneous determination of ^{210}Pb and ^{210}Po (Vajda *et al.*, 1997; Vrecek *et al.*, 2004). PbSpec is a modified version of SrSpec with

reduced selectivity for Pb thus allowing easier removal from the resin.

The basic procedure is described in the Eichrom method for ^{210}Pb and ^{210}Po (Eichrom, 2014b). When loaded in 2 M HCl, Bi and other interfering radionuclides are not absorbed onto the column, whereas Po and Pb is retained. Non-retained ions are washed from the column with 2 M HCl. Po is stripped with 6 M HNO_3 and prepared for counting by spontaneous deposition. Pb is stripped with 6 M HCl. Milder reagents, which are less corrosive, are also used for stripping ^{210}Po (1 M HNO_3) and ^{210}Pb (0.1 M citric acid) (Vajda *et al.*, 1997).

Pb is precipitated as oxalate or sulphate or evaporated, mixed with liquid scintillation cocktail and counted directly by LSC. Because LSC offers some resolution the ^{210}Pb and ^{210}Bi peaks can be separated with careful selection of the pulse decay discriminator settings (L'Annunziata, 2003). Alternatively the Pb fraction can be kept for 14 days for ingrowth of ^{210}Bi (counted by LSC or GFPC); or six months for ingrowth of ^{210}Po (counted by alpha spectrometry).

Po and Pb is quantitatively recovered from the columns. Chemical recovery of ^{210}Pb is determined by addition of a stable lead carrier measured gravimetrically or with AAS. It is preferred to use "radioactive free" or ancient lead, since stable lead carriers are known to contain ^{210}Po and ^{210}Pb *e.g.* analar lead nitrate may contain up to 500 Bq.kg^{-1} ^{210}Pb (Ham *et al.*, 1997). Compared to spontaneous deposition results are produced faster but at the cost of more laboratory work and a loss in sensitivity

Determination of ^{210}Po by spontaneous deposition

^{210}Po, as a pure alpha emitter, can be determined only by alpha-spectrometry. Chemical separation of ^{210}Po is required because there is interference with its alpha spectrum (*e.g.* ^{234}U and ^{228}Th alpha emissions overlap). A source preparation step is necessary in order to deposit polonium in a thin layer on a disk or a filter.

The method of spontaneous deposition of ^{210}Po onto a silver disc has first been documented in the1960s (Figgins, 1961; Flynn, 1968) and still remains the generally preferred choice in many laboratories worldwide (Clayton & Bradley, 1995; Fernandez *et al.*, 2012; Ham *et al.*, 1997; Matthews *et al.*, 2007), mainly due to the ease of use of this straightforward method.

Po, a noble metal will be deposited by electrochemical displacement, under suitable conditions on the surface of a less noble metal such as Ag. The theoretical rate of polonium deposition on a rotating silver disc can be expressed as:

$$dN/dt = K_1(A\ \omega^{0.5} / V)(N_0 - N_s)\ exp\ (K_2T)$$

where dN/dt is the rate of deposition; K_1 and K_2 are constants; T is the absolute temperature; A is the active disc area; V is the volume of solution; ω is the angular velocity of rotation of the disc; and N_0 and N_s are the concentrations of polonium in the bulk liquid and at the disc surface respectively (Smith & Hamilton, 1984).

Following from this expression it is clear that the rate of deposition is directly proportional to: (1) the ratio of disc area to solution volume (A/V); (2) the concentration difference between the bulk solution and the solution at the disc surface ($N_0 - N_s$); (3) the square root of the angular velocity of rotation of the disc and (4) the exponential of the absolute temperature. This indicates that optimum plating conditions would require high temperatures and angular velocity, and small solution volume.

Optimization of the experimental parameters for source preparation has been evaluated in many studies since 1961 (Smith & Hamilton, 1984; Vesterbacka & Ikaheimonen, 2005). The findings can be summarized as follows:

- Ag has been the metal of choice for most investigators because of its selectivity for Po only. Ni extracts both Po and Bi and also became discolored more easily. Yields of 61% on average were found on Ni compared to 99% on Ag (Eichrom, 2006). However, some authors still prefer use of Ni, probably due to costs and easier availability (Puchkova & Bogdanova, 2015).
- Po deposits readily on Ag from dilute HNO_3 or HC1 solution, but proceeds more smoothly and is more efficient from HCl than from HNO_3, which tends to attack the disc.
- Small amounts of ferric ion inhibit the deposition, but this can be overcome by reduction with ascorbic acid or hydroxyl ammonium hydrochloride.
- Rate of deposition varies directly with the surface area of the Ag, and inversely with the volume of solution. Fillings or powder can be used to provide a larger deposition area.

— Experimental conditions of major importance for optimal recovery include temperature, extraction time and acidity of the solution. Recoveries vary but are typically better than 90%. Slight variations occur in literature, but optimum yields are typically obtained by plating for three hours at a pH of 1.5-2 at 85-90 ^{o}C.
— One side of the disc must be covered to prevent plating on both sides to increase counting efficiency.

Auto-deposition produces a thin, uniform layer, which is essential for maximum resolution in alpha spectrometry. Other alpha emitters are not expected to deposit in any significant amounts. Either ^{209}Po or ^{208}Po is usually added as yield tracer. ^{208}Po is more easily available and there is less contamination of the detectors due to more rapid decay, but spectrum resolution is a problem because of the close proximity of the alpha energy to that of ^{210}Po. ^{209}Po has better resolution from ^{210}Po.

Sample preparation for ^{210}Po analysis

Relative clean aqueous samples do not require chemical clean-up prior to deposition of Po. For complex samples with high salt concentrations (*e.g*. hydraulic fracturing fluids), a pre-cleanup is required. One possibility is to use TRU resin. Po is not retained in 2 M HNO_3 (low k'). Deposition is done on the eluate. This has been used with success in some samples with complex matrices (see 4.8.1).

For solid samples many studies have been done to investigate procedures for digestion and chemical separation. Loss of Po (as chloride) can occur during dry ashing; therefore acid digestion is normally used (Longworth *et al.*, 1998). Organics must be completely decomposed since the presence of any organic material may result in reduced recoveries (Seiner *et al*., 2014). The choice of dissolution technique depends on the required sample mass and sample matrix. Some authors prefer traditional digestion on hot plates; whereas others use microwave digestion (Begy *et al.*, 2015; Sanchez-Cabeza *et al.*, 1998). Planisek, Benedik & Smodis (2013) found similar recoveries when comparing three different dissolution techniques for biological samples, *i.e*. classical wet ashing, digestion in an Erlenmeyer flask and microwave digestion.

Samples are evaporated to dryness to ensure complete nitrate removal. Losses of Po may occur by absorption onto glassware or by volatilization; therefore care must be taken when

evaporating. After evaporation the residue is transferred into the chloride form with concentrated HCl.

Bateman equations for data reduction

^{210}Pb can be determined by separation (deposition) of Po on time t_1, followed by a second deposition after a sufficient time for the growth of ^{210}Po from ^{210}Pb to be significant. Most authors in literature use simplified Bateman equations (Friedlander *et al.*., 1981) to obtain the ^{210}Pb activity from the measured ^{210}Po activity assuming that at time t_0 there is a certain activity of the parent Pb and none of the decay products present. The delay between sampling time (t_0) and time of first deposition (t_1) should be at least five weeks to ensure that Bi is in equilibrium with its parent Pb at time t_1. Trying to solve an equation with three unknowns (Pb, Bi and Po), but doing only two measurements (Po at times t_1 and t_2), is impossible, therefore the simplification of assuming Bi equilibrium.

The second deposition (at time t_2) provides data on the ^{210}Pb activity of the samples and hence on the extent to which the initial ^{210}Po was supported by its grandparent. Uncertainty of Pb (t_0) decreases as the time interval (t_2-t_1) increases. Where great accuracy for lower activity samples is needed, it is necessary for the Po to be as close to equilibrium with its parent Pb as possible. One year is the typical ingrowth period used with a Pb concentration of 0.2 mBq (Clayton & Bradley, 1995) – see Figure 2-24.

Using the method of spontaneous deposition most authors prepare consecutively the two sources from the same aliquot. When two measurements are made on the same aliquot one has to assume that the first deposition proceeded quantitatively and that all Po present at the second deposition is from ingrowth of Pb. This is seldom the case, and yields, even though high (>80%), is seldom complete. Fernandez *et al.*, (2012) and Garcia & Garcia (2002) describe procedures where the two measurements of Po are made on two different aliquots separated by sufficient time for the growth of ^{210}Po from ^{210}Pb to be significant. When two separate aliquots are used, there is no need to remove Po from solution after the first measurement, thus avoiding possible contribution to error.

2.13.11 Determination of Uranium

A number of analytical techniques can be used to measure uranium. It can be chemically measured, where the concentration is expressed as $mg.L^{-1}$ U, or it can be radiologically measured in terms of the α-particle radiation activity, where the concentration is expressed in units of $Bq.L^{-1}$.

Measurements of total (chemical) uranium do not provide the relative isotopic abundance of the uranium isotopes, which might be important when the origin of the uranium has to be assessed (*e.g.* natural, depleted or enriched). More than 99% of the uranium mass is provided by ^{238}U (see Table 2-1). In case of natural uranium, for which the $^{238}U/^{235}U$ ratio is well known, the mass results can be easily converted into activity results (equation 2.17). Where the equilibrium has been disturbed the isotopic concentration or the $^{234}U/^{238}U$ ratio is required to have an accurate conversion from mass to activity, or vice versa.

Chemical Measurement

Chemical techniques include spectrophotometry, fluorometry and kinetic phosphorescence (KPA). KPA has been used in some laboratories for analysis of water and urine samples (ASTM D5174-02; Elliston *et al*., 2005; Hedaya, Birkenfeld & Kathren, 1997). It allows for the measurement of small amounts of uranium (as low as 0.1 $\mu g.L^{-1}$) with good precision and accuracy (less than 20% expanded uncertainty) in a variety of matrices. Calibration is required using a set of external standards. The method is susceptible to matrix effects.

ICP-MS provides an excellent tool for the rapid and straightforward measurement of low concentrations of U in water and urine (Hou & Roos, 2008; Shi *et al*., 2013). Measurements can be done on virtually unprocessed samples with a high sensitivity in an analysis time of less than 2 minutes. Detection limits for ^{235}U and ^{238}U (~1 $pg.ml^{-1}$) are lower than those obtained by α-spectrometry. Although the use of ICP-MS for analysis of U by laboratories worldwide has increase in recent years, many radio-analytical laboratories still prefer radiochemical separation followed by alpha spectrometry, especially if quantification of the individual uranium isotopes is needed (e.g. ^{238}U, ^{235}U or ^{234}U).

Radiometric measurement

Radiometric techniques focus on the radiochemical toxicity of uranium. Gamma

spectrometry is preferred for relatively high activities of uranium due to the speed and convenience of the direct non-destructive measurement. U is measured via decay products due to lack of suitable, high abundance gamma lines emitted by the long-lived U isotopes (2.13.4). In environmental media where activity concentrations are usually low, the standard radiometric method is alpha spectrometry after pre-concentration and chemical separation.

NAA is an excellent technique for determination of low concentrations of U in solids due to the high sensitivity and low blanks. ^{238}U is measured via ^{239}Np after irradiation of the sample in a nuclear reactor (Benedik & Byrne, 1995). Delayed neutron activation analysis is a method sensitive for measurement of ^{235}U only. Uranium irradiated in a nuclear reactor produces nuclear fission of ^{235}U, which emits delayed neutrons after removal from the reactor. The number of neutrons are measured and converted to ^{235}U concentration.

Radiochemical separation of uranium

When using alpha spectrometry, chemical separation procedures are required for separation of nuclides with un-resolvable alpha energies such as ^{231}Pa (4.73 MeV) and ^{230}Th (4.69 MeV) and ^{235}U (4.78 MeV), as well as ^{232}U (5.32 MeV) and ^{210}Po (5.30 MeV).

Classical methods for chemical separation such as precipitation and liquid-liquid extraction (LLE) are still used in some laboratories (Casacuberta *et al.*, 2012 and Mola *et al.*, 2013). Ion exchange chromatography (IEC) has been widely used for separation of actinides since the 1960's, and is still used by many laboratories (Popov, 2016; Taddei *et al.*, 2001). The separation and purification of uranium is attained by adsorption with strong base anion exchange resin in hydrochloric acid media. U is absorbed in 8 M HCl on Dowex 1X8, while Th (and Ra) is not retained; U is then eluted with a low concentration of HCl (0.1 M or 0.5 M).

Extraction chromatography has become increasingly popular over the last two decades. Due to the difference in binding strength in HCl and HNO_3 (see 2.13.11), U and Th can be easily separated from one another. Separation of U on the commercially available resin, UTEVA, is widely implemented (Baik *et al.*, 2015; Casacuberta *et al.*, 2012; Dirican & Sahin, 2016; Mola *et al.*, 2013; Prabhath-Ravi *et al.*, 2016; Siddeeg *et al.*, 2015). In the recommended procedure (Eichrom, 2014a) U is retained on the resin in 3 M HNO_3-1M $Al(NO_3)_3$ (3 M, or 8 M is also used by other authors), Th is removed with 5 M HCl-0.05 M oxalic acid (5 M HCl

or 9 M HCl also used), U is then stripped from the column with 1 M HCl (or 0.01 M HCl). Most authors reported good chemical recoveries (65–86%) and depending on counting time LODs of 0.1–1 mBq have been reported.

TEVA and TRU resin has also been used in methods for U. Both Th and U are strongly bound on TRU resin in concentrations of 0.5 to 3 M HNO_3. Using TEVA in 4 M (or 6 M) HCl, U and Pa are retained on the column, whilst Th is eluted. Following the removal of residual Th, Pa can be stripped with 4 M HCl-0.1 M HF (because Pa forms a soluble Pa fluoride complex). U is then eluted with 0.1 M (or 1 M) HCl (Tagami&Uchida, 2004).

A combination of more than one column is often required for sequential separation of all the elements of interest (U, Th, Ra, and Ac). Burnett & Yeh (1995) describes a procedure for sequential separation of U, Th and Pa using a combination of TRU and cation exchange. Sample is loaded onto TRU resin in 2 M HNO_3 in which the common ions are not retained. The k' values for U and Pa are high and they are strongly retained. The column is converted to a chloride system, after which Th is eluted in 1 M HCl (80-90%). The Th fraction is very pure. U and Pa is eluted with 0.1M HCl-0.1 M HF and then further purified on a cation column. A method based on this separation has been implemented, but has recently been replaced by a method based on the Eichrom recommended method using UTEVA (see Chapter 4).

Alpha spectrometry

From a spectroscopy point of view alpha spectroscopy presents few problems for uranium determination and good spectrums are obtained (see Figure 2-25). Due to the low specific activity of the long-lived ^{238}U (12.3 Bq per mg), there is an upper limit as to how much U can be accepted on the filters before degradation of the alpha spectrum due to self-absorption of the alpha particles in the source. Keeping the mass of U on the filter to less than 100 µg, the FWHM will be less than 60 keV.

Tracer solution (^{232}U) is readily available and do not disturb other peaks in the spectrum. Use of a self-cleaning ^{232}U tracer is recommended (Eichrom, 2014e). $BaSO_4$ precipitation is used to remove ^{228}Th and daughters before an aliquot is taken for uranium tracer. ^{210}Po can cause interference under the ^{232}U tracer peak if not adequately removed during the chemical separation, resulting in overestimation of the yield.

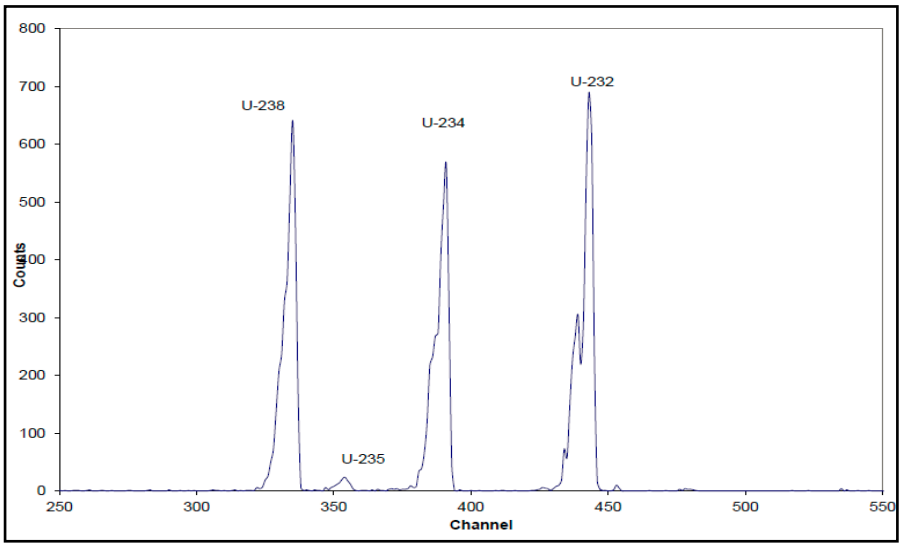


Figure 2-25: Typical alpha spectrum for natural uranium

Samples preparation for analysis of Uranium

The chemical separation procedures described above can be used for solids after suitable digestion. Complete dissolution of the solid mineral samples is required because uranium is usually incorporated into the crystal lattices of the oxides of Si, Zr, Al, and Fe. Leaching with HNO_3 or aqua regia is not sufficient (Hill *et al.*, 2004; Jia *et al.*, 2008; Lee & Lee, 2001; Maxwell *et al.*, 2015) and is suitable only for solid samples from biological origin - grass, algae, fish, milk, bones and some bottom sediments, which do not contain silicates (Benedik & Byrne, 1999). Fusion is often the most effective sample dissolution technique to use for determination of U in soil (Dirican & Sahin, 2016; Jia *et al.*, 2008).

2.13.12 Determination of Thorium

Elemental thorium (^{232}Th)

^{232}Th has a long half-life (> 10^9 y) and is the only one of the Th-nuclides with significant mass to be readily determined with good precision and accuracy by non-radiometric instrumental techniques. Spectrophotometry, using thorin as a chromogenic reagent and measuring the absorption at 544 nm, is a classical method used for Th (Khan *et al.*, 1994). ICP-MS has been routinely used for the elemental analysis of ^{232}Th in a wide variety of matrices (Shen *et al.*, 2002). No chemical separation of Th from the sample matrix is required, although less matrix affects are observed with a purer sample. There are usually no

spectroscopic interferences in natural samples.

NAA is a very sensitive and reliable analytical method for determination of ^{232}Th, and is also used at our laboratory. It allows direct measurement of Th in solid samples via the (n,ϒ) reaction and subsequent decay of the short-lived ^{233}Th (22.3 min) product to ^{233}Pa (27d). The 311.8 keV characteristic gamma line of ^{233}Pa is counted using a HPGe detector (Benedik & Byrne, 1995). No chemical separation of ^{233}Pa is required, although it can be separated from matrix elements after neutron activation to reduce the LOD (Glover *et al.*, 1998).

As discussed in 2.13.4 direct measurement of ^{232}Th by gamma spectrometry is not possible due to the weak intensity of the 63.8 keV peak. Measurement is done indirectly by measuring the short-lived progeny isotopes, if equilibrium can be assumed.

Determination of other thorium isotopes of interest

Determination of the shorter-lived Th isotopes is of particular concern if the ^{232}Th decay series is in a state of disequilibrium. Measurement of ^{228}Th will provide information on the equilibrium of ^{232}Th with its daughter decay series, and is required by the NNR (NNR, 2013). The long-lived Th isotopes can be easily assayed using α-spectrometry, which is the method of choice for analysis of water samples. However, application of this method requires chemical separation of thorium from other alpha emitters and preparation of thin alpha sources.

^{228}Th is readily determined with gamma-spectrometry (see 2.14.4), which is the most suitable technique for detecting ^{228}Th in solid samples. ^{230}Th cannot be measured directly via gamma spectrometry, but is determined via ^{226}Ra progeny products (^{214}Pb at 352keV, ^{214}Bi at 609keV). Samples have to be sealed in air-tight containers to avoid emanation of the precursor ^{222}Rn.

Radiochemical separation of thorium

Chemical separation of thorium is mostly done using procedures based on ion exchange chromatography or extraction chromatography.

Th forms absorbable nitrate complexes in nitric acid solutions over a wide range of concentrations with maximum adsorption at 8 M HNO_3 and will be retained on an anion

column in HNO_3 while U is not. Th and other cations are eluted with 1 M HCl, since Th is not absorbed in HCl medium. Ra, Ac and Po, which will interfere with α-spectrometry, will elute with Th and has to be separated on a second (cation) column (Hrnecek & Irlweck, 1995). When a solution containing U and Th is loaded onto a cation column, Th is strongly retained in all concentrations of HCl, while U and other elements are rapidly eluted (Hyde, 1960).

As discussed for uranium separation TEVA, TRU and UTEVA resin, or combinations thereof, can be utilized for separation of Th from U, Ra and other progeny for low-level environmental radioanalytical measurements. The Eichrom recommended procedure uses TEVA resin (Eichrom, 2014c). Th is retained in 3 M HNO_3 and then eluted with 9 M HCl. The load conditions of 3 M HNO_3 on TEVA and 8 M HNO_3 on UTEVA are based on the high retention of Th on the respective resins, with a distribution coefficient k'>100 (Horwitz *et al.*, 1995). Less than 0.1% Th was detected in the load and rinse fractions of TEVA and UTEVA (Ivanov *et al.*, 2017). No cations such as Fe, Ca and Ra are retained. Th(IV) does not form anionic complexes in hydrochloric acid, which makes HCl, a highly efficient stripping agent for thorium elution. On TRU almost 98% of all Th was eluted in 1 M HCl with no cross contamination, whereas lower HCl (0.5 M HCl) resulted in breakthrough of small amounts of U and Pa (Burnett & Yeh, 1995). Using UTEVA resin, Th and U can be eluted with 6 M HCl and 0.025 M HCl, respectively.

Alpha spectrometry

Different tracers can be selected to use for chemical recovery. ^{228}Th occurs in nature and can only be used if a correction is made assuming equilibrium between ^{232}Th and ^{228}Th. The contribution of ^{228}Th from the sample is then simply obtained by subtracting the peak area of ^{232}Th from the ^{228}Th sum peak. Or two aliquots of samples are measured, one with tracer and one without.

^{234}Th can be prepared from a uranium salt. UO_2 is dissolved in concentrated HNO_3 and converted to uranyl nitrate. The solution is loaded onto an anion exchange column in 8 M HCl on which U is retained and Th eluted. There is very little movement of the U band. Because of the short half-life of 24 days, Th is expected to be in equilibrium after 240 days at which time another "milking" can be performed. Repeated purification of the Th solution

may be required and the solution has to be standardized. Advantages are that ^{234}Th can be prepared in the laboratory and is convenient to handle due to the short half-life. It is a beta emitter, and is determined by either gamma spectrometry of liquid scintillation counting. To avoid interference from naturally present ^{234}Th the added tracer activity has to be high.

^{229}Th is generally used as tracer. It has a long half-life (7340 y) and is available as a certified standard solution. Disadvantages are recoil contamination of the detectors with short-lived α-emitting progeny (^{225}Ac and daughters), which can interfere with ^{228}Th measurement. Low probability (0.3%) ^{229}Th emissions are present in the ^{230}Th ROI, which must be corrected for. Resolution of the peaks of ^{229}Th and ^{230}Th can be problematic. Resolution must be less than 30 keV FWHM because of proximity of ^{229}Th tracer peaks to ^{230}Th. For good resolution a mass of 40 µg added lanthanide is recommended for source preparation (Eichrom, 2014d). A bit of overlap between ^{230}Th and ^{229}Th peaks is found, even when using electro-deposition to prepare sources for counting (Jia *et al*., 2008).

Determination of thorium in solids after digestion

Gamma spectrometry is often preferred for analysis of thorium in solid samples. However, direct measurement of all isotopes of interest, *e.g.* ^{230}Th is not possible with gamma spectrometry, in which case alpha spectrometry, after suitable digestion of the solid sample, is the preferred technique. As for U great care must be taken in any digestion where Th concentrations are desired, to ensure a complete digestion. Th resides in the small mineral inclusions of environmental samples, which are particularly resistant to acid attack (Jia *et al.*, 2008; Maxwell *et al.*, 2015). For analysis of Th in excreta and vegetation samples, co-precipitation with oxalate before column separation, is recommended to eliminate interferences (Taddei *et al.*, 2001).

2.13.13 Determination of Radium

Methods for determination of ^{226}Ra include radon emanation, liquid scintillation, gamma spectrometry and alpha spectrometry following radiochemical separation. Reviews on methodology for determination of radium have been published by the IAEA (2010b) and Jia & Jia (2012).

Due to the higher background of LSC compared to α-spectrometry, direct measurement using LSC is most often only used as a screening technique for ^{226}Ra and ^{228}Ra in drinking water

(IAEA, 2010b; Jia & Jia, 2012).The classic radon emanation method (Kirby, 1964) is an indirect method based on measurement of ^{222}Rn produced by ^{226}Ra. ^{222}Rn is extracted into an organic scintillation cocktail and counted with LSC after equilibrium has been established (Method 903.1, EPA 1980; Forte *et al.*, 2015). The method is easy to use, but a drawback is the waiting period of three weeks required for in-growth of the ^{226}Ra daughters.

Direct gamma ray spectrometry using the 186.1 keV gamma ray emitted from ^{226}Ra is convenient and rapid, but is insensitive due to the low abundance and interference from ^{235}U, as discussed in 2.13.4. Indirect gamma-ray spectrometry of the radon progeny, ^{214}Pb and ^{214}Bi is the preferred method for solid samples. The sample must be sealed in a radon tight contained and aged for at least three weeks to ensure secular equilibrium between ^{226}Ra and its progeny. The LOD is improved by measuring the daughters because of less interference and higher abundance of these gamma rays, but is still not sensitive enough to be used for analysis of ^{226}Ra in water samples, unless very large volumes of samples are used. For example, to measure at the required LOD of 0.04 Bq.L^{-1} for ^{226}Ra (EU, 2013a), using a HPGe detector of 30% efficiency, it would be necessary to use at least 30 L of water to achieve the desired sensitivity. Our laboratory does not use gamma spectrometry for analysis of water samples (see Table 4-21).

Alpha spectrometry is the most sensitive of the radiometric methods and is used to determine ^{226}Ra with high precision and accuracy. The LOD of 0.0001 Bq.L^{-1} is about two orders of magnitude lower than that of gamma spectrometry or LSC (Jia & Jia, 2012). It is a direct method with no waiting period for equilibrium of ^{226}Ra with daughters. Chemical separation of Ra from chemically similar elements (Ca, Ba, Sr), as well as from spectral interferences (Th), is required.

Radiochemical separation

Methods to isolate and purify Ra include co-precipitation, extraction and ion exchange.

From the literature survey, the most popular technique for separation of Ra is micro-precipitation of radium-barium-sulfate, based on the research done by Sill (1987b). $BaSO_4$ co-precipitation is used to prepare a counting source for alpha spectrometry as the final step after chemical separation of Ra from the bulk of the elements has been done. Ba carrier is added to the sample and Ra is co-precipitated as $Ba(Ra)SO_4$ from sulfuric acid. The solution

containing the precipitate (not visible) is filtered through a polypropylene filter of 0.1μm. The method is relatively easy to perform and very good yields (better than 75%) and sources of sufficient quality (FWHM 50-60 keV) are obtained when appropriate conditions are used (Decaillo *et al.*, 2004; IAEA, 2010b; Lozano *et al.*, 1997). This method has been used for a wide range of sample types.

In a modified version of the micro-precipitation procedure, Pb is added to the solution and Ra is concentrated from water by co-precipitation with Pb sulphate, using Ba as carrier (Benedik, 2016; EPA Method 903.0, 1980). Ra and the added carriers (Pb, Ba) are co-precipitated with sulphuric acid. Small amounts of Th, U and other radionuclides are also precipitated in this step, so further decontamination is required. The $PbSO_4$ precipitate is dissolved in 0.1 M ethylene diamine tetra acetic acid (EDTA). EDTA is added as a complexing agent to improve selectivity of Ra in the purification step (Kirby, 1964). $Ba(Ra)SO_4$ is precipitated by addition of Ba^{2+} carrier, saturated $NaSO_4$ solution and adjusting the pH to 4.5-5.0 with acetic acid; as a result the precipitate does not adsorb U, Th and Pb. The $Ba/RaSO_4$ is mounted on a filter to be counted and washed with mildly acidic sulphuric acid to remove any trace of radionuclides. This is also the procedure used at our laboratory (see 4.8.5).

Ion exchange, usually by using a combination of more than one column, has been used by some authors for separation of Ra from interfering elements (Crespo, 2000). On anion exchange Ra is not retained, but can be separated from interfering nuclides, which are retained in strong acid (U in 8 M HCl, and Th in 8 M HNO_3). Cation exchange is used to separate Ra from Ba, which is a crucial interference in source preparation for alpha spectrometry (Hrneck & Irlweck, 1995). Extraction chromatography in combination with ion exchange is proposed by some authors. Ra is first separated from interfering ions such as Mg, Ca, U and Th and then further purified using SrSpec (Benedik, 2016; Maxwell & Culligan, 2012). Decaillon *et al.* (2004) used TRU resin to separate Ra from other α-emitters prior to the $BaSO_4$ co-precipitation separation.

Alpha Spectrometry

If determination of all Ra isotopes is required, a spectrum with high resolution is required to minimize peak overlap. The determination of alpha activity of ^{226}Ra is based on the counts in the ^{226}Ra region (doublet at 4.602 MeV; 5.55% and 4.785 MeV; 94.45%). Alpha counting

must take into account the rapid in-growth of the radioactive progeny of ^{226}Ra (^{222}Rn, ^{218}Po and ^{214}Po), which will also be present in the spectrum (see Figure 2-26). The main possible source of spectral interference is from ^{234}U, which occurs at 4.773 MeV and cannot be resolved from the ^{226}Ra peak. This is not expected to be a significant problem, since U is chemically separated from Ra. The spectrum should be examined for contaminant ^{238}U (4.194 MeV); if not detected one can be confident that no ^{234}U is contributing to the ^{226}Ra signal. For the other radium isotopes such as ^{224}Ra there will be overlapping from ^{226}Ra descendants. ^{224}Ra can be determined via the short-lived progenies ^{216}Po, ^{212}Po and ^{212}Bi, assuming equilibrium and applying Bateman equations^{225}Ra or ^{133}Ba are most often used as tracers for chemical yield determination. Both have their associated problems. Parallel samples, where one sample is spiked with ^{226}Ra can be analysed, if no suitable tracer is available.

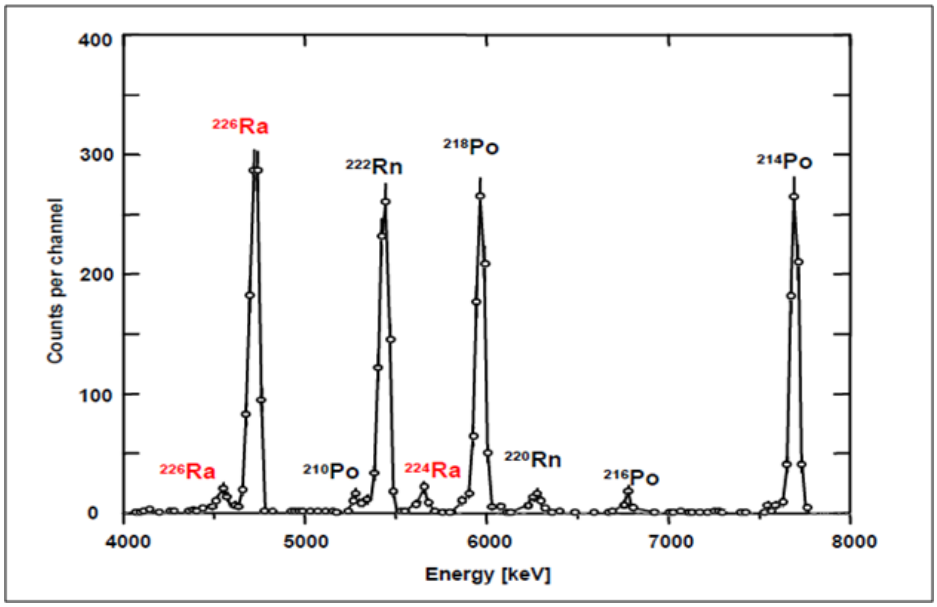


Figure 2-26: Alpha spectrum of ^{226}Ra and progeny

^{225}Ra (as daughter of ^{229}Th) does not occur naturally and can be used if available (Benedik, 2016; Blanco *et al.*, 2002; Crespo, 2000; Maxwell & Culligan, 2012). ^{225}Ra (14.9 d) is a beta emitter and decays to ^{225}Ac, which in turn decays to a series of short-lived alpha emitting daughters. Chemical recovery is determined from the ^{217}At peak (7.07 MeV) in the α-spectrum, which occurs in a region of the spectrum where no interference from other daughters of natural isotopes of radium is expected (see Figure 2-27). A suitable ingrowth period must be allowed for ^{225}Ac, which reaches a maximum after 17 days. Due to the short

half-life of ^{225}Ra there is only a short window for optimal counting of the ^{217}At. ^{225}Ra introduces several peaks into the spectrum, which complicates determination of ^{224}Ra and ^{223}Ra. Even with good resolution, overlapping between peaks occurs, which requires de-convolution processes. Therefore use of the non-radium tracer ^{133}Ba is often preferred.

^{133}Ba (10.53 yr) is presumed to have the same chemistry as radium. When using ^{133}Ba as tracer the sample has to be counted by both alpha spectrometry and an alternative technique for ^{133}Ba. In most publications ^{133}Ba is measured by gamma spectrometry (HPGe or NaI) using the 356 keV peak (Benedik, 2016; Decaillon *et al.*, 2004), but it can also be counted by GFPC. The added ^{133}Ba is compared to a ^{133}Ba standard containing an equivalent amount of tracer as the samples. Regardless of the similar chemistry, use of a non-isotopic tracer may be prone to error (Lozano *et al.*, 1997; Sill, 1987b). Since an external tracer is used, accurate alpha efficiency values are required. Very high activities of ^{226}Ra in the samples can produce enough activity in daughters (^{214}Bi and ^{214}Pb) with spectral lines that will interfere with the ^{133}Ba energy regions, leading to an overestimation of the yield. If this is suspected, then counting the sample source immediately after the deposition is required to assess the ^{133}Ba activity before ingrowth of ^{226}Ra daughters.

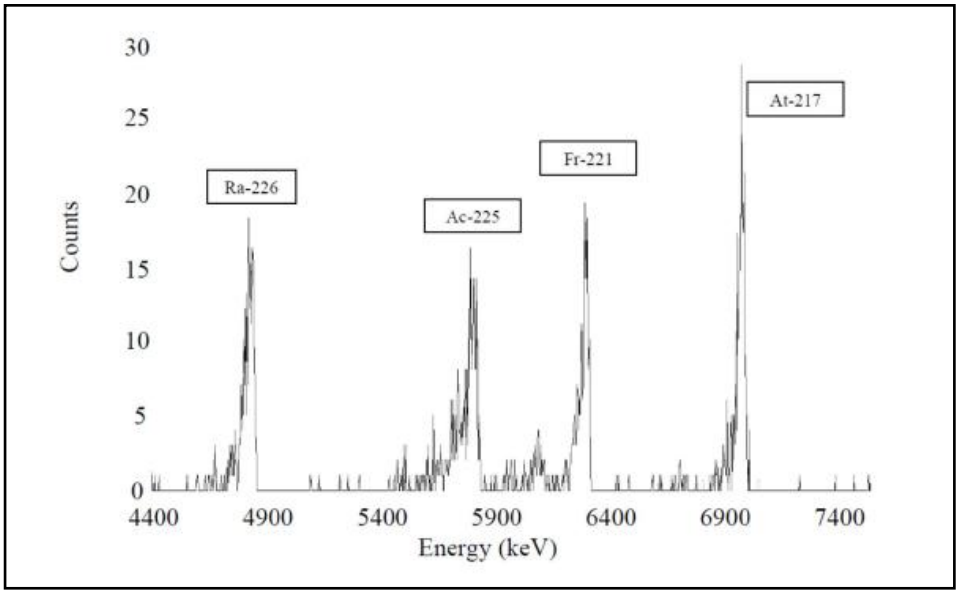


Figure 2-27: Spectrum of ^{226}Ra with ^{225}Ra as tracer

Chapter 3 RESEARCH METHODOLOGY AND LIMITATIONS

3.1 Introduction

Knowledge of the radiological properties and the occurrence of NORM in environmental media and industries of regulatory concern are essential to understand any environmental impact. A literature background to the most relevant information concerning NORM has been presented in Chapter 2. An overview of available radiometric techniques for measurement of the radioactivity concentrations of the various natural nuclides of interest was also given.

The radio-analytical data generated at our laboratory are used for routine environmental monitoring, impact assessments, modelling and dose evaluation. The data is used by radiation protection specialists and other decision makers in various industries to evaluate the potential impact of the radioactivity on workers, the public and the environment. Some of the applications are discussed in Chapter 5. Case studies are presented, using results of a large number of samples of different origin and matrices analysed at our laboratory.

The main focus of this thesis is the development and implementation of the radio-analytical techniques, which are used to produce reliable radio-analytical data, as signified by the title: "*Radio-analytical chemistry in support of the NORM industries in South Africa*". The author of this thesis has been responsible for the implementation of several of these methods, specifically all radiochemical development currently used for routine analysis in the laboratory. Chapter 4 addresses the development and implementation of these methods and can be considered as the core of this thesis.

3.2 Research Method

The process used for this thesis is categorized under the following main activities:

- Initiation: Complementary to the aims mentioned in 1.3, the research strives to provide a clear picture of how NORM industries in South Africa contribute to radioactivity in the environment and how this can be accurately measured and assessed.
- A framework is created to use for conducting the research. Therefore, parameters for

reviewing the radiological impact of the NORM industries in South Africa were identified, prioritized and systematically analyzed using international regulations and benchmarking for NORM industries worldwide.

— The final document is compiled from the collection of data and information originating from the framework.

3.3 Research Limitations

Achievement of the set objective and aims of this research is limited mostly by restrained access to specific data and information from the NORM industries. This is because these industries in South Africa are very sensitive.

The research is confined to:

— Application of radiometric techniques for routine measurement of natural radioactivity in various types of samples.

— General use of accumulated radioactivity data of samples analysed over a few years. No single specific study area is investigated.

— First order radiological impact assessments for some industries to illustrate the application of the data and to gain an appreciation of the extent of NORM occurrence in South Africa.

— Illustration of the use of dose assessment models to assess the radiological risk in non-human biota.

The above proposed methodology is suitable for this study because it will enable evaluation of the suitability of implemented radiometric methods for environmental assessments. Use of specific case studies will illustrate the significance of accurate radio analytical measurements in support of the NORM industries.

Chapter 4 EXPERIMENTAL DEVELOPMENT AND IMPLEMENTATION OF RADIOMETRIC TECHNIQUES

Theoretical background of the radiometric techniques was given in 2.13. Chapter 4 presents the practical aspects of the work done for this thesis. It focuses on the development and the implementation of analytical techniques for the measurement of radioactivity. The chapter is concluded with a summary of the final techniques used in the case studies of which the results are presented in Chapter 5.

4.1 Introduction

The methods currently used at our laboratory are fit-for-purpose and have been implemented over a period of 20 years. Methods are periodically updated taking into consideration the latest and most applicable technology available. One of the basic principles of ISO-17025 is that only validated methods can be used. Even where methods are available in literature they must be validated in the laboratory using them. Since RA is a SANAS (South African National Accreditation System) accredited laboratory the majority of the analytical methods used in the laboratory are validated and documented.

This chapter presents the analytical techniques and radiochemical methods used during the course of this study. Only some aspects of the experimental work done during evaluation, development and validation are discussed. Where the author has not as such been responsible for the method development of a specific technique, *e.g.* gamma spectrometry, neutron activation analysis and gross alpha/beta counting, less detail is provided.

4.2 Analysis of environmental samples

The NNR regulatory guide (NNR, 2013) requires analysis of the following nuclides:

- Alpha emitting radionuclides: ^{232}Th, ^{228}Th, ^{224}Ra , ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Po; and
- Beta emitting radionuclides: ^{228}Ra and ^{210}Pb.

The methods routinely used at our laboratory for analysis of these nuclides in environmental samples and typical LODs obtained with the radiometric techniques are summarized in Table 4-21. Both destructive and non-destructive techniques are included. Destructive

(radiochemical) techniques require sample preparation (filtration, drying, ashing, milling, grinding), sample dissolution, pre-concentration by either evaporation or co-precipitation with iron hydroxide or calcium oxalate/ phosphate, purification (chemical separation: precipitation or extraction chromatography), source preparation (LaF_3 precipitation or deposition) and measurement of the activity using nuclear instrumentation. Non-destructive techniques require less sample preparation than the destructive techniques. Depending on the type of sample, it is dried, ashed, grinded or milled.

4.3 Sample preparation

The aim of sample preparation is to convert field samples (whose size and form are determined by the object sampled) into laboratory samples (whose properties are suitable for the analytical method to be applied).

4.3.1 Aqueous samples

The purpose of radionuclide analysis of water is usually to determine the potential exposure that people will receive should they regularly consume the water from the area being investigated. Only the residual liquid phase (particles less than 0.45 µm) is analysed.

Water samples are filtered and acidified only after arrival at the laboratory and not in the field as prescribed in literature (MARLAP, 2004). Before filtration the TDS (total dissolved solids) of the water sample is determined using a conductivity meter with a conversion scale for micro ohms per cm to mg. This information is helpful when deciding on appropriate volumes to use for radiochemical analysis (4.4.1). The amount of salts dissolved in water is measured by the TDS or dry residue value. A low TDS value of less than 1 $mg.L^{-1}$ is typical for rainwater, whereas a range of 195 - 1 100 $mg.L^{-1}$ can be expected in water in contact with sedimentary rock formations. For drinking water the acceptable limit specified in SANS 241:2015 is 1200 $mg.L^{-1}$.

Samples received for water are filtered through both a 0.8 µm and a 0.45 µm membrane filter. The latter is kept should it be required that the radioactivity of the suspended matter be analysed. This will be the case if the objective of the analysis is to determine the concentration of any insoluble nuclides, such as Th in the suspended matter (MARLAP, 2004). The residual liquid is put back into the original container and acidified with nitric acid

(2 ml nitric acid per litre).

Acidification of aqueous samples to pH<2 with nitric acid immediately after collection are commonly recommended to prevent absorption of trace elements onto the container (L'Annunziata, 2003). However, acidification is done only after filtration since adding acid to the unfiltered sample may leach radionuclides from non-dissolved matter increasing the radioactivity concentration of the water fraction. It was found that the suspended matter does not contain significant levels of radioactivity and that the bulk of the radioactivity resides in the water fraction (5.1.4).

Analysis of samples is often only completed about 4-6 months after filtering and preservation. In a study conducted to determine whether the sample integrity is maintained when samples are kept for a prolonged period before analysis, it was found that the sample remained stable for at least eight months even if not refrigerated (4.11.1).

Water samples for radiochemical analysis are most often pre-concentrated by evaporation. A sample volume is used, optimally containing an analyte activity of about 0.05-0.5 Bq. The sample is gently evaporated to near dryness. Samples with TDS value of up to 1 $g.L^{-1}$are evaporated without any problems. Calcium phosphate co-precipitation has also been evaluated when validating the methods for U and Th and can be used when using larger volumes of sample.

4.3.2 Biological samples

Sample preparation is determined by the objectives of the study. Food samples analysed for evaluation of the ingestion pathway are reduced to edible portions (*i.e*. head, fins, bones, intestines and other non-edible parts are removed). The outer leaves, cores and seeds of vegetables are also removed). Vegetables are washed to remove all surface contamination. If the purpose of the work is to monitor contamination of the environment or impact on non-human biota the whole organism (fish, animal, plant) is analysed. Dust on the leaves of plants should be included and the material is therefore analysed as received.

Fresh plant and animal material is usually cut into smaller pieces, and then dried to preserve it and concentrate all the constituents to be analysed. The material is pulverised (for homogeneity). The material is dry-ashed to pre-concentrate for lower detection limits depending on which analyte has to be determined. The sample is first dried at 100-150 ^{o}C and

then ashed in a muffle furnace at typically 500-550 ^{o}C. When analyzing for ^{210}Po, dry-ashing cannot be used, as the element is volatile and is lost at temperatures of 300 ^{o}C (Bock, 1979). Analysis of ^{210}Po is done on the dried fraction, or for milk samples directly on the fresh milk (4.8.1).



Figure 4-1: Typical biological samples received for analysis

The concentrations are usually reported as activity in Bq per kg wet weight. The weight loss when being dried or ashed is measured and the moisture content calculated to convert activity concentrations either to a dry mass or fresh mass basis (ash:dry:wet ratio).

Concentrated HNO_3 is used for wet ashing of biological samples. To completely destruct any organic material, drops of H_2O_2 are added. Disadvantages of hot plate digestion are the possibility of charring and formation of insoluble salts during evaporation. The process has to be closely monitored, and have a risk of cross-contamination and exposure to acid fumes. Any remaining fat debris may interfere with the chemical separation. For complete dissolution of biological samples, several days may be required, especially if it contains fat (Clayton & Bradley, 1995; Ham *et al.*, 1997). Microwave digestion may be used to speed up the digestion process, but has had limited application in the radiochemical laboratory because of the constraint on sample size, usually limited to 0.5 g dry weight, due to pressure limitations for the vessel (Kingston & Hasswell, 1997). Conditions can be controlled when using open vessel microwave digestion, thereby preventing many of the mentioned problems (Faanhof & Louw, 2001).

4.3.3 Soil and geological samples

Solid samples received for analysis of natural nuclides are all treated in a very similar manner. These types of samples include soils, sediment, samples from building industry, coal industry and various others. Samples are dried overnight at 105 ^{0}C and then milled and homogenised. The moisture percentages of the samples are determined form the fresh and dry weight. Soils are well mixed after removing materials such as roots and pieces of stones and gravel. Samples in the form of large blocks such as rock, concrete, brick and stone are first converted into a fine powder with particles less than 50 to 100 μm in diameter to ensure a homogeneous material for analysis.



Figure 4-2: Solid samples received for analysis (tailings, crushed brick)

4.4 Gross alpha/beta determination

Gross αβ-counting is a relatively fast, inexpensive and sensitive technique used to screen large numbers of samples in order to identify anomalies that require nuclide-specific analyses. Its application is limited mainly by the fact that the technique cannot identify the different nuclides present in the sample (2.14.3). This technique is employed at our laboratory for screening of water, solid and filter samples.

RA uses a Canberra Oxford series 5 gas-flow proportional counter. This instrument has the capacity to carry 50-100 planchettes with its sample changer. The counting gas consists of a mixture of argon (90 %) and methane (10 %). Eclips LB software is used for data acquisition and calibrations for efficiency, plateau, background and spillover. Optimization of the instrument includes pulse height discrimination settings to ensure limited spill-over between

α and β channels. Typical spill-over was less than 20% for alphas and less than 0.5% for betas. Measured background was about 0.2 cpm for alphas and 1.2 cpm for betas. Data reduction includes background-, efficiency-, as well as cross-talk correction. Details of the calculations are not shown here.

The efficiency of the detector was determined with calibration sources of ^{241}Am (at 5.48 MeV) and ^{90}Sr/Y (at 0.546 MeV). ^{241}Am is used because the energy of the particle is in the range covered by decay products of U and Th, and the long half-life of 432.2 years. ^{90}Sr, in equilibrium with ^{90}Y, is preferred for β calibration because of its "average" energy and long half-life (28.74 years). The counting efficiency for thin calibration sources on the 47 mm filter was about 25% for alpha and 45% for beta.

It is assumed that the calibration values can be applied without correction to other nuclides emitting α- and β- particles with different energies. The radionuclide composition of field samples is usually not known, and the analyst has no means to evaluate how appropriate the selection was. The contribution to uncertainty can be more than 50 % for soft β-emitters (betas with low energy). This confirms that gross alpha/beta measurements are not as accurate and precise as radiochemical separations, but are only intended to be used for rapid screening to indicate an event that may warrant investigation.

4.4.1 Determination of gross alpha/beta activity in water samples

The method used at our laboratory for gross alpha/beta analysis of water samples is similar to that of EPA Method 900.0 (EPA, 1980). In this method radon and its short-lived decay products are eliminated from the samples. As discussed in 2.13.3 gross beta measurements include the ^{40}K contribution.

Samples are filtered and acidified as in 4.3.1. A known volume of the filtered water is evaporated directly into a shallow tray or dish (typically about 50 mm in diameter with a 3 mm rim), which also serves as the counting container. The mass of the material residue left in the planchette after evaporation is recorded and used for self-absorption corrections. The measured TDS value (4.3.1) is used to assess the maximum value of water to be used for the analysis, keeping in mind the problems with self-attenuation if the mass of residue on the planchet is too thick (2.13.3). It was found that samples subject to gross αβ-counting should normally not exceed a total mass of 300 mg to avoid too much loss in sensitivity due to self-

absorption.

A specific sensitivity for a gross α/β analysis is required to meet the requirements for dose evaluation. As most likely larger sample volumes will be used, which have to be evaporated, the residual solid mass may prove to be a restricting factor. A suitable LOD is usually considered to be at least one-fifth of the required screening level. To reach the required detection limits the following protocols are used:

Protocol followed for water from NORM industries

A sample aliquot of 25 ml is evaporated. The samples are counted for 20 minutes to reach a LOD of 1.4 and 2.2 $Bq.L^{-1}$ for GA and GB respectively. To reduce the counting time and increase sample throughput larger volumes are used if possible. The LOD increased to about 5.5 $Bq.L^{-1}$ GA and 2.3 $Bq.L^{-1}$ GB at a residual mass of 300 mg.

Protocol followed for drinking water analysis

For water samples received from the bottled water industry, for which a low LOD is required, an aliquot of at least 300 ml of water is evaporated. The LOD for GA and GB was 0.1 $Bq.L^{-1}$ for a 300 ml volume and 5 hour counting time. The results are evaluated to comply with WHO criteria. The U concentration of samples with GA > 0.5 $Bq.L^{-1}$ is determined by KPA to confirm that the high GA activity is due to the presence of U. If GB > 1 $Bq.L^{-1}$ the sample is analysed for K and the contribution of ^{40}K subtracted from the GB activity.

Protocol followed for monitoring of radioactivity in water from DWS

As surface and ground water in South Africa show a wide range of TDS-values between 1 and 10 000 $mg.L^{-1}$ (DWS, 1996b) one should for routine applications either use a fixed maximum volume for known sampling sites, or adjust the volume and accordingly the counting time of a sample, based on the TDS. The analytical protocol for samples for the DWS NRMP is as follows:

Depending on the TDS an appropriate volume is taken for evaporation - a volume of 300 ml is used if the TDS is below 1000 $mg.L^{-1}$ and 50 ml if the TDS is higher. The filtered water is first evaporated to a small volume, which is then transferred to a planchette for evaporation to dryness. The residue is oxidised in an oven at 600 ^{o}C before counting for five hours. The GA

and/or GB of the measurement are evaluated for the possibility of further investigation. If it does not meet the criteria for a first-order screening as given in Table 4-1 the filter residue is stored for future measurements.

Table 4-1: Water quality classification/assessment based on screening results (DWS, 2006b)

Screening Result	α/β ratio	α activity (Bq.L^{-1})	β activity (Bq.L^{-1})	Class
α < 1.5 Bq.L^{-1} **And** β < 2.5 Bq.L^{-1}	Any ratio	< 1.5	< 2.5	Green
α > 1.5 Bq.L^{-1}	> 5	> 1.5	< 10	Orange
And/or	1 – 5	< 10	< 10	Green
β > 2.5 Bq.L^{-1}	< 1	> 10	< 10	Orange
		N/A	< 10	Orange

The screening criteria in Table 4-1 have been set to ensure that if they are not exceeded, the water will definitely fall within the green or blue class, which means that the dose over a lifetime average use of the water will be < 1 mSv.a^{-1} irrespective of the radionuclides that cause that activity (see 2.2.7). If the water falls within an orange class, its quality must be confirmed by measurement of the individual isotopes, in order to calculate the dose, which in turn will facilitate assessment according to the criteria as set out in Figure 2-4.

The use of gross measurements for estimating the dose will result in unacceptably large uncertainties in the final dose determination, due to the large uncertainties, typically about 20% to 30%, inherent in the determination of gross activity. For accurate dose calculations individual measurement of the important contributing radionuclides, especially those with high dose conversion factors, is recommended. If it can be experimentally established by analysing a significant number of samples over an extended period, as has been done for DWS samples (5.1.4), that a strong correlation exists between gross alpha measurement and a specific nuclide, for example ^{238}U, or gross activity and dose, it may be possible to use gross alpha activity for an estimation of dose.

4.4.2 Gross alpha/beta determination of solids

Powders are obtained from rocks, bricks and other building material that are first broken into smaller pieces before grinding. When organic material (plants, animal tissue, milk *etc.*) are ashed, the product is usually in the form of a coarse powder. This material is ground to a

very fine powder (typically 10 μm) to ensure that it is homogeneous. Particle size can have a significant effect on the self-absorption of α-particles in the powder.

Approximately 1-3 g of sample is weighed out and transferred to a tarred 47 mm planchette, for a thickness of about 0.2 $mg.cm^{-2}$. The sample is spread uniformly and compressed using a hydraulic press. Samples are routinely measured for three hours. The estimated detection limit of the method was about 1 and 0.1 $Bq.g^{-1}$ for alpha and beta activities, respectively.

As mentioned in 2.13.3 for prepared samples with thickness of > 0.2 $mg.cm^{-2}$, the energy loss of a particle becomes significant and corrections for attenuation are required. Calibration samples prepared in $CaSO_4$ equivalent matrices are used to determine the self-absorption in relation to sample thickness and density. This is used as a correction factor for solid samples.

4.5 Gamma spectrometry

4.5.1 Gamma spectrometry at RadioAnalysis

Gamma spectrometry has been used at our laboratory for more than twenty years for measurement of natural radionuclides in various matrices. A high purity germanium detector (HPGe) was used for the analysis of the majority of the solid samples in this study. The detector (Canberra model PGC2519) has a relative efficiency of 25% with energy resolution 1.92 keV at the 1332 keV line of ^{60}Co. Pb is used to shield the detector and to reduce unwanted radioactivity from background sources. The considered energy range is 200-1500 keV. A Canberra DSA 1000 signal processing unit is used for collecting the pulse height data. An energy and efficiency calibration is performed using a ^{152}Eu source with an activity of about 50 kBq. ^{152}Eu has multiple energy peaks (*i.e.* 121.77, 344.29, 778.90, 963.39, 1112.07 and 1408.01 keV) covering a large energy region and is therefore suitable to be used as calibration source. The efficiency calibration is carried out using full energy peaks from ^{152}Eu sources prepared in $CaSO_4$ (representing high density samples) within containers of geometries identical to those of the samples. Corrections for self attenuation are done.

The spectrum analysis is performed using gamma software (Canberra Genie 2000). Identification of individual nuclides is done based on their gamma ray energies. RA relies in this regard on data contained in the Genie master libraries, which are obtained from the NUDAT database (NUDAT, 2017). Corrections are made for decay, self-absorption and

sum-coincidence. Details of the calculations are not shown in the thesis. The counting uncertainty of the activity concentration is automatically calculated by the Genie software. Using the root-sum-of-squares rule the total uncertainty is calculated by combination of the counting uncertainty and the efficiency uncertainty. The "Quality Assurance Editor" program analyses and keep record of Quality Control (QC) data. The laboratory measures the ^{152}Eu source on a weekly basis to monitor performances of detectors. The peak position (peak centroid), peak shape (FWHM) and peak area (or efficiency) for the lines 121 keV, 964 keV and 1408 keV are recorded for QC evaluation.

A broad energy gamma ray spectrometric system was used for measurement of vegetation- and food samples. The system consists of an n-type coaxial high purity germanium (HPGe) detector (Canberra BE 6530) with a 1.69 keV resolution at 1332 keV and relative efficiency of 50%. A lead castle containing less than 10 Bq.kg^{-1} of ^{210}Pb is used to reduce background radiation. Laboratory Sourceless Calibration Software (LabSOCS) is used for efficiency calibration. A point source of ^{152}Eu with activity of 3 kBq and known full-peak energies is used for energy calibration over the range of 46-2000 keV.

4.5.2 Analysis of naturally occurring radionuclides in solids

Samples of building material and other solids are crushed, pulverized to a fine powder and homogenized. A weighed quantity is used for gamma spectrometry, typically 200-250 g for the "honey bottle" geometry (330 ml) and 10-15 g for the "60 mm polytop" geometry. The samples are sealed and stored for 3-4 weeks to confine radon gas, which is the first progeny of radium. This is important to ensure radioactive equilibrium between ^{226}Ra and its short lived daughters, whose high intensity gamma emissions are utilized for analysis (see Figure 4-3). Different methods for sealing the samples have been investigated of which the best seem to be sealing in glass with epoxy glue (see Figure 4-4). Too low values for ^{214}Pb and ^{214}Bi may be obtained due to loss of ^{222}Rn, resulting in underestimation of ^{226}Ra, if containers are not gas tight. This was typically observed for some proficiency exercises, where samples were not sealed (4.11.2).

As commonly used according to the literature study (2.13.4) ^{226}Ra was quantified using the emissions of ^{214}Bi and ^{214}Pb. Using a low-energy gamma detector the full-energy peak at 46.54 keV was used to determine ^{210}Pb. For solids, equilibrium with ^{210}Po was assumed. In the Thorium-232 series ^{228}Ra was determined via ^{228}Ac and ^{228}Th via ^{208}Tl. The gamma-ray

peak corresponding to 1461 keV was used to determine the activity of ^{40}K. A typical gamma-ray spectrum of a solid sample is shown in Figure 4-5. Samples are routinely counted for 24 hours, to obtain an overall uncertainty of less than 10%. The detection limit of the detector system used is typically about 2 $Bq.kg^{-1}$ (see Table A-4, Appendix A).

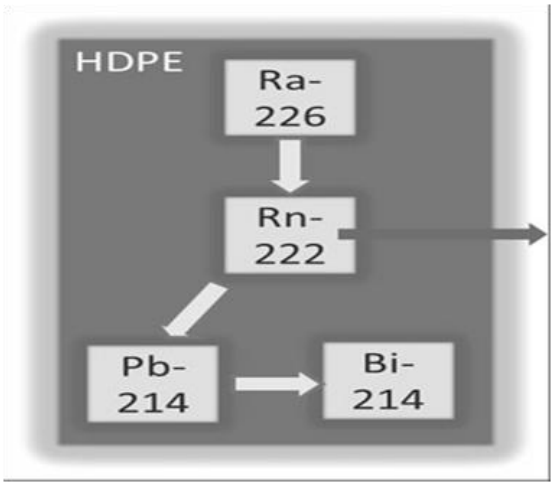


Figure 4-3: Measurement of ^{226}Ra via radon progeny (dark arrow represents leakage)



Figure 4-4: Sealed environmental samples prepared for gamma counting

For most of the solid samples analysed poor correlation was found between measured gross alpha/beta and the expected total alpha and beta activities calculated from the gamma spectrometry results (see 5.4.2). As explained this is due to limitations to the efficiency calibration of the gross alpha/beta technique. Validation of accuracy of measurement of

NORM in solid samples is proved by regular participation in proficiency exercises. Typical results are shown in Table 4-18.

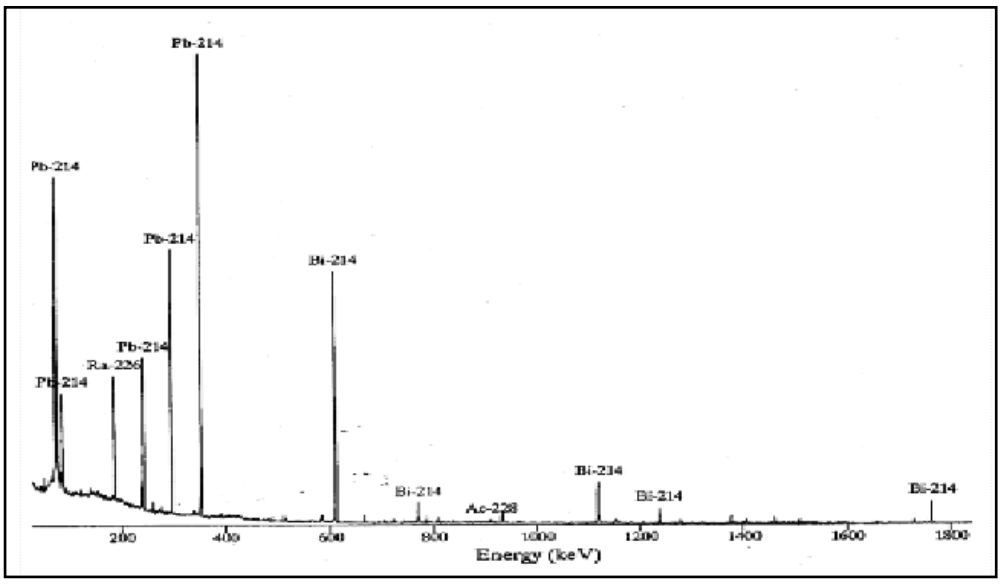


Figure 4-5: A typical gamma spectrum of natural radioactivity

4.5.3 Analysis of naturally occurring radionuclides in food

The same basic principles as described above for solid samples, apply for counting of food samples. In the first few years after gamma spectrometry has been established at our laboratory the natural nuclides in food samples were determined by high- and low energy gamma spectrometry. In recent years food samples have been counted using the broad energy detector, with much better sensitivity. Due to the broader energy range determination of ^{210}Pb with low energy peak at 46.5 keV is also possible.

A hydraulic press is used to compress the dry/ashed samples in a prescribed geometry for the broad energy gamma spectrometer (a "lid-dish" container of 70 mm diameter x 0.5 mm height). Samples are properly sealed for radon density (see Figure 4-4). Food samples are counted on the broad energy detector for about 12 hours per sample, depending on the required sensitivity based on the mass of the samples after compression. The detection limits are about 0.1-1 Bq.kg^{-1} for ^{226}Ra and ^{210}Pb respectively compared to that of 2 and 10 Bq.kg^{-1} for the high- and low energy detectors respectively. The improvement in results obtained with this detector and the effect on dose calculation for food are discussed in 5.2.3.

4.6 Neutron Activation Analysis and Delayed Neutron Counting

In most laboratories naturally occurring radionuclides, including ^{238}U and ^{232}Th in raw materials and by-products of the NORM industries are routinely measured by gamma spectrometry assuming equilibrium. However, if disequilibrium exists, with a large difference between for example ^{238}U and ^{226}Ra in the U series and ^{232}Th and ^{228}Ra in the Th series, gamma spectrometric results will not be accurate. Therefore the preferred technique for measurement of ^{232}Th, as well as ^{238}U, at our laboratory is Neutron Activation Analysis (NAA).

Two techniques are used at RA –DNC and NAA. NAA exploits the following (n,ϒ) reactions: (L'Annunziata, 2003):

^{238}U (n,ϒ) → ^{239}U (23.5 min) → ^{239}Np (2.35d)

^{232}Th (n,ϒ) → ^{233}Th (22.3 min) → ^{233}Pa (27d)

Sub-samples of 200 mg are used for determination of the U concentration. The samples are irradiated in specially designed capsules in the RINGAS (Routine Instrumental Neutron and Gamma Analysis System) facility in the SAFARI-1 (South African Fundamental Atomic Reactor Installation No 1) research reactor. Nuclear fission of ^{235}U is caused by the irradiation process. To determine the concentration the emitted delayed neutrons are counted after removal of the sealed capsule from the reactor (DNC). The observed counts are converted to the equivalent amount of ^{235}U by subtracting the background, and dividing the result with the sensitivity value for the calibration standards (*i.e.* counts for 1 µg of U). For NAA the same samples are allowed to cool for 7 days before counting with a HPGe detector for one hour. For ^{238}U the 228.12 keV gamma of ^{239}Np is measured (using the 277.6 keV line for confirmation); for ^{232}Th the 311.9 keV line of ^{233}Pa is used.

DNC is based on the fission of ^{235}U, and it is therefore sensitive to the isotopic composition of the uranium in the sample. Calibration is performed with certified natural uranium, and it is assumed that the samples all have natural isotopic abundance. Assuming natural isotopic abundance the DNC results can be converted to ^{234}U, ^{235}U and ^{238}U activity concentrations. The results will be in error if the ^{234}U in the sample is enriched. DNC results are usually

confirmed by NAA (which measures ^{238}U), which is the preferred technique if isotopic enrichment in the sample is suspected.

Uranium and thorium determined by INAA/DNC produce mass concentrations. Results are then converted to activity concentrations for reporting purposes and dose rate calculations using the specific activity values in Table A-1 (Appendix A), as discussed in 2.13.2. A common error made in some reports is to use the measured elemental concentration to convert to activity concentration of ^{238}U only, thereby under-estimating the activity in the sample.

4.7 Alpha spectrometry

Our laboratory uses alpha spectrometry (2.13.6) for full nuclide analysis of water samples and digested solid samples. An alpha spectrometer (Alpha Analyst, Canberra, USA) is used for measurement of prepared sources of the U, Th and Ra isotopes (^{238}U, ^{235}U, ^{234}U, ^{230}Th, ^{228}Th, ^{227}Th,^{226}Ra, ^{224}Ra, ^{223}Ra), as well as ^{210}Po. The spectrometers each have 12 chambers housing PIPS semiconductor detectors. The planchet containing the filter with deposited sample is put on a detector platform and kept in position at a specific distance from the detector by a specially manufactured geometry rig (see Figure 4-6). Genie 2000 spectroscopy system software is used for data acquisition. Samples are counted for 24 hours in the recoil suppression mode. Radiochemical recovery is determined by addition of a suitable yield tracer.

The detectors are calibrated using a ^{241}Am source purchased from Amersham with alpha activity of (839±84) Bq deposited onto a stainless steel disc. The mean counting efficiency was 20.9 ± 2.1 % for a 20 mm source, and 8.6 ± 1.2 % for a 36 mm source placed 6 mm from the detector, with a resolution of 20 keV for the 5.486 MeV alpha particles of ^{241}Am.

Quality Control on the detectors is done weekly and the data plotted on control charts. A performance test is done to check the efficiency of the detector, using the ^{241}Am source and also checks for low-energy tailing. A pulsar test is used to check the resolution of the peaks. The width of the pulsar peak (FWHM) at 5 MeV is monitored to detect any degrading in the detector. The energy of the peak is monitored to detect any energy shifts in the detector electronics. The background count rate for the region of interest from 3 MeV to 9.4 MeV is used to check for contamination of the detector. The accepted upper boundary is

set as 24 counts per 24 hours. The background was about 5.9 ± 4.5 counts in the total energy region. A second higher energy region (> 7 MeV) is used to monitor for contamination from radon daughters, *i.e.* ^{212}Po and ^{214}Po. For a clean detector, there are usually no counts in this area. It is advisable to use spectrometer systems with recoil suppression for counting to prevent recoil contamination of the α-detectors. Despite counting in recoil suppression mode, contamination of detectors was a serious problem, as seen from the occasional increase in detector background (see 4.11.1).

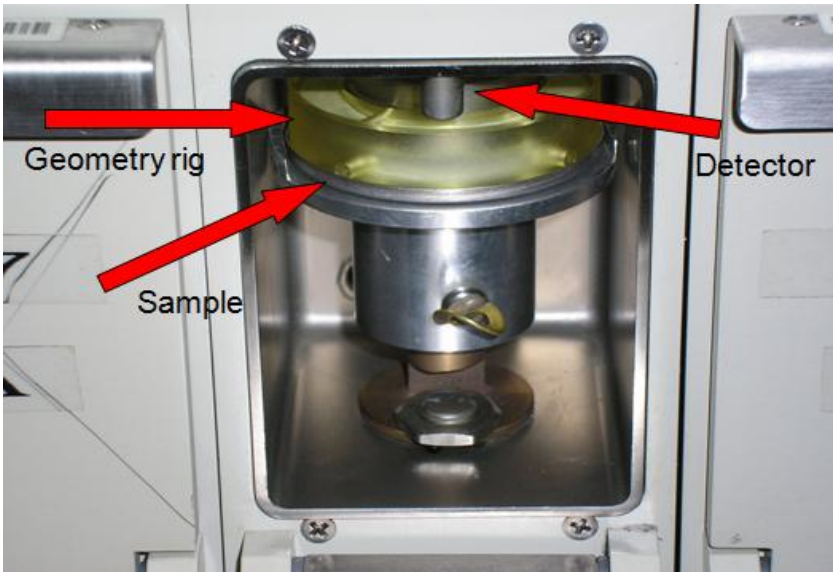


Figure 4-6: Inside of the alpha spectrometer detector chamber

LaF_3 precipitation and filtration is used to mount uranium and thorium for analysis by alpha spectrometry. This method has proved to be successful, quick, inexpensive and reproducible and is used by many other radio analytical laboratories (2.13.6). Although LaF_3 precipitation worked well for most samples, problems were sometimes experienced with the resolution, especially for Th. Resolution of many spectrums were so poor that the peaks could not be resolved. For better resolution electro-plating might be a better option, but unfortunately the equipment is not available at our laboratory. The very specific electrochemical properties of ^{210}Po allow spontaneous deposition onto a silver disk (4.8.1). ^{226}Ra sources are prepared by $BaSO_4$ precipitation (4.8.5).

4.8 Radiochemical separations

For accurate estimation of annual dose one should be able to analyse nuclides like ^{210}Po,

^{210}Pb, ^{227}Ac, ^{231}Pa, ^{228}Ra and ^{232}Th at a LOD of about 0.01 Bq.L^{-1} in drinking water (Table 4-23). For those samples where the sensitivity of instrumental techniques is not sufficient to meet requirements, it is necessary to chemically separate the analyte to improve the sensitivity and/or selectivity of the method.

In principle radiochemical procedures can be used for any sample, which can be brought into solution, however, some analytical challenges must be overcome for environmental samples, as discussed in 2.13.8. Radiochemical techniques require mineralization (sample preparation/pre-concentration), chemical separation, source preparation followed by α-spectrometry. The radiochemical methods described in this section were evaluated, validated and implemented by the author of this thesis. Details of implementation and validation of some of the methods are shown in the validation reports in Appendix D, which forms an integral part of the work submitted for this thesis. Validations were done according to recommendations as in the SANAS technical guide TG 07-01 (SANAS, 2012).

The aim of this work was to implement routine procedures with an acceptable accuracy and precision and a sufficient capacity at a reasonable turnaround time. Generally the following requirements were set:

- Accuracy better than 10% (expressed as bias or percentage error)
- Precision better than 20% (expressed as relative standard deviation (RSD) of replicate measurements; *i.e.* repeatability/reproducibility uncertainty)
- The method uncertainty should be evaluated
- Recovery (chemical yield) should be better than 20%

A RSD of 5-15% and bias of 10-20% is typical in radiochemical methods (Betti & Aldaveded las Heras, 2004).

4.8.1 Method for determination of ^{210}Pb and ^{210}Po

Since ^{210}Po is one of the most radiotoxic isotopes to humans it is often required to quantify the amount of ^{210}Po that humans are exposed to. Analysis of ^{210}Po at our laboratory is performed not only in water, but also in various foods such as fish and milk.

Polonium in water

The procedure for the radiochemical separation of polonium used at RA is based on the

procedure developed by Flynn (1968). Polonium is pre-concentrated from solution acidified with hydrochloric acid by spontaneous electro-deposition onto a polished silver disc. The solution is warmed to a temperature of just below boiling point (90^0C) on a hot plate-stirrer, and stirred to induce deposition of ^{210}Po on one side the disc. The other side of the disc is covered to prevent plating. The silver disc is removed from the solution, washed and air-dried. The yield of the deposition is determined by addition of ^{209}Po as tracer. The sample is counted by alpha spectrometry to determine the alpha activities of ^{209}Po and ^{210}Po. Measurement of ^{210}Po is done through its 5.30 MeV alpha particle emission. A typical spectrum is shown in Figure 4-7. ^{210}Pb is determined from the ^{210}Po activity concentration by doing a second deposition on a new aliquot of the sample after an in-growth period of four to six months.

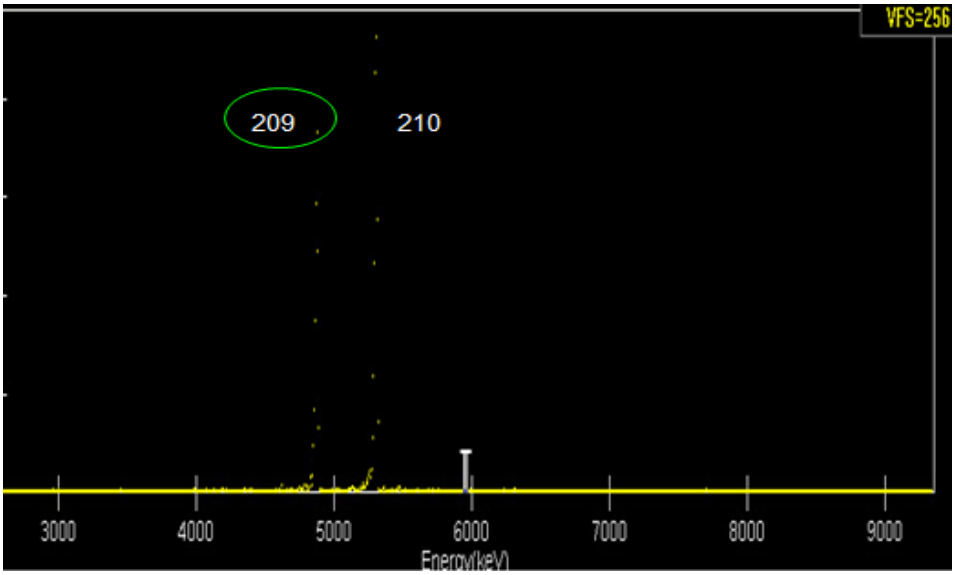


Figure 4-7: Typical energy spectrum for polonium analysis showing the peaks for ^{209}Po and ^{210}Po

A control sample, prepared from a certified solution obtained from Amersham, containing ~ 0.3 Bq of ^{210}Pb-^{210}Bi-^{210}Po in equilibrium was used for validation. During optimization experimental parameters such as temperature, pH, deposition time, disc size, stirring method and addition of reducing agents were investigated. The average recovery (as determined by the ^{209}Po tracer) was 64±14 % when deposition was done for four hours at 85-90^{o}C in 0.05 M HCl at pH 1-2. The MDA for the method for a counting period of 24 hours was about 0.005 Bq.L^{-1} for a sample size of 0.2 L, chemical yield of 0.4 and counting efficiency of 0.3. The target concentration to evaluate the exposure level at 0.025 mSv.a^{-1} for adults for a daily

intake of 1.7 L daily is about 0.035 and 0.060 $Bq.L^{-1}$ for ^{210}Po and ^{210}Pb respectively (see Table 4-23).

The accuracy of the method was acceptable with a bias of less than 15 % for ^{210}Pb and less than 20% for ^{210}Po provided that the first extraction (t_1) is done within two months after sampling (t_0). The precision depended on the concentration level, as well as ingrowth period, and was less than 20% with a time interval (t_2-t_1) of longer than 100 days. The chemical recovery during routine use of the method over the last five years was 48 ± 15 %, which was low compared to initial implementation results, and especially when compared to what is commonly found in other laboratories worldwide (2.13.10). The reason for this could not be identified and therefore the laboratory is currently in the process of re-optimizing the plating conditions.

The method is suitable for environmental water samples and any digested solid sample. It can be used for sample volumes ranging from 100 to 2000 ml by first pre-concentrating the larger samples. For quantitative plating the final volumes shouldn't exceed 200 ml.

Bateman equations for data reduction

Activity of ^{210}Po re-growing from ^{210}Pb is obtained from Bateman equations (2.13.10). Bateman equations can usually be applied with the assumption that at t=0 the parent substance alone is present (Friedlander *et al.*, 1981). In the series ^{210}Pb-^{210}Bi-^{210}Po the Bateman equations are simplified assuming that there is equilibrium between ^{210}Pb and ^{210}Bi at time of sampling, since ^{210}Bi with short half-life of five days will grow into ^{210}Pb very quickly. In most cases this assumption causes only small errors.

The calculations used are shown in Appendix B. In environmental samples ^{210}Po is often not in equilibrium with its ^{210}Pb parent. At sampling time, t_0, the following scenarios are possible:

- $^{210}Po = ^{210}Pb$ radioactive equilibrium
- $^{210}Po < ^{210}Pb$. The interpretation is then that ^{210}Po is growing into ^{210}Pb
- $^{210}Po > ^{210}Pb$. One can conclude that the excess ^{210}Po is not supported by ^{210}Pb.

Pb and Po at time t_0 can be calculated using equations as in Appendix B.3:

- $Pb_0 = (Po_1C_4 - Po_2C_2) / (C_1C_4 - C_2C_3)$ and
- $Po_0 = (Po_2C_1 - Po_1C_3) / (C_1C_4 - C_2C_3)$

Where C_1 and C_3 represent ingrowth of ^{210}Po from ^{210}Pb from time of sampling ($t_{0)}$ to first deposition (t_1) and from first deposition (t_1) to time of second deposition (t_2) respectively; and C_2 and C_4 is the decay of ^{210}Po over the same periods.

Scenario 1 ($^{210}Po=^{210}Pb$): Daughters will decay with half-life of mother. Difference in decay from t_0 to t_1 and t_0 to t_2 is negligible due to the long half-life of ^{210}Pb, therefore measured ^{210}Po activities at t_1 and t_2 will be the same, $Po_1 = Po_2$, which is the decayed value of ^{210}Pb. Best estimates of ^{210}Po and ^{210}Pb activities will be $Pb_0 = Po_0 = (Po_1 + Po_2)/2$ or alternatively the sample need only be measured once. This scenario is applicable to the ^{210}Pb control sample.

Scenario 2 ($^{210}Po < ^{210}Pb$ at time t_0): The ^{210}Po activity will change considerably from its initial value at sampling, due to the production of ^{210}Po from ^{210}Pb decay and the decay of ^{210}Po itself, according to $Po(t) = Pb\,(1 - e^{-\lambda 1 t}) + Po.e^{-\lambda 3 t}$. The $1\text{-}e^{-\lambda t}$ factor approximates the real situation with ^{210}Pb and ^{210}Bi decay sufficiently well. ^{210}Pb has a relatively long half-life and decays slowly; decay of ^{210}Po is ignorable because of the low activity of ^{210}Po at the start. For scenario 2 it will therefore be expected for the ingrowth factors of ^{210}Po from ^{210}Pb (C_1 and C_3) to be the main contributor to the final activity of ^{210}Po in the sample at any time. The activity of ^{210}Po at any time t after sampling will be a factor of the initial concentration of ^{210}Pb in the sample until equilibrium is reached (see Figure 4-8). At time of equilibrium (1380d) it can be expected that $Po_1 = Po_2 = Pb.e^{-\lambda 1 t}$.

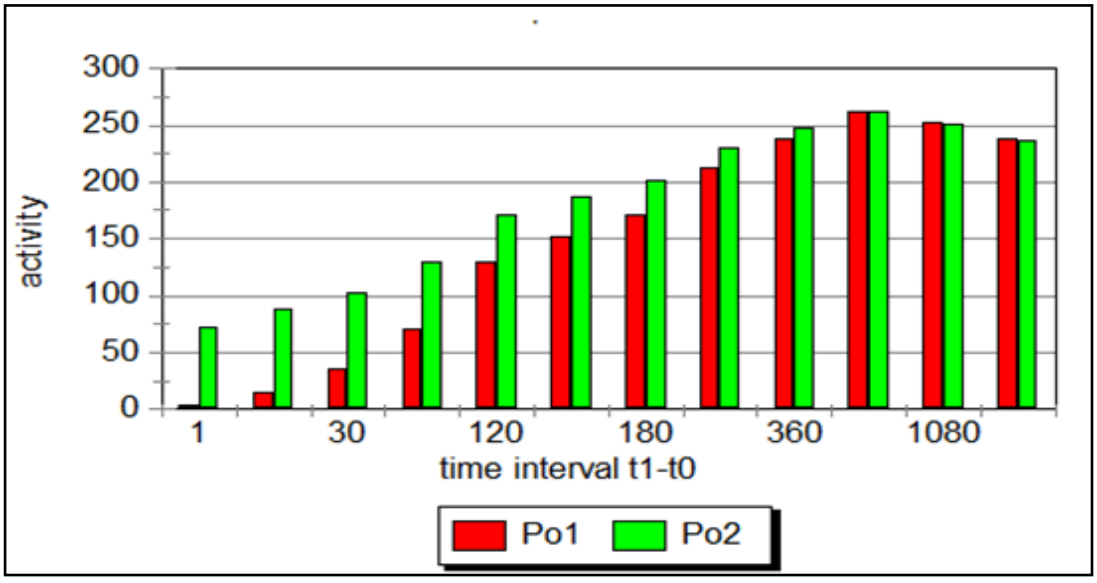


Figure 4-8: Scenario 2 - Expected activities for Po_1 and Po_2 (Initial Pb=0.3Bq)

Scenario 3 (^{210}Po>> ^{210}Pb at time t_0): Given limited information one assumes that the excess ^{210}Po is unsupported. The equation describing this situation is $Po(t) = Pb + Po.e^{-\lambda 3t}$. This means that where only ^{210}Po is present at sampling time, the ^{210}Po present at time of plating will be as a result of decay of ^{210}Po (C_2 and C_4) only (see Figure 4-9). Because of the low initial activity of ^{210}Pb, ingrowth of ^{210}Po due to ^{210}Pb will be insignificant. The ^{210}Pb activity will remain constant and low over time.

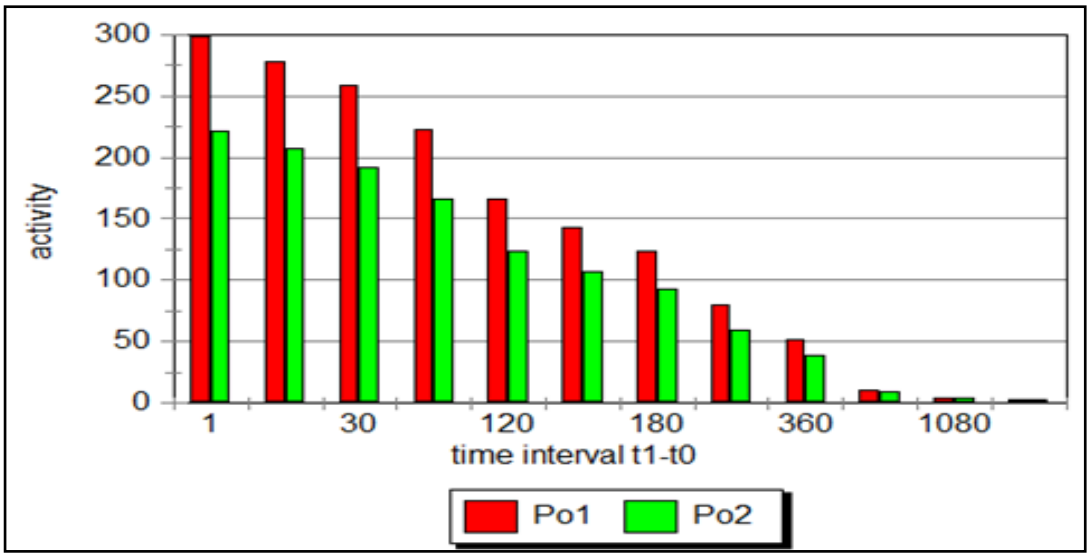


Figure 4-9: Scenario 3 - Expected activities for Po_1 and Po_2 (Initial Po = 0.3 Bq)

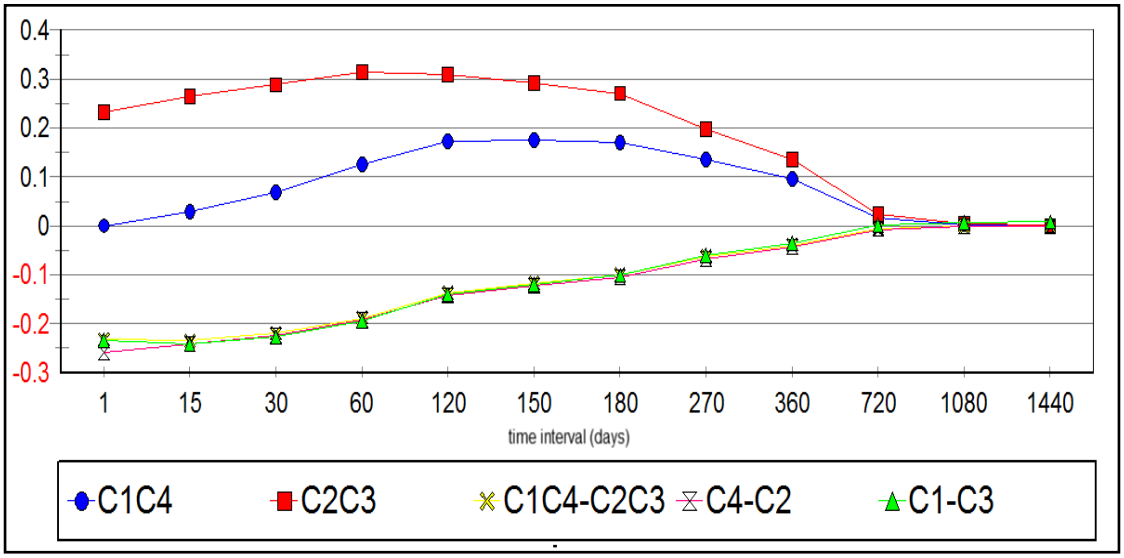


Figure 4-10: Decay and ingrowth of Po as function of t_1-t_0 (t_2-t_1=60 d, Pb=Po= 0.3 Bq)

Looking at the simplified equation where C_1 and C_3 are ignored, $Pb = (Po_1C_4 - Po_2C_2) / (C_4 - C_2)$, it is clear that a small difference between $e^{-\lambda.t1}$ (C_2) and $e^{-\lambda.t2}$ (C_4) will result in division by zero. As can be seen from Figures 4-10 it will only be zero with t_1-t_0 exceptionally long (1440 days), and t_2 relatively short thereafter (less than 60 days), in which case Scenario 1 applies.

Error estimations

The purpose of the error estimations was primarily to aid in whether or not the activities of ^{210}Pb and ^{210}Po were statistically meaningful. Since both the first and second depositions have a variety of sources of variance associated with it, the errors tend to be large. Large errors in either of the two measurements will result in a large error in the final activity calculations.

The uncertainty in ^{210}Pb determination at low activity levels (0.01 and 0.001 Bq) was predicted to be large (> 50%) using Bateman equations. It was therefore decided to do only a single deposition for samples with low activity concentrations. Alternatively the time interval for in-growth (t_1-t_2) should be longer than 100 days for the uncertainty for ^{210}Pb determination to be less than 20%. For samples where t_1-t_0 >> 1 year (typically the ^{210}Pb control sample), Pb_0 and Po_0 are calculated as the average of the measurements at t_1 and t_2. For all other cases the mathematics using Bateman equations gave accurate results and can be applied. For better statistics the ingrowth period between depositions (t_2–t_1) should be as long as possible to be as close to equilibrium as possible. One year is preferred, but due to analytical constraints a period of at least four months is used. Uncertainties can also be minimized by keeping the time delay between sample collection and analysis as short as possible.

Alternative radiochemical methods for determination of ^{210}Po

A method using SrSpec resin for simultaneous determination of ^{210}Po and ^{210}Bi as described in 2.13.10 is currently under investigation and will be implemented in the immediate future. The biggest advantage will be the shorter time needed for in-growth of Bi. The achievable sensitivity may however not be as good as that of the spontaneous deposition method.

Analysis of ^{210}Po in food and biological samples

Polonium in different foodstuffs and biological samples can be analysed as for water after suitable digestion of the dried material. Because of the volatility of Po, care must be taken

during the digestion procedure to avoid losses. Recovery may vary when the digested samples contains organic material, which will result in charring when evaporating the nitric acid (Holtzman, 1987).

The deposition method was evaluated for fish samples. Edible parts of the fish were used. Initial sample preparation included drying (at a temperature less than 70 ^{O}C to prevent losses of volatile polonium), milling and homogenisation of the material. Drying of samples served as a pre-concentration step to improve sensitivity. A typical dry/wet ratio for fish samples is 0.27 (see Table A-10, Appendix A). The samples were spiked with a known activity of approximately 0.100 Bq ^{210}Po.

Optimum conditions for digestion of the samples were investigated. A Milestone Ethos Touch Control open vessel microwave, which allows continuous addition of fixed volumes of acids during the digestion procedure, was used (Figure 4-11). The digested solution was converted to chloride form by evaporating to dryness. Wet-ashing on a hot-plate was compared to microwave digestion. Organic residues persisted in samples digested on a hot plate with a combination of HNO_3 and H_2O_2, whereas a clear solution containing little residue was obtained when using the microwave. Addition of H_2O_2 was essential for complete oxidation of organic residue.

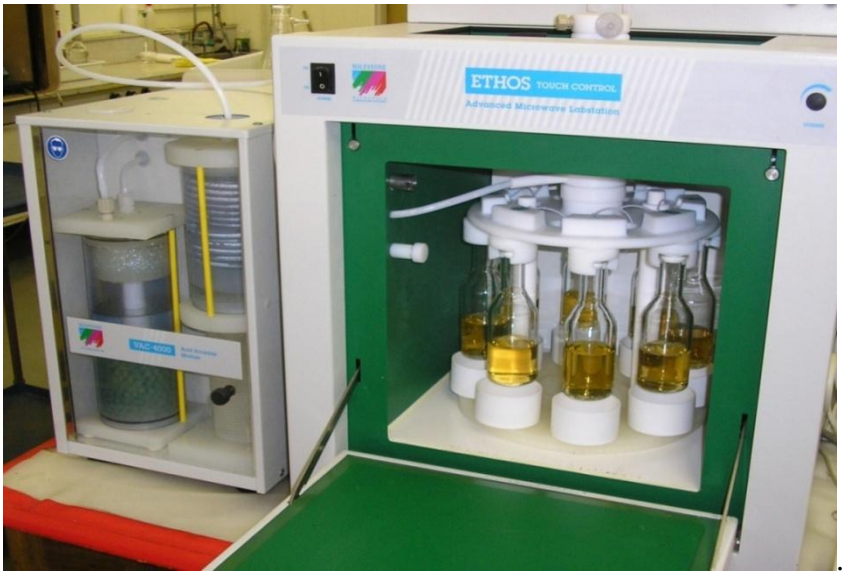


Figure 4-11: Using an open vessel microwave for digestion of fish

The accuracy of the method was acceptable with a bias of less than 15%. Chemical recovery was 66±17%. Since this is similar to the average recovery for plating in water (64±14%), it was concluded that no losses of polonium occur during digestion. The recovery was similar to what were reported by Saito & Cunha (1997) for fish (46-75%) and by Vajda *et al.* (1997) where samples were dissolved on a hot plate by repetitive addition of HNO_3, HCl and H_2O_2. For 1 g of sample, the MDA for ^{210}Po was calculated as 1.34±0.94 Bq.kg^{-1} (dry weight), assuming 60% chemical recovery and counting for 24 hours. By digesting 3 g of fish the MDA can be decreased to 0.5 Bq.kg^{-1}. Based on NNR consumption values for fish, the required MDA to evaluate at a dose of 0.025 mSv.a^{-1} is 0.83 Bq.kg^{-1} (see Table 4-23).

The optimized open-vessel microwave procedure was used for digestion of dried samples of other biological samples including bone, hay, meat and vegetation samples, for which the results are presented in 5.2. Good spectral quality and chemical recoveries proved that minimum interference of matrix effects occurred in the spontaneous deposition experimental procedure.

For milk samples analysis was done directly on the fresh milk sample. Milk was treated with acids to eliminate proteins from the aqueous phase. 100 ml concentrated HNO_3 was added to 100 ml of sample and heated for one hour. The fat fraction was separated using a separation funnel. The remaining solution was heated with addition of H_2O_2 to a light yellow colour. The sample was evaporated to dryness with 2 M HCl. The evaporation was repeated twice after which the solution was made up to a volume of 200 ml and Po plated on a silver disc as described for water. The mean chemical recovery of polonium was 26 ± 2 %, which is lower than for water samples, indicating that losses occur during the procedure. The results obtained for control samples were acceptable with a negative bias of about 10% (Table 4-2). Results for milk samples using this method are shown in 5.2.

Table 4-2: ^{210}Po activity concentrations for milk control sample (mBq)
[Expected = 123 mBq]

Control sample	Measured	Bias	Yield
S1	114.7	-6.7	0.27
S2	108.0	-12.2	0.23
S3	112.4	-8.6	0.26
S4	111.3	-9.5	0.27

Polonium in geological samples

Geological solid samples received for analysis are usually analysed for ^{210}Pb using gamma spectrometry (4.5.2), assuming equilibrium of ^{210}Pb and ^{210}Po. The LOD of direct determination by gamma spectrometry is about 10-100 Bq.kg^{-1} (Table 4-21). When lower LODs are required, or when specifically requested, ^{210}Po is determined by alpha spectrometry after digestion of the samples. Closed microwave digestion was used for digestion of coal and samples from the building industry, similar as discussed for Th (4.8.4). Due to microwave restrictions sample mass was limited to 300 mg. Geological samples may contain high concentration of iron, which may interfere in the analysis. Fe(III) is reduced to Fe(II) by addition of hydroxyl ammonium chloride to limit interference. Analysis of ^{210}Po in soil samples is not routinely done, but accuracy of the method for soil has been shown by analysis of proficiency samples (Table 4-19).

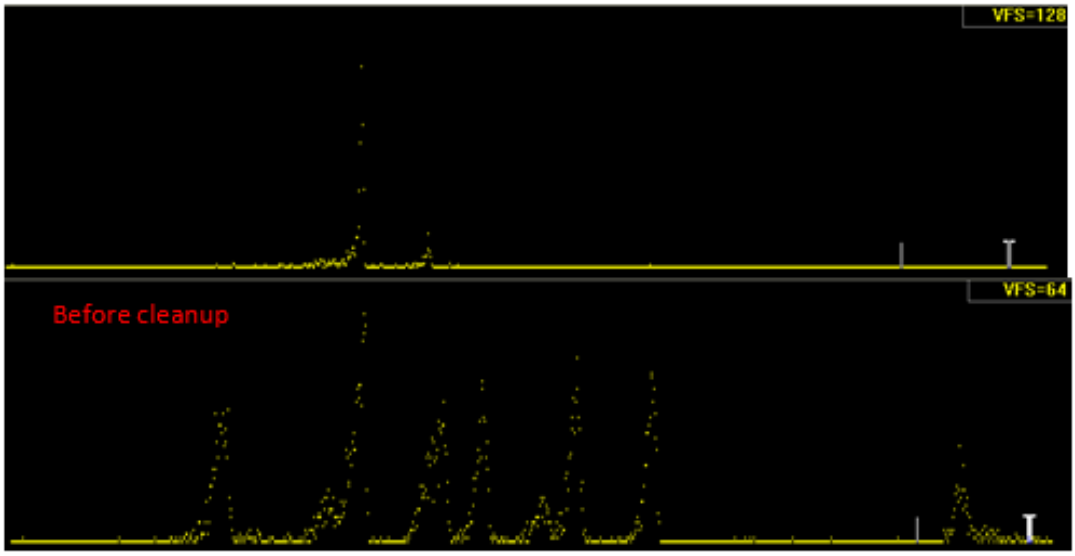


Figure 4-12: Spectrum of ^{210}Po showing interference of high Th concentration removed by TRU resin

Polonium in samples containing high Th

The procedure of spontaneous deposition of ^{210}Po is very specific, and except for Fe, relatively free of interference. Although Th is not expected to precipitate on the silver discs, problems were experienced in the laboratory with the analysis of samples from the phosphate industry containing very high Th concentrations. A pre-cleanup was done using TRU resin;

Po is not retained in 2 M HNO_3 (low k'), whereas Th is strongly retained (2.13.10). Deposition was done on the eluate after evaporation and conversion to 0.1 M HCl. The spectra before and after the cleanup step are shown in Figure 4-12.

4.8.2 Isotopic determination of Uranium (^{238}U, ^{235}U and ^{234}U)

For samples with elevated ^{234}U (as often occurs in water samples), the exposure to alpha-emitting radionuclides is larger than perceived from measurement of the chemical uranium concentration, and assuming a natural isotopic ratio of unity, and dose will be underestimated. On the other hand, where the ^{234}U/^{238}U ratio is less than one, (not normally expected in the natural environment) the U activity will be overestimated. Therefore it is recommended that all three isotopes of uranium (^{238}U, ^{235}U and ^{234}U) are measured in water samples.

The method for nuclide specific analysis of U in environmental samples utilizes extraction chromatography resin (2.13.9). This section discusses optimization and implementation of the method. For many years the separation has been performed using a combination of TRU resin and cation exchange (based on method by Burnett & Yeh, 1995). This has recently been changed to separation using UTEVA as per the recommended method of Eichrom (Eichrom, 2014a).

For TRU separation a column is prepared containing 0.7 g of TRU resin (100-150 µm) in 2 M HNO_3. The sample solution (after appropriate pre-concentration as in 4.3.1) is transferred to the column. The first 10 ml 2 M HNO_3 rinse contains Ra, Po, Pb and other cations such as Ca and Fe. Concentrated HCl is used to convert the column to the chloride form, after which Ac and Th are eluted with 4 M HCl followed with 1 M HCl. The U/Pa fraction is eluted from the column with a mixture of 0.1 M HCl and 0.1 M HF (see Figure 4-13). The U/Pa fraction is evaporated and the residue dissolved in 0.1 M HCl, which are transferred to a column containing 1.0 gram of cation exchange resin in 0.1 M of HCl. The column is first rinsed with 0.1 M HCl/0.01 M HF, followed by 0.1 M HCl, which contains Pa. Elution of uranium is done with 2 M HCl (see Figure 4-13). For UTEVA separation the samples are evaporated to dryness, dissolved in 3 M HNO_3-1 M $Al(NO_3)_3$ and selectively sorbed onto the column. The analysis sequence as illustrated in Figure 4-14 is followed.



Figure 4-13: Separation of Uranium using extraction chromatography and cation exchange chromatography

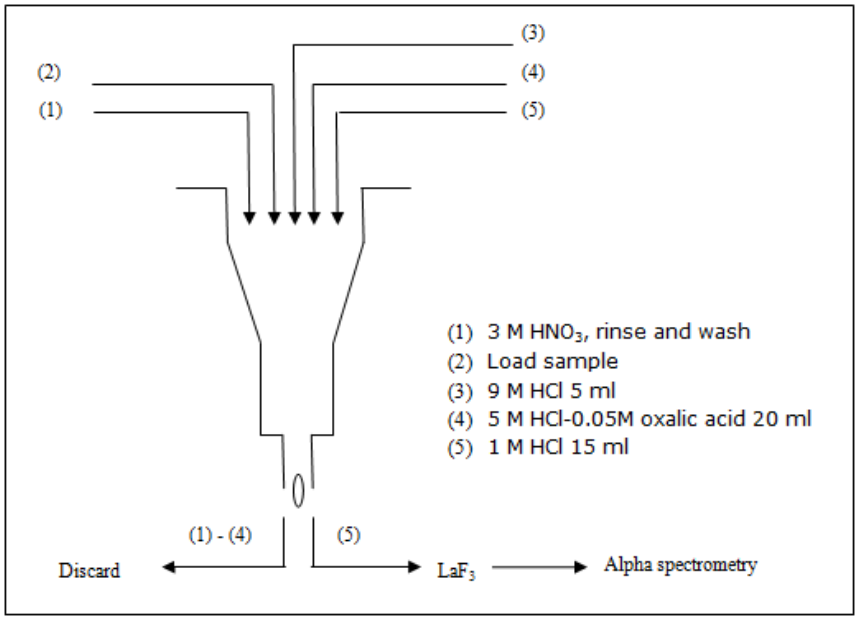


Figure 4-14: Analysis sequence for separation of U on UTEVA resin

After separation $TiCl_3$ is added to the sample for reduction of U(VI) to U(IV). The counting source is prepared by lanthanum fluoride micro-co-precipitation (Figure 4-15). Filtration is done through a 0.22 µm filter loaded with a 0.2 mg LaF_3 suspension. The lanthanide fluoride precipitation does not proceed quantitatively for uranium quantities in excess of 100 µg (1.2 Bq) - see Figure 4-16. This is as what has been reported at a Eichrom user's group meeting that recovery decreases from 100-70% with increase in mass of 100 to 200 µg (McAllister, 2014). Therefore, for samples with expected uranium activities higher than 5 $Bq.L^{-1}$ (*i.e.* 1 Bq in a 200 ml aliquot), a smaller aliquot was taken for analysis to ensure a total activity on the filter of less than 1.2 Bq (~100 µg).

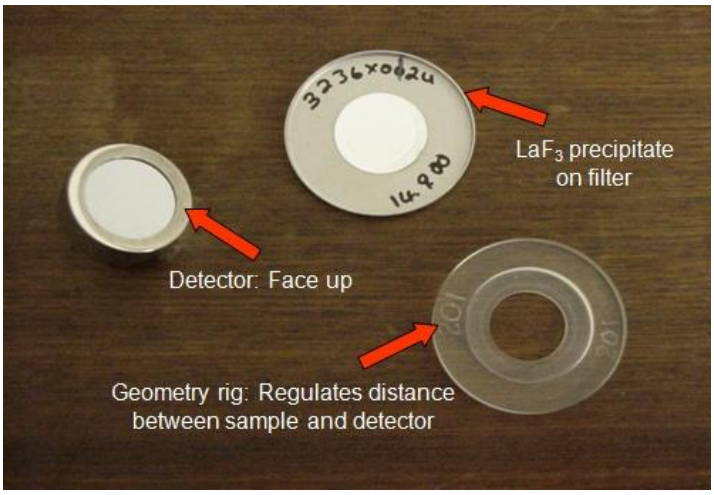


Figure 4-15: Prepared counting sources for alpha spectrometry

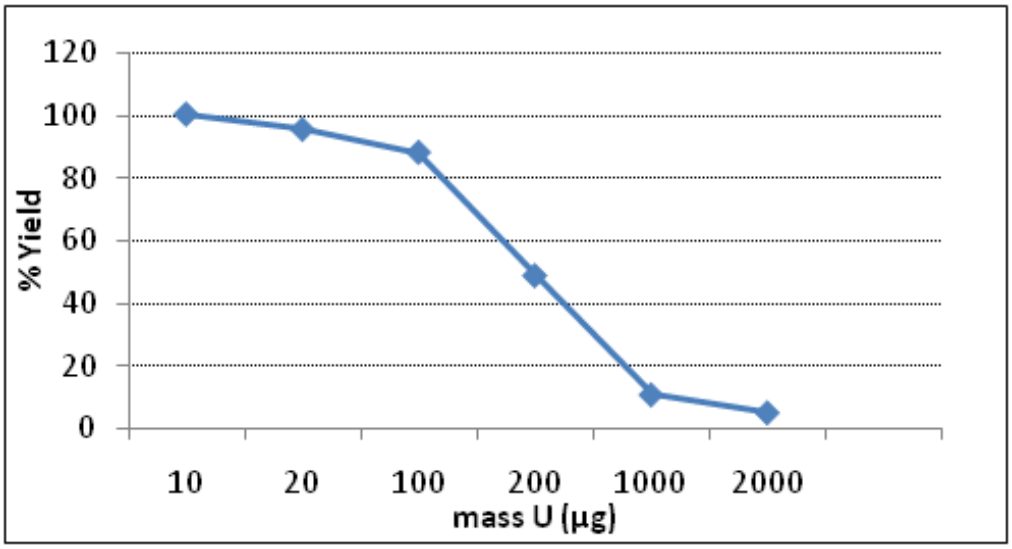


Figure 4-16: Influence of mass of U on LaF_3 precipitation recovery

The samples are counted on an alpha spectrometer to determine the alpha activities of ^{238}U, ^{235}U and ^{234}U. Typical spectra for depleted and natural uranium are shown in Figure 4-17. Resolution was typically less than 100 keV, with good spectra having a resolution of 50-65 keV, which is as expected from literature (2.13.6). Spectrum A in Figure 4-17 is for the control sample, which was prepared from depleted uranyl nitrate with the ^{238}U concentration almost a factor 10 higher than that of ^{234}U. This ratio is not expected in environmental water samples. The more common spectrum for undisturbed water samples look similar to spectrum C with higher ^{234}U concentrations; ratios higher than two are common (2.1.2). Spectrum B

shows a natural ratio of uranium and is typically an indication of water, which has been contaminated by an external uranium source (Skwarzec *et al.*, 2001).

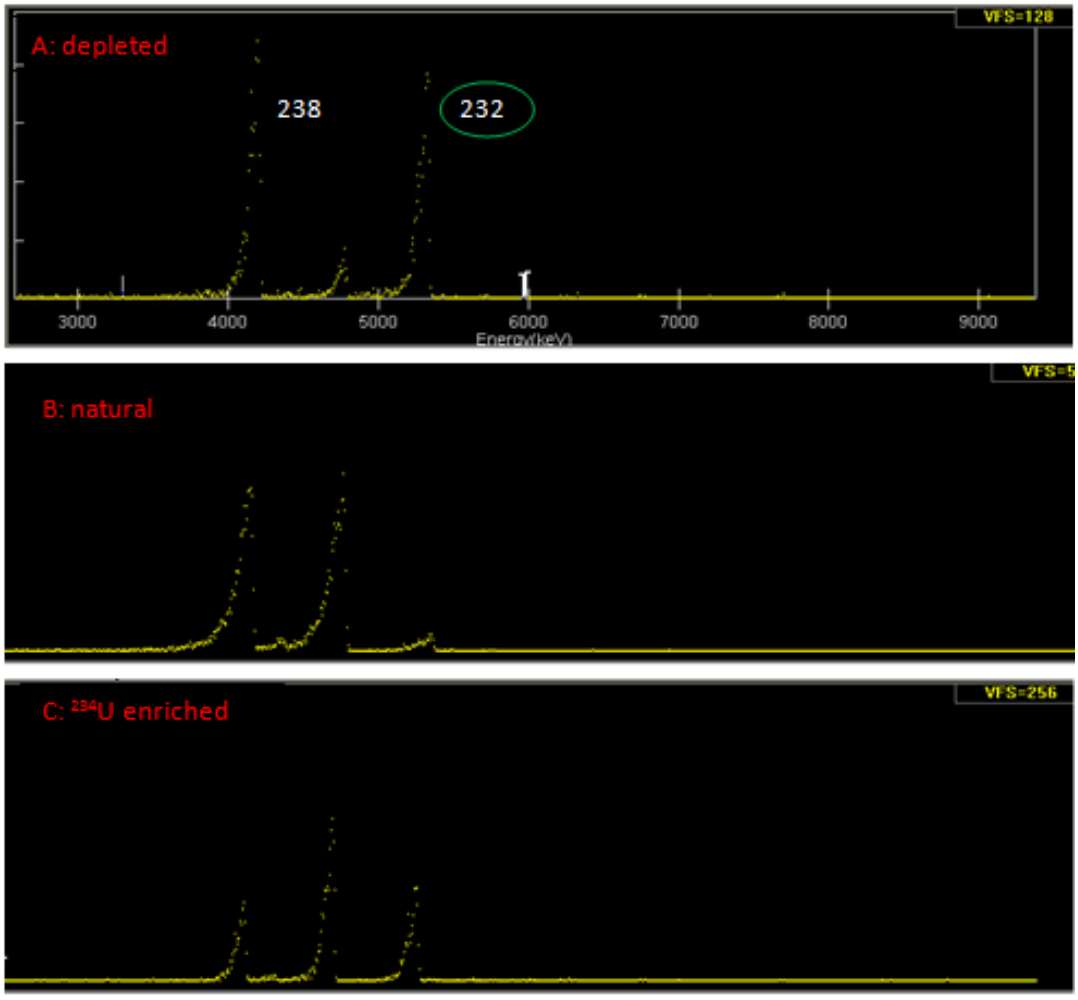


Figure 4-17: Typical energy spectra for uranium analysis showing the peaks for ^{238}U, ^{235}U, ^{234}U and ^{232}U

Chemical recovery was determined by addition of ^{232}U (with ^{228}Th in equilibrium) as tracer. The average recovery during original implementation was 70±15%. The method is suitable for sample volumes ranging from 100 to 2000 ml by first pre-concentrating the larger samples. Two alternatives methods for pre-concentration were evaluated - evaporation and calcium phosphate co-precipitation (4.3.1) - both gave good results. A high salt content may prevent the sample from being evaporated to a small enough volume for quantitative loading of the sample onto the column, in which case co-precipitation is preferred or alternatively a smaller aliquot is loaded directly onto the column. The method is suitable for environmental water samples and any digested solid sample, although the preferred method for solid

samples is NAA (4.6).

Table 4-3: Comparison of results for Uranium control samples separated on TRU and UTEVA resin *Expected value for ^{238}U = 254±25mBq; ^{234}U = 27.3 ± 2.7mBq*

Sample	Yield	^{238}U	Bias	^{234}U	Bias
UTEVA RESIN					
1	0.19	247 ± 8	-2.7	24.4 ± 3.2	-10.7
2	0.99	249 ± 4	-1.8	25.6 ± 1.4	-6.3
3	0.71	256 ± 4	+0.7	24.2 ± 1.5	-11.4
4	0.67	261 ± 4	+2.7	24.4 ± 1.5	-10.6
5	0.56	252 ± 4	-0.9	23.2 ± 1.7	-15.0
6	0.73	245 ± 4	-3.5	23.2 ± 1.4	-15.0
7	0.56	259 ± 5	+2.2	24.9 ± 1.7	-8.9
8	0.99	261 ± 4	+2.7	26.6 ± 1.5	-2.5
9	0.55	252 ± 5	-0.7	26.5 ± 2.0	-3.1
10	0.64	270 ± 4	+6.5	26.9 ± 1.7	-1.3
11	0.68	248 ± 4	-2.3	27.8 ± 1.6	+1.8
Average	0.66	255 ± 8 (3.0%)	+0.26	25.2 ± 1.5 (6.1%)	-7.5
TRU RESIN					
1	0.43	228 ± 5	-10.4	23.4 ± 1.8	-14.1
2	0.43	237 ± 5	-6.9	20.8 ± 1.8	-23.7
3	0.32	231 ± 6	-8.9	24.7 ± 2.5	-9.7
4	0.38	228 ± 6	-10.3	25.1 ± 2.3	-8.0
5	0.37	257 ± 6	+1.3	24.9 ± 2.1	-8.8
6	0.36	246 ± 5	-2.9	21.7 ± 2.0	-20.6
7	0.45	260 ± 6	+2.2	26.1 ± 2.1	-4.6
8	0.33	258 ± 6	+1.5	29.7 ± 2.4	+8.6
9	0.30	247 ± 6	-2.6	25.4 ± 2.3	-7.1
10	0.28	241 ± 7	-5.1	25.8 ± 2.7	-5.5
11	0.23	227 ± 7	-10.8	27.1 ± 2.7	-0.6
Average	0.35	242 ± 13 (5.3%)	-4.8	24.9 ± 2.4 (9.8%)	-8.5
QC data 201405-201502	N= 50	248± 59.4 (23.9%)	-2.4	28.6 ± 10.2 (35.5%)	+4.8
QC data 201502-201508	N=29	251± 17.6 (7.0%)	-1.2	26.4 ± 5.9 (22.3%)	-3.3

Both methods (using TRU or UTEVA) separated the uranium isotopes effectively from all interfering alpha emitters. The results for control samples are presented in Table 4-3. Also shown is the average of the control sample in water monitored over two periods in 2014-

2015. The accuracy of both methods was good, with that of UTEVA slightly better than TRU. The average chemical recovery on UTEVA (66%) was also better than on TRU (35%).

The precision for both methods was good with a RSD of less than 10%. The ^{238}U results for a series of water samples from the mining industry (n=43) ranging in activity concentration from 11.6 to 2310 mBq.L^{-1} and analysed with both methods are graphically represented in Figure 4-18. Good correlation was obtained for the results obtained with the two methods with linear regression R^2 = 0.992. The slope does not differ significantly from one, which indicates that the intrinsic accuracy of both methods is good. The MDA was calculated as 0.01 Bq.L^{-1} using 200 ml of sample (and 2 Bq.L^{-1} using 1 ml of sample), chemical yield of 0.6 and counting efficiency of 0.2. The target concentration to evaluate the exposure level at 0.025 mSv.a^{-1} for adults for a daily intake of 1.7 L daily is about 0.9 Bq.L^{-1} for ^{238}U and ^{234}U (see Table 4-23).

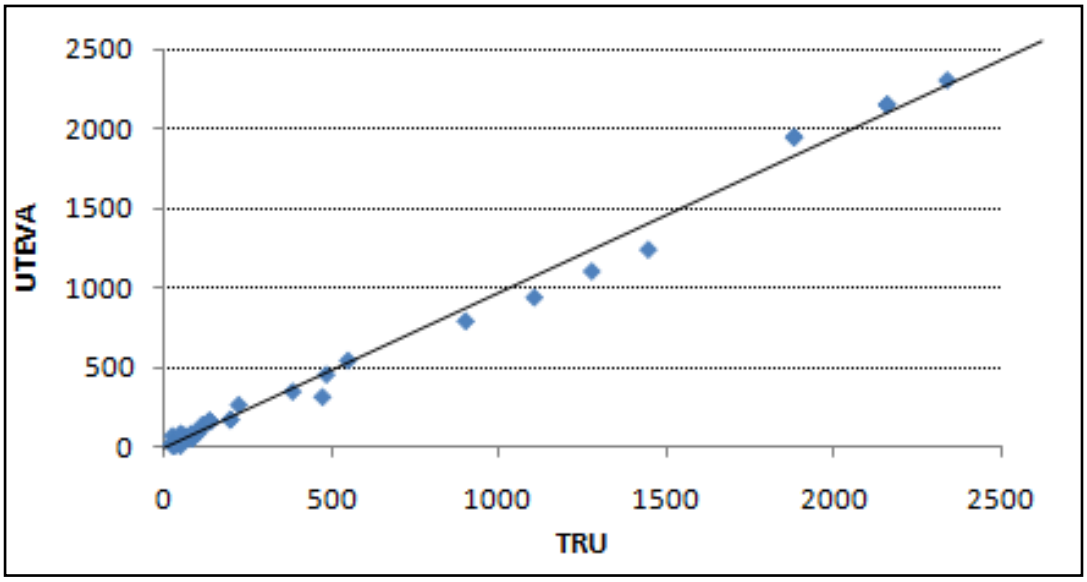


Figure 4-18: Comparison of ^{238}U results for water samples from the mining industry obtained with two different resins
[y = 0.98X - 3.38 (R^2 = 0.992)]

Re-use of UTEVA resin

Due to the high costs, extraction chromatography resins are re-used in many laboratories. According to the manufacturers UTEVA resin is sufficiently stable to be re-used, since lost of extractant is negligible (2.13.9). The procedure described in Casacuberta *et al*. (2012) was followed. UTEVA resin was cleaned by rinsing with 0.1 M oxalic acid after U and Th had

been eluted. Re-use of the resin is feasible if no traces of U and Th are retained in the column. Results showed that the column can be used at least three times before fingerprinting effects occurred.

Uranium in soil samples

Implementation of a destructive (radiochemical) method for the analysis of soil was investigated. Wet acid digestion on a hot plate was compared with results obtained using microwave digestion. For hot plate digestion 1.0 g aliquots of the soil sample were digested by repeated additions of concentrated HF, HCl and HNO_3. For microwave digestion the sample size was limited to 0.5 g. After addition of the acids (9 ml HCl, 3 M HNO_3), the vessel was closed and completely digested in the Milestone Ethos Touch microwave using a suitable program. The digestion was repeated with small volumes of HNO_3, HF and HCl to obtain a colorless solution. After digestion the samples were filtered through a glass microfiber filter and dissolved in 2 M HNO_3 before proceeding with the radiochemical separation as for water using UTEVA.

Soil proficiency test samples provided by the Department of Energy of the USA for the Mixed Analyte Performance Evaluation Program (MAPEP) were analysed after digestion using these methods. The recoveries were comparable to those obtained for water samples and well resolved spectra were obtained. The results compared well with the expected values (see Table 4-4), especially for those samples where microwave digestion was used.

Table 4-4: Results for uranium in soil samples for MAPEP Proficiency Exercise (Bq.kg^{-1})

Study	^{238}U			^{234}U		
	Reference	**Measured**	**Bias**	**Reference**	**Measured**	**Bias**
*Mapep 28	281	253 ± 8	-10.0	62.5	62.3 ±4.0	-0.3
*Mapep 29	34.0	38.7 ±3.2	+13.8	30.0	36.8 ±3.2	+22.7
Mapep 31	259	188 ± 7	-27.4	89	38.0 ±3.7	-57.3
Mapep 32	201	169 ± 6	-15.9	52.5	35.2 ±2.9	-33.0

**microwave digested*

Results for MAPEP 31 and 32 samples, which were digested on a hot plate, were not accepted with large negative bias indicating incomplete dissolution of refractory particles in the samples. Although mineral aids have been shown to be effective leaching agents for

specific samples, elements included in a refractory matrix will not be removed completely without total dissolution of the matrix as pointed out by Sill & Sill (1995).

4.8.3 Chemical determination of uranium

Analysis of elemental U in water samples is required as per the DWS protocol (see 4.4.1). Based on this analysis, and the gross alpha/beta screening results, sampling points are identified for which full nuclide analysis is performed. The WHO guideline value for U in drinking water is 30 $\mu g.L^{-1}$ based on its chemical toxicity for the kidney (WHO, 2011).

In this study the use of KPA for analysis of U was implemented. KPA uses a computer controlled, laser induced, time resolved luminescence analyser. A sample aliquot is mixed with a complexing agent (uraplex) and injected into the KPA cell. A laser is used to stimulate uranium ions in reference and sample cells; de-excitation of the ions results in emission of photoluminescence photons that are converted to an electronic signal by photomultiplier tubes. The light intensity as a function of time is directly related to the uranium concentration. A uranium reference solution is used to correct for instrumental variations. The KPA instrument subtracts the background and calculates the concentration of uranium according to calibration curves. All the data reduction (*i.e.* calculation of the uranium concentration values from the intensity readings, dilutions, standard additions) is done in the KPA database. The final uranium concentration in $\mu g.L^{-1}$ is reported. The result is converted to $mBq.L^{-1}$ ^{238}U assuming a natural ratio .This method has been validated - a summary from the validation is presented here.

The specified reporting range is from 0.01 to 5 $mg.L^{-1}$ (Chemcheck, 2009). The instrument can be used with both a low and high calibration and is calibrated every time when new complexing solution (uraplex) is prepared, usually weekly. The instrument was calibrated using a series of five standards prepared from a primary uranium solution (NIST standard). Good linearity was obtained in the two ranges calibrated for *i.e.* 1–10 $\mu g.L^{-1}$ ($R^2 > 0.995$) and 50-1000 $\mu g.L^{-1}$ ($R^2 > 0.9998$). When a 20 $\mu g.L^{-1}$ standard was included in the low calibration range the regression coefficient decreased with curvature occurring towards the upper end.

It was found that the instrument background was very sensitive to any U in the ambient atmosphere and fluctuated from day to day. This has been better controlled by moving the instrument to another laboratory and introducing a rinse cycle at shutdown. Cross-over

contamination from previous samples was less than 0.1%. The method detection limit was determined by repeated analysis of a standard with concentration close to the expected detection limit of the method (0.01µg.L^{-1}). The LOD was calculated as three times the standard deviation of the replicate measurements. Using this approach the calculated LOD was 0.05 µg.L^{-1} of uranium by direct injection of one ml of sample. The limit of quantitation (reporting) of the method was set at 10 times higher than the LOD; *i.e.* 0.5 µg.L^{-1}.

Control samples with concentrations of 0.1, 1 and 10 µg.L^{-1}, prepared from a U certified solution, were measured periodically during the course of this study. The data were used to determine the accuracy and method uncertainty or reproducibility. The uncertainty was about 15% at concentrations of 1 and 10 µg.L^{-1}, with the main contributor the calibration as indicated by the relatively large bias of about 10% observed for the calibration check standards. The repeatability as determined by repeated analysis of a sample on the same day was 2% and 6% at a concentration of 10 µg.L^{-1} and 1 µg.L^{-1} levels respectively with a bias of less than 10%. Instrument precision was about 1.2%, which corresponds with the manufacturer's specification of 1-3% for instrument precision (Chemcheck, 2009). Since this is much lower than the method uncertainty, it was decided that all samples will be analysed in duplicate, with probable error reported as the standard deviation of two measurements rather than precision of a single reading as given by the instrument. The accuracy of the method was acceptable with a bias of less than 10%. Both the bias and relative standard deviation increased at the reporting level for the method (0.5 µg.L^{-1}).

Results for the many water samples analysed by KPA over the last 5-10 years are presented in the case studies in Chapter 5. Most of the samples analysed for the DWS study (5.1.4) were analysed in the low calibration range. Samples with a higher concentration were adjusted to the working range by dilution. Samples requiring a dilution of more than 25 times (> 250 µg.L^{-1}) were analyzed using the high calibration range. Samples containing high levels of interfering substances (resulting in non-detectable results) were either diluted or pre-treated with concentrated nitric acid and peroxide before analysis. During routine use of the method additional sample preparation was often required for groundwater samples, whereas surface water samples were mostly analysed without problems.

Some of these water samples were also analysed by other analytical techniques, such as fluorometry (FLM), DNC, ICP-MS and alpha-spectrometry. When comparing KPA and

FLM, the percentage difference of the results was less than 10%. There was also excellent comparison between the KPA and DNC results. Results obtained with both KPA and DNC were however much lower than the expected uranium concentration as calculated from the gross alpha results. This lower-than-expected-concentration was found for almost all groundwater samples (see 5.1.4). It confirms that the groundwater samples probably contain high ^{234}U activity, which is not reflected in the conversion to mass concentration and that a natural ratio can therefore not be assumed for the groundwater samples. Results for DWS surface-and groundwater, analysed with both ICP-MS and KPA, showed good correlation, especially at concentrations higher than 10 $\mu g.L^{-1}$ (see 5.1.4).

A few inter-laboratory studies were conducted with independent laboratories. Table 4-5 shows results for mine effluent samples analysed at with KPA and FLM. It was also analysed with ICP-MS by two other laboratories. The samples were analysed directly as received, and was not filtered or acidified at the laboratory. It was therefore assumed that U is present as soluble U(VI). With some exceptions, the results obtained with the different techniques compared very favourably. The concentrations were high and had to be diluted 100-500 times to fall within the analytical range of FLM, whereas it was only diluted 10 times to fall within the high calibration range of KPA. Analysis by KPA is therefore preferred.

Table 4-5: Inter-laboratory study of mine effluent samples - U in $\mu g.L^{-1}$

Sample	RA Fluorometry	RA KPA	PAL ICP-MS	DD SCIENCE ICP-MS
x001	4170	1890	2100	2040
x002	1440	1550	1410	1330
x003	2260	2170	543	2100
x004	309	245	272	276
x005	1130	1290	1220	1240
x006	490	545	590	580
x007	2920	2370	2440	2560
x008	72	104	88	86

4.8.4 Method for determination of thorium isotopes (^{232}Th, ^{230}Th, ^{228}Th, ^{227}Th)

Analysis of the long-lived thorium isotopes is required for compliance with NNR regulations (4.2). As is clear from Table 4-21, which shows the comparative LOD for the various

analytical methods available at RA, alpha spectrometry has the best sensitivity among the available methods for measurement of thorium.

Thorium in water

RadioAnalysis routinely determines thorium isotopes in water samples using extraction chromatography and α-spectrometry. Samples for U and Th determination are separately prepared to avoid interference from the ^{232}U tracer (which contains ^{228}Th) in the Th analysis. The method has been in use since 1998, but has been modified several times since then. Until recently the separation was performed using a combination of TRU resin and cation exchange. The results obtained have always been reliable and accurate, but the method is rather long and expensive. In 2017 the method has been changed to separation using TEVA resin as per the recommended method of Eichrom (Eichrom, 2014c). Both methods separate the thorium isotopes effectively from all interfering alpha emitters. The TEVA method is about 2-3 hours shorter than the method using TRU resin. TEVA resin is also slightly cheaper than TRU resin. The cost of the analysis is further reduced by the elimination of the cation exchange separation, which is no longer required.

The separation using TRU resin is similar to that of U and is illustrated in Figure 4-19. A column is prepared containing 0.7 g of TRU resin (100-150 µm) and pre-conditioned with 2 M HNO_3. After loading of the pre-concentrated sample the column is rinsed with 10 ml of 2 M HNO_3, 2 ml of concentrated HCl, 10 ml of 4 M HCl (to elute Ac) and then with 3 ml of 1 M HCl. The thorium/uranium/protactinium fraction is eluted from the column with 15 ml of a mixture of 0.1 M HCl and 0.1 M HF. The eluted fraction is loaded onto an ion exchange column containing 1.0 gram of cation exchange resin in 0.1 M of HCl. The cation column is rinsed with 10 ml of 0.1 M HCl/0.01 M HF, which contains Pa followed by 10 ml of 2 M HCl, which contains U. Th is eluted with 15 ml of 2 M H_2SO_4. For TEVA separation the sample is evaporated to dryness, dissolved in 10 ml 3 M HNO_3-1 M $Al(NO_3)_3$ and loaded onto the column. U is removed from the column with 40 ml 3 M HNO_3. The fraction containing Th is eluted with 9 M HCl.

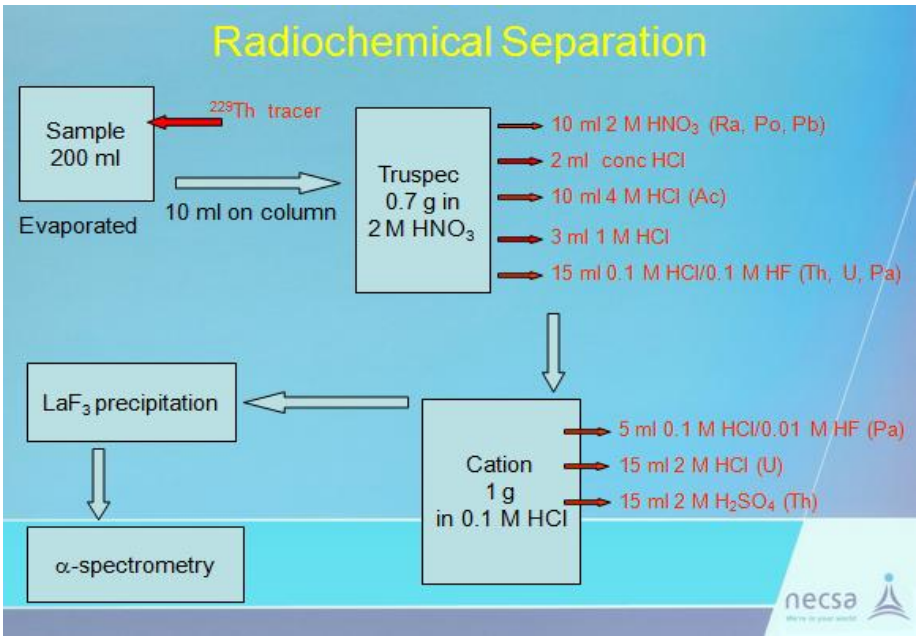


Figure 4-19: Schematic presentation of method for Th determination using TRU resin

After separation the counting source is prepared by lanthanide fluoride micro-precipitation. The sample is counted by alpha spectrometry to determine the activities of the thorium isotopes. A typical spectrum is shown in Figure 4-20. Daughters isotopes of ^{228}Th are also present in the spectra at energies higher than 5.5 MeV. The FWHM was about 60-100 keV, showing acceptable resolution of the ^{229}Th tracer and ^{230}Th peak allowing reliable quantification of ^{230}Th in the sample. A good resolution between these two peaks, which have alpha energies close to each other, was however not always obtained and seemed to be analyst dependentThe method can be used for samples volumes ranging from 100 to 2000 ml by first pre-concentrating the larger samples. Pre-concentration by both evaporation and calcium phosphate co-precipitation was evaluated. Using calcium phosphate precipitation recoveries were better than 60%. Both methods can be used, but evaporation is preferred due to ease of use. The breakthrough volume of the extraction column is 50 FVC (~65 ml) (Horwitz *et al.*, 1993). Therefore the volume to be loaded onto the column was restricted to 10 ml to 20 ml.

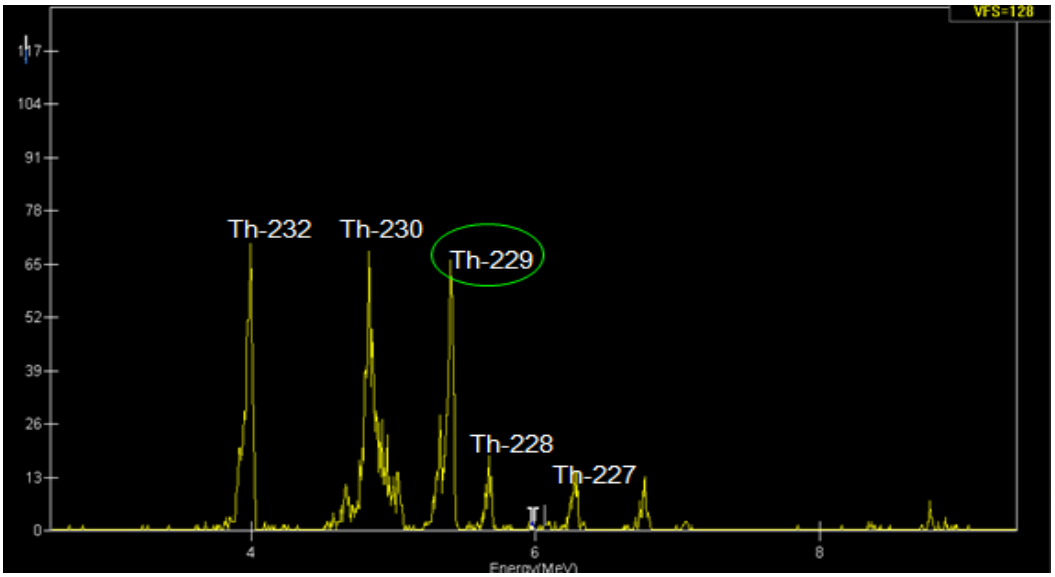


Figure 4-20: Typical energy spectrum for thorium analysis showing the peaks for ^{232}Th, ^{230}Th, ^{229}Th, ^{228}Th and ^{227}Th

A control sample with expected activity of about 0.040 Bq ^{232}Th/g, prepared from a thorium nitrate salt was used for development and implementation. The average recovery (as determined by the ^{229}Th tracer) during implementation was 70 ± 27%. The accuracy of the method was acceptable with a bias of less than 15%. The precision of the method was acceptable with a RSD of less than 10 % at levels of 0.040 Bq.L^{-1} and less than 20% at levels of 0.020 Bq.L^{-1}. The MDA's for the thorium isotopes were about 0.005 Bq.L^{-1} calculated using detector background values for a counting period of 24 hours, volume 200 ml, recovery 60% and counting efficiency of 20%. Based on the average blank counts in the region of interest (ROI) for ^{230}Th, the MDA for ^{230}Th was calculated as 0.050 Bq.L^{-1}. The target concentration for drinking water to evaluate the exposure level at 0.025 mSv per year for adults for a 1.7 L daily intake is about 0.18, 0.19 and 0.58 Bq.L^{-1} for ^{232}Th, ^{230}Th and ^{228}Th respectively (see Table 4-23).

The standard deviation on replicate analyses (about 10 %) was larger than the probable error calculated from counting statistics only (about 4 %) indicating that other factors are contributing to the uncertainty.

Tracer solutions

Suggested tracers to be used for thorium include ^{229}Th and ^{234}Th (2.13.12). Use of both tracers was investigated during the experimental development. ^{234}Th was originally used in

the laboratory, but it was later changed to ^{229}Th mainly due to disadvantages such as generation of additional waste (liquid scintillation vials and cocktail), frequent preparations, as well as presence of about 20 mBq of ^{228}Th as impurity in the prepared tracer solution.

^{229}Th was purchased as a certified solution from Amersham. The main disadvantage of the use of ^{229}Th is the close proximity of the main energy peak of 4.84 MeV to the peak of ^{230}Th at 4.69 MeV. ^{229}Th progeny (^{225}Ac) will also interfere with determination of ^{227}Th if samples are not counted directly after preparation. Another disadvantage of using ^{229}Th is recoil contamination of the detector with short-lived, alpha-emitting progeny.

A ^{234}Th tracer solution was prepared by milking a uranyl nitrate solution loaded onto an anion column (Ag1X8). The following equilibrium exists in a natural U solution:

^{238}U (4.468x10^{9} a) $\Rightarrow$ ^{234}Th (24.1 d) $\Rightarrow$ ^{234m}Pa (1.17 m) $\Rightarrow$ ^{234}U (2.4x10^{5} a)

In principle a pure ^{234}Th solution can be obtained by separation of U and Th. From one gram of ^{238}U an equilibrium mass of 1.4x10^{-5} μg ^{234}Th is produced. Therefore a micro quantity of Th has to be separated from a macro quantity of U. The capacity of an anion resin is about 75 g U per 500 ml resin bed. U forms chloride complexes in 8 M HCl and is retained, whereas Th and other cations elute (Berman *et al*., 1960). Th was quantitatively eluted with 8 M HCl. The column can be milked a few times before minimum quantities of uranium start breaking through. When the U-impurity level in the tracer increased to more than 50 mBq, the uranium was eluted with 0.1 M HNO_3, evaporated to dryness, re-dissolved in 8 M HCl and loaded onto a freshly prepared column.

For standardization the activity concentration of the ^{234}Th solution was determined by adding 15 ml Ultima Gold AB to 0.1 g fractions and counting with LSC. The measured value compared well with the expected calculated value (see Table 4-6). The purity of the prepared tracer solution was determined by preparing LaF_3 counting sources and counting with α-spectrometry. $TiCl_3$ was added for reduction of U(VI).

The use of two different uranium solutions was investigated: a NBS standard and a U_3O_8 salt. It was found that the NBS 950b standard (with natural uranium ratio) contained high concentrations of ^{230}Th, and it was therefore not suitable for use as a source for preparation of ^{234}Th. A prepared tracer solution of 1 kBq ^{234}Th contained approximately 2 Bq ^{230}Th (0.2%) and 0.1 Bq of ^{232}Th and ^{228}Th, whereas a 1 kBq ^{234}Th tracer prepared from a U_3O_8 salt

contained only 0.010 Bq ^{230}Th as impurity. The lower contamination in the salt was due to the fact that this material, as is the case for most commercially available uranium salts, contains depleted uranium (less ^{234}U and therefore also less ^{230}Th than natural U ore, since ingrowth from ^{234}U will be minimal). Impurities decreased with further milking of the column due to the slower rate of ingrowth for ^{232}Th, ^{230}Th and ^{228}Th compared to ^{234}Th.

Table 4-6: Standardization of ^{234}Th tracer solution

Mass	Cpm	Activity (Bq.g^{-1})
1.0812	1008	7.46
1.0858	999	7.36
1.0722	1009	7.54
Average		7.45 ± 0.09 (1.19%)
Calculated		7.44 Bq.g^{-1}

When using ^{234}Th as tracer a known amount of the β-emitting isotope ^{234}Th (in excess of the activity that might be present as daughter of ^{238}U), is added to the sample. High activities of tracer (> 200 Bq) must be added to the sample, so that the natural contribution of ^{234}Th in uranium-rich samples can be ignored (~ 1 Bq level). The gross β-activity of the prepared LaF_3 counting source is determined by LSC after completion of α-counting. LSC counting efficiency for alpha emitters is typically 100%. The method does not provide any selectivity for the analyte, and all β-activity is ascribed to ^{234}Th. It is possible to discriminate against α-emitters to a limited extent by using the αβ-discrimination facility of the LSC (2.13.3). The optimum pulse discriminator setting (PDS) was established by calculating alpha and beta misclassification at different PDS settings (Zapata-Garcia *et al*., 2012). A pure α-emitter (^{241}Am) and pure β-emitter (^{234}Th) was used for the optimization (L'Annunziata, 2003). From Figure 4-21 it is clear that with a setting of 110, miss-classification of both α and β will be less than 20%. A PDS was selected that discriminates more against beta events because it was expected that sample beta activity will be much higher than alpha activity. A PDS setting of 150 was chosen for determination of ^{234}Th; where less than 1% of β's was observed in the α channel.

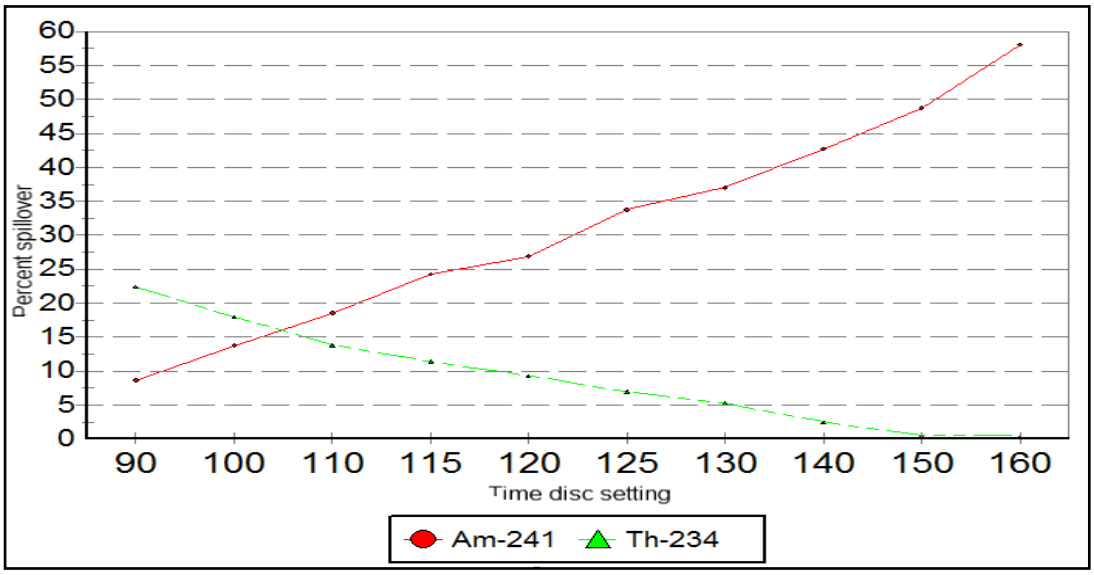


Figure 4-21: Time discriminator setting chart: Percentage spill versus pulse discriminator setting

Source preparation and counting

Rare-earth micro precipitation is commonly used to prepare counting sources for α-spectrometry (Sill, 1987a). Thorium was co-precipitated with lanthanide fluoride. The recovery from both 10 ml 1 M HCl and 15 ml 2 M H_2SO_4 was almost quantitative (> 85%). Losses of Th occurred if the flow rate during filtration was too high. The yield also decreased with an increase in volume of the sample. The recovery was optimum for 100 µg lanthanum carrier.

When spectrum resolution was poor as a result of a poorly prepared source there was low energy tailing from peaks with high energy *e.g.* ^{229}Th in the ^{230}Th peak area. These spectra had to be resolved manually, leading to poor reproducibility. Counts from ^{229}Th in the ^{230}Th region must be accounted for. If not, it will cause underestimation of the yield resulting in incorrectly high results reported for ^{230}Th. Overlap of ^{229}Th and ^{230}Th peaks in samples with poor resolution contributed significantly to the uncertainty of measurement for ^{230}Th. Total propagated uncertainty, rather than the uncertainty based on counting statistics, is therefore reported for ^{230}Th (Appendix B5). The use of Eichrom resolve-TM filters (Eichrom, 2005) was evaluated, but no improvement in the resolution was observed. Future plans in the laboratory include investigation of the use of electrodeposition (with better resolution) as an alternative for source preparation.

Investigation of elution behaviour of Th on TRU resin

To optimize separation conditions, elution curves for Th, U, Po and Ra on TRU resin were compiled by step-wise elution of 3 ml aliquots into liquid scintillation vials for direct counting by LSC. Known activity concentrations of about 10 Bq ^{238}U, ^{226}Ra, ^{234}Th and ^{209}Po were evaporated to dryness, dissolved in the column loading solution and eluted from the column with: 10 ml 2 M HNO_3; 2 ml 9 M HCl; 10 ml 4 M HCl; 25 ml 1 M HCl and 10 ml of 0.1 M HCl/0.1 M HF. These experiments were done to determine the maximum volume of acid for peak elution, and no attempt was made to assess or correct for quench or background. A counting efficiency of 100% was assumed for all nuclides. Elution curves are complicated by presence of decay products, which are always present to some extent. From the elution curve shown in Figure 4-22 the following was observed:

Radium: All elements in the radium solution were eluted in the first 30 ml, of which 73% was eluted in the first 20 ml and a further 12% in the 10 ml 4 M HCl. No activity was observed in the 1 M HCl and HCl/HF fractions.

Polonium: No activity was observed in the 1 M HCl or HCl/HF fractions; 50% eluted in the first 20 ml and a further 21% in the 10 ml 4 M HCl.

Thorium: No activity was observed in the first 20 ml HNO_3, 10 ml 4 M HCl and the first 10 ml of 1 M HCl. 72 to 76% eluted in the next 15 ml of 1 M HCl (fractions 13-17), and 19 to 22% in the HCl/HF fraction (18-20). Recovery increased to 84% when using 40 ml of 1 M HCl. However, the elution volume should be kept as low as possible, since increased volumes will reduce the LaF_3 precipitation yield. The activity observed in the HCl/HF fraction was measured in the beta channel of the LSC and was due to the decay product ^{234m}Pa and not ^{234}Th. Using 40 ml of 1 M HCl as eluant this peak was absent and only appeared once switching to HCl/HF as eluant.

Uranium: No activity was observed in first 20 ml 2 M HNO_3 and 10 ml 4 M HCl. Separation between U and Th was incomplete when using only 15 ml 1 M; using 25 ml, 90% of Th eluted in 1 M HCl and 86% of U in the HCl/HF fraction. The activity observed in the 1 M HCl fraction was measured in the beta channel of the LSC and was due to the decay product ^{234}Th, which is present in equilibrium activities with U, and not due to U. Small amounts of U co-eluting with Th will not interfere since the U-LaF_3 precipitate only forms after reduction

to U(IV) with $TiCl_3$. Additional uranium decontamination of Th fraction can be achieved by adding a small volume of H_2O_2, ensuring that the uranium is present as U(VI).

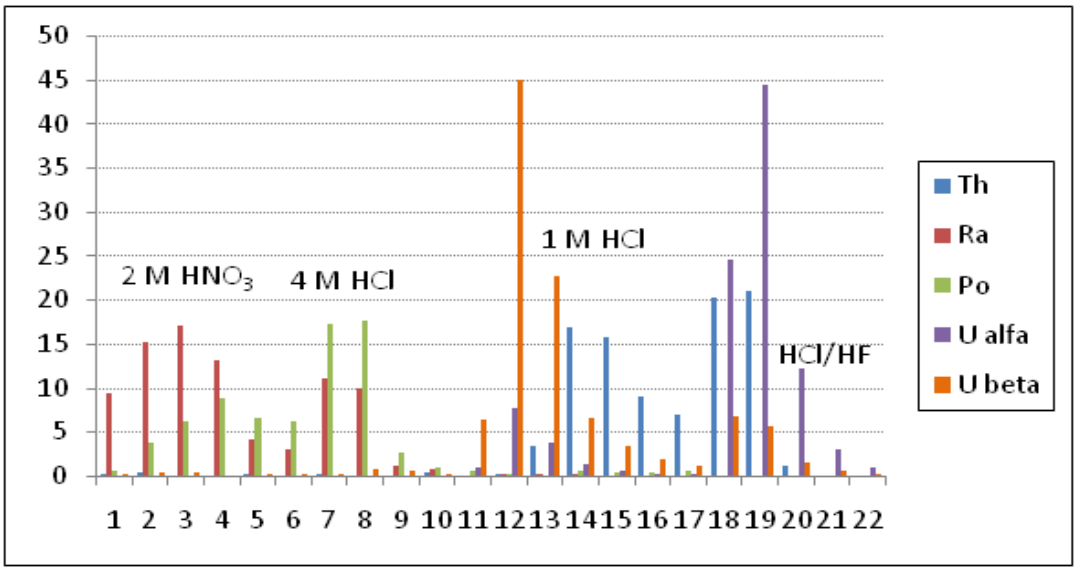


Figure 4-22: Elution curves showing behaviour for the nuclides of interest on TRU resin *(1-5:2 M HNO_3; 6-9:4 M HCl; 10-17:1 M HCl; 18-20:0.1 M HCl/0.1 M HF)*

Development of a separation procedure for thorium

Many changes had been made to the thorium method since first implementation. The method first implemented in the laboratory was based on a method from literature used for the separation of Pa (Burnett & Yeh, 1995.) Cations such as Fe, Ca and Ra are not retained by the TRU resin in 2 M HNO_3, whereas Th is retained and eluted in 1 M HCl with no cross contamination. Based on the elution curves in Figure 4-22, with the original implementation, 30 ml of 1 M HCl was used for elution, of which the first 10 ml was discarded and the next 20 ml (containing 72-76 %) kept for Th source preparation.

Due to problems experienced with reproducibility of results and low recoveries during routine use, it was decided to use a more rugged method, in which Th, Pa and U were eluted as a batch with further separation on an AG50W cation column. Based on the elution curves (Figure 4-22), 5 ml of 1 M HCl was discarded before switching to HCl/HF for elution; 100% of Th was eluted with 0.1 M HCl/0.1 M HF as eluant. U and Pa was also quantitatively eluted (90%) and further separation of the three isotopes on a second column was therefore required. Using cation separation, Pa and U was quantitatively removed from the cation column with

0.1 M HCl/0.01 M HF and 2 M HCl respectively, whereas Th was very strongly retained and only eluted with H_2SO_4. Due to problems with deterioration of alpha PIPS detectors, possibly caused by corrosion, the eluant for Th was later changed to 5 M HNO_3-0.1 M HF identified from a literature study as a suitable eluant to elute Th from the cation column.

In 2017 the Eichrom recommended procedure using TEVA resin (Eichrom, 2014c) was evaluated. TEVA resin has high retention of Th(IV) in 2-4 M nitric acid media, whereas interfering nuclides such as Ra, Po, Pb and hexavalent U are not retained. Thorium is removed from the column with 9 M HCl. No interference from any nuclide is expected in the thorium fraction. No additional separation on cation exchange resin is required, thereby resulting in savings in both cost and time. The results for control samples analysed using TEVA are presented in Table 4-7. For comparison the average of the control sample in water, as monitored over the period 2015-2016 using TRU resin, is shown.

Table 4-7: Thorium activity concentration in control samples using TEVA resin (mBq)

Sample	Yield	^{232}Th	Bias
1	0.97	57.2 ± 1.8	-3.8
2	0.59	53.5 ± 2.3	-10.1
3	0.87	52.7 ± 1.7	-11.4
4	0.41	52.3 ± 2.4	-12.1
5	0.93	66.1 ± 2.1	+11.1
6	0.33	53.5 ± 3.1	-10.1
7	1.05	57.3 ± 1.8	-3.7
8	0.69	58.0 ± 2.3	-2.5
9	0.84	48.5 ± 2.1	-18.5
10	0.63	59.9 ± 3.7	+0.2
11	0.82	50.3 ± 1.7	-15.5
12	1.06	54.3 ± 1.6	-8.7
Average	0.77±0.24	55.4 ± 5.0 (9.0%)	-6.9
QC data	N= 30	52.0 ± 4.8 (9.2%)	-12.7

Expected value for ^{232}Th = 59.5 ± 6.0 mBq

The accuracy of the method exceeded the required specification of a maximum bias of 20% and was similar to those obtained with the method using TRU. With a single exception (data point 5), both methods have a negative bias, which may be due to an overestimation of the yield, resulting in a too low value being measured. The precision for both methods was good

with RSD less than 10%. The average yield for the method using TEVA was better than 70%. Yields higher than 80% should be regarded with suspicion and the spectrum integrated manually to ensure that no counts of the ^{230}Th ROI were accidentally included in the ^{229}Th ROI due to poor spectrum resolution. Results for the analysis of a proficiency exercise sample from the National Physics Laboratory (NPL) are shown in Table 4-32. The results obtained with the two different resins were comparable, but both with a negative bias.

The results for a number of mine water samples (n=31) analysed with both resins are graphically represented in Figure 4-23. The correlation between the two methods was not very good with correlation coefficient, $R^2 = 0.677$. Mine water samples often contain ^{230}Th at higher concentrations than in the control samples, resulting in peak overlap of ^{230}Th and ^{229}Th, which are not sufficiently resolved, and which influences the yield determination. The variability between the results obtained with the two resins was therefore more likely to be a result of peak overlap and operator dependence on resolving the spectra, than on any difference due to the resins itself. To improve accuracy for field samples, the source preparation has to be optimized to improve spectrum resolution.

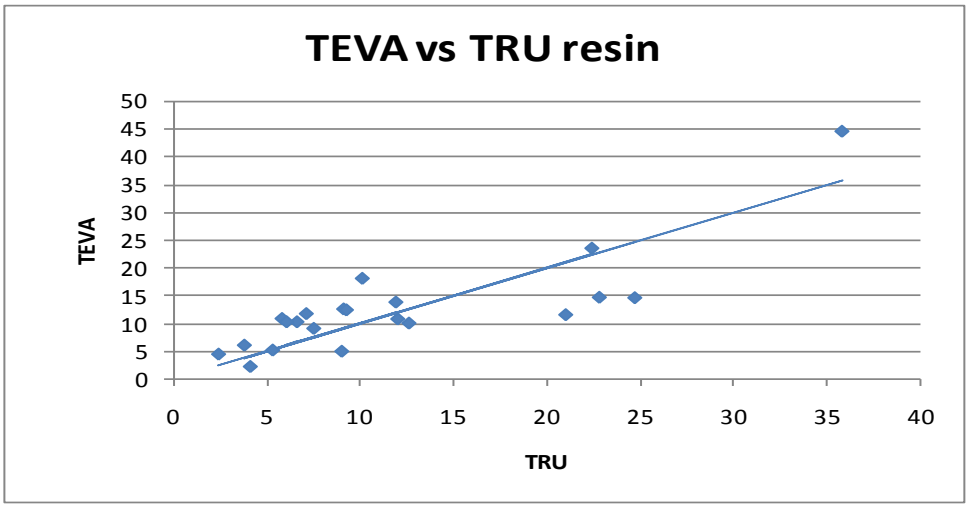


Figure 4-23: Comparison of ^{232}Th results in mine water samples separated on TRU and TEVA resin (solid line represents 1:1 correlation between results obtained with the two different resins)

Data reduction

Ingrowth of progeny of ^{229}Th and ^{228}Th during counting complicates the calculations (Appendix B5). The following thorium isotopes from the natural decay series can be present in the separated Th source:

- ^{234}Th (from ^{234}U): β-emitter. Can affect the yield determination if ^{234}Th is used as tracer, but no daughters will be present after separation.
- ^{230}Th (from ^{238}U): Ingrowth of the daughter ^{226}Ra ($t_{½}$ = 1600 a) after separation will be insignificant.
- ^{232}Th (from ^{232}Th): Ingrowth of the daughter ^{228}Ra ($t_{½}$ = 5.75 a) after separation will be insignificant.
- ^{228}Th (from ^{232}Th): ^{224}Ra ($t_{½}$ = 3.66 d; Eα = 5.69 en 5.45 MeV) will grow in and can interfere in ROI for ^{228}Th (5.42 MeV) and ^{227}Th (5.6-6.03 MeV). The rest of the series will be in equilibrium after a short time. Ingrowth is corrected for by counting ^{212}Po (8.78 MeV).
- ^{231}Th (from ^{235}U): β-emitter. Only low activities present in the sample. No daughters will be present after separation.
- ^{227}Th (from ^{235}U): ^{223}Ra ($t_{½}$ = 11.4 d; Eα = 5.60 and 5.96 MeV) will grow in and interfere with ^{227}Th (5.42 MeV). The rest of the series will be in equilibrium after a short time. Ingrowth is corrected for by counting ^{215}Po (7.39 MeV). Will be present in low concentrations only.

Determination of thorium in a uranium matrix

The analytical procedure described above was adjusted for analysis of Th in ammonium - diuranate (ADU) samples. An additional column separation was required to separate the small amount of Th from the bulk (U) matrix, similar to that described for preparation of ^{234}Th tracer. An aliquot of the sample was dissolved and ^{229}Th tracer was added for yield determination. The solution was loaded onto an anion exchange column to separate the bulk of the uranium. The fraction containing thorium was purified by extraction chromatography using TRU resin. Thorium was co-precipitated with lanthanum fluoride to prepare the source for alpha spectrometry analysis.

The alpha spectra obtained from the thorium analysis are shown in Figure 4-24. The dominant peaks in the spectra are those of ^{230}Th and ^{228}Th. To confirm the ^{228}Th peak, the source was recounted after approximately a week. The second count shows the increase in the peak intensities of decay products of ^{228}Th (^{224}Ra, ^{212}Bi, ^{220}Rn, ^{216}Po) formed from ^{228}Th during spectrum accumulation. From the graphs it was confirmed that Th isotopes were successfully isolated from the bulk of the U matrix.

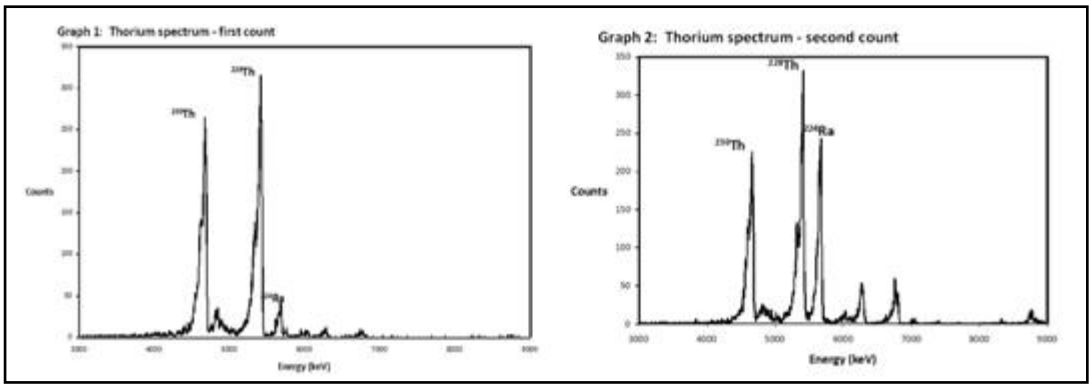


Figure 4-24: Alpha spectrum of thorium in ammonium -diuranate

Determination of thorium in solids for building-and coal industries

Although NAA and gamma spectrometry is the preferred method for analysis of ^{232}Th and ^{228}Th in most solids, alpha spectrometry has been used occasionally. To achieve the required sensitivity in radiochemical procedures, larger sample sizes (5-10 g) are usually required, which limits the use of microwave digestion. However, because of the relatively high activity concentrations present in solids from the building- and coal industries, microwave digestion becomes an option. The use of microwave digestion to prepare samples from the cement industry for radiochemical analysis was evaluated. The samples were analysed for ^{210}Po, ^{232}Th, and ^{228}Th, and the results compared with those obtained by the instrumental nuclear techniques, *i.e*. INAA (^{232}Th), HE gamma spectrometry (^{228}Th) and LE gamma spectrometry (^{210}Pb).

Samples were milled and homogenised after drying overnight at 105 ^{0}C. A Milestone Ethos Touch Control microwave system was used to dissolve a 0.3 gram of sample, including slag, silica fume, gypsum, cement and fly-ash. Use of a mixture of concentrated HCl, HNO_3 and HF in a two-step procedure at 200 ^{o}C proved to be the most satisfactory procedure to dissolve most of the samples. The resulting solution was clear, pale yellow with a small amount of

flocculent precipitate observed in some samples. Dissolution of the silica fume and slag samples were improved by addition of H_3PO_4. This acid is however not compatible with the radiochemical method, since Th will not be retained on TRU resin in 1 M H_3PO_4, with absorption about four magnitudes lower than in 2.5 M HNO_3 (Nour *et al*., 2002). The digested samples were evaporated on a hot plate, filtered and dissolved in the suitable acid medium for radiochemical analysis. The removal of excess quantities of HF and HCl prior to analysis is desirable, because both may interfere with the analytical methods.

A maximum mass of 0.3 g of sample could be digested. The MDA of the method is thus limited to 5-10 $Bq.kg^{-1}$, which is sufficient to evaluate samples against the 500 $Bq.kg^{-1}$ criteria for building material. The average yields of 53% (±16%) and 57% (±14%) for Th- and Po- analysis respectively compared well with yields routinely obtained for water samples indicating negligible losses from digestion. In general, there was good agreement between results obtained by microwave digestion and chemical separation and those obtained using non-destructive nuclear techniques. These results for building material are discussed in more detail in 5.5.

Coal and fly ash samples were digested using a closed microwave digestion procedure as in Table 4-8. For coal samples a clear solution was obtained, but a small amount of undissolved blank materials remained in the fly ash samples. Addition of HF was essential for more complete digestion of the silicates in coal and fly ash. Although the results were promising, the lower results obtained with the radiochemical procedure after microwave digestion compared to the values obtained using non-destructive nuclear techniques suggest that the samples were not quantitatively digested. These results are discussed in more detail in 5.6.

Table 4-8: Digestion procedure for coal and fly ash

Procedure	Reagents	Microwave program
Fly ash	0.25 g sample 1 ml HCl, 7 ml HNO_3, 1.5 ml HF	1: 3.5 min 200 ^oC 2: 3.5 min 200 ^oC 3: 4 min 240 ^oC 4: 20 min 240 ^oC
	Ramping occurs in 4 steps because of very sharp increase in vessel temperature	
Coal	0.25 g sample 6 ml HNO_3, 2 ml HF	1: 10 min 220 ^oC 2: 20 min 220 ^0C

4.8.5 Method for determination of Radium isotopes (^{226}Ra, ^{224}Ra, ^{223}Ra)

The NNR regulatory guide requires analysis of ^{226}Ra and other long-lived alpha emitters at a sensitivity level and accuracy acceptable to the NNR (NNR, 2013). Analysis of ^{228}Ra is not routinely included in the scope of analysis. Determination of ^{226}Ra is commonly performed in ground- and surface water as part of environmental water monitoring for protection of people and the environment. Results for ^{228}Ra are reported on request only by measuring ^{228}Ra via ^{228}Th (1.91 a) after a six month ingrowth period.

Determination of ^{226}Ra

The radiochemical separation method is based on EPA method 903.0 (EPA, 1980) and ASTM method D2460-97 using a radium/barium/lead sulphate precipitation. Similar to these methods pre-concentration of Ra is done by quantitative precipitation of Ra with $Pb(Ba)SO_4$. The precipitate is dissolved with EDTA at pH 8-9 and finally the very fine final $Ba(Ra)\ SO_4$ precipitate is formed by lowering the pH to 4.8 by adding acetic acid.

The activities of the different radium isotopes in the sample are determined by counting the final precipitate by α-spectrometry, measuring the number of counts in the relevant energy regions of the pulse height spectrum. The fraction of Ba (and Ra) present in the sample and recovered in the final precipitate, is determined by adding a known activity of ^{133}Ba tracer to the sample, and measuring the precipitate by GFPC. The theoretical MDA based on a background value of 5 counts, chemical yield of 60%, counting efficiency 16%, counting period of 24 hours and sample volume 500 ml was 0.002 $Bq.L^{-1}$.

The chemical separation process

The co-precipitation of lead, barium and radium can be either enhanced or suppressed by exploiting the following properties:

— The solubility of the respective sulphates differs, as can be seen from the values of their solubility in water at 20 ^{0}C:

$PbSO_4$: 4.25 mg/100 ml

$BaSO_4$: 0.25 mg/100 ml

$RaSO_4$: 0.002 mg/100 ml

— The effective concentration of EDTA, which forms strong complexes with the cations being discussed, can be adjusted by controlling the pH of the solution:

$EDTA^{-} + H^{+} \leftrightarrows$ H-EDTA

By increasing the pH (*i.e.* reducing the concentration of H^{+}) more free EDTA-ions are formed. These will then complex the cation, and increase the solubility of the precipitated sulphate.

— The solubility of the sulphate precipitates can also be manipulated by heating the solution, and by changing the SO_4^{-2} concentration.

During the first phase of the process radium is selectively and quantitatively separated from the bulk of the other dissolved components in solution by adding lead (and barium) carriers, and precipitating these as a mixed sulphate:

$Pb^{+2} + Ba^{+2} + Ra^{+2} + SO_4^{-2} \leftrightarrows Pb(Ba,Ra)SO_4$ *Precipitate* pH = 1.0

Precipitation of Ra is done by addition of citric acid and adjusting the pH to 8-9 with NH_4OH. After addition of Pb and Ba carrier the precipitate is formed by adding ammonium sulphate and lowering the pH to 1 with H_2SO_4. The liquid is stirred continuously while the precipitate is being formed to ensure homogeneous and quantitative precipitation.

This precipitate is purified (from other cations and anions present in the aqueous solution) by washing, and then dissolved again by adding EDTA (as complexing agent) and heating the sample. The solution obtained in this manner now has a smaller volume and is free from all ions that might interfere in the separation process. Washing the sample with dilute sulphuric acid (pH =1) and not with denim water, resulted in a more consistent value for the chemical yield and less sample being lost.

The radium is then co-precipitated on the barium sulphate, leaving the lead carrier in solution. This separation is accomplished by carefully lowering the pH and decreasing the available EDTA-ions.

$Pb^{+2} + Ba^{+2} + Ra^{+2} + SO_4^{-2} \leftrightarrows Ba(Ra)SO_4 + Pb^{+2}$ pH = 4.8

The lead provides a bulky precipitate on which the Ra^{+2} can adsorb during the initial steps, and which can be separated from the large sample volume, and purified with minimal loss. In the subsequent phases it acts as hold-back carrier for the lead isotopes, preventing the radium sulphate precipitate from becoming contaminated with other radioactive lead species *e.g.*

^{210}Pb. This step has been found to be quite critical in the procedure with the yield of 67% at pH 4.8 decreasing to less than 1% at pH 6.

The Ba(Ra)SO_4 precipitate is filtered from the solution and counted. Quantitative collection of the small amount of material (about 0.1 mg of Ba only) presents serious practical problems, and is perhaps the most critical aspect of the method. Every effort is made to minimise this loss by leaving the precipitate for a reasonable time at room temperature to allow the microscopic crystals (that might pass a 0.45 μm filter) to dissolve and larger crystals to grow and removing the precipitate mechanically from the inner walls of the glass container and transferring it quantitatively to the filter.

Data Manipulation

The following isotopes of radium can initially be present in the barium/radium sulphate freshly prepared from a field sample:

^{223}Ra	Decay: α	E:	5.71 MeV (50 %) 5.60 MeV (24 %) 5.23 MeV (10 %)	11.4 d
^{224}Ra	Decay: α	E:	5.49 MeV (5 %) 5.69 Mev (95 %)	3.64 days
^{226}Ra	Decay: α	E:	4.60 MeV (5 %) 479 MeV (95 %)	1600 years
^{228}Ra	Decay: β	Not important for α-spectrometry		

The decay products of these will grow in, and can reach radioactive equilibrium with their precursors if the barium/radium sulphate is allowed to stand for a while. The following α-emitting nuclides should be considered:

ex ^{223}Ra^{219}Rn	E: 6.81 MeV (82 %)	3.9 seconds
^{215}Po	E: 7.36 MeV (100 %)	1.8 ms
^{211}Bi	E: 6.62 MeV (83 %)	2.13 m
ex ^{224}Ra^{220}Rn	E: 6.29 Mev (99 %)	55.6 seconds
^{216}Po	E: 6.78 MeV (99 %)	0.14 seconds
^{212}Po	E: 8.78 MeV (100 %)	0.3 μs and 48 seconds
ex ^{226}Ra^{222}Rn	E: 5.59 Mev (99 %)	3.82 days
^{218}Po	E: 6.00 MeV (99 %)	3.05 minutes
^{214}Po	E: 7.69 MeV (99 %)	164 μs

Self-absorption of the α-particles in the sample causes peak broadening in the spectra, and sometimes creates serious overlap of peaks (*eg.* ^{224}Ra at 5.69 MeV and ^{223}Ra at 5.71 MeV). This situation is aggravated by the peaks from the decay products, which start to grow into the spectrum. The peaks of ^{215}Po (from decay of ^{223}Ra), of ^{212}Po (out of ^{224}Ra) and of ^{214}Po (out of ^{226}Ra) are at much higher energies and relatively free from interference. In the method used, these high energy peaks from the decay products are used to supplement data obtained from the primary nuclides.

Performance study for the implemented method

A solution with nominal activity of (234±8) ^{226}Ra mBq.L^{-1} was prepared and five replicates were analysed by three different analysts. The added tracers (*i.e.* ^{226}Ra and Ba spikes) were weighed to determine the precision and accuracy of the pipetting process, and to quantify the reliability of the volumetric work. The results are presented in Table 4-9.

The agreement between the results obtained by the different analysts was acceptable. The precision on volumetric work was about 0.5 % on average. The standard deviation on replicate analyses (about 10 %) was better than the required precision of 20% required for radiochemical methods. It was however larger than the probable error calculated from counting statistics only (about 4 %) indicating that there are other factors contributing to the uncertainty. This difference cannot be explained by the error on volumetric values (less than 1 % total) or by variation in the yield values (which is compensated for). The average measured ^{226}Ra value of (183 ± 19) mBq.L^{-1} differed by -22% from the certified value of (234 ± 8) mBq.L^{-1} for the control sample.

A set of six control samples were analysed under strictly controlled conditions: on the same day, from the same set of solutions, under the same laboratory conditions (temperature *etc*.), and by the same analyst. The average measured value for the suite was found to be (231±13) mBq.L^{-1}, *i.e.* RSD=5.6 % and error= -1.3 %. The same experiment was repeated with less control (*i.e.* different times and personnel), and the measured value was (217±16) mBq.L^{-1}; RSD=6.8 % and error= -7.3 %. Even though it would appear that the precision of the method can be improved by careful attention to every detail, the results for the control sample analysed at regular intervals since original implementation, as shown in 4.11.1, indicate that the best that can be attained in practice, is still in excess of the probable error calculated from the counting statistics.

Table 4-9: Performance results for determination of ^{226}Ra in water

	Sample	Liquid measured (gram ^{226}Ra spike (1 ml)	Ba spike (3 ml)	Yield	^{226}Ra (mBq.L^{-1})
A	001	1.0285	3.0349	1.05	167 ± 5
	002	1.0308	3.0556	1.10	176 ± 5
	003	1.0217	3.0219	1.06	183 ± 6
	004	1.0427	3.0281	1.11	224 ± 6
	005	1.0211	3.0367	1.09	188 ± 6
	Ave	*1.029 ± 0.008*	*3.035 ± 0.011*		*188 ± 22*
	RSD	*0.76 %*	*0.37 %*		*11.6 %*
B	001	1.0268	3.0535	0.82	174 ± 8
	002	1.0275	3.0238	1.02	171 ± 7
	003	1.0224	3.0393	1.01	191 ± 7
	004	1.0339	2.9856	0.80	187 ± 8
	005	1.0317	3.0304	1.15	136 ± 5
	Ave.	*1.028 ± 0.004*	*3.027 ± 0.023*		*172 ± 22*
	RSD	*0.39 %*	*0.75 %*		*12.6 %*
C	001	1.0320	3.0176	099	187 ± 7
	002	1.0362	3.0201	1.04	173 ± 7
	x003	1.0396	3.0153	0.88	207 ± 8
	x004	1.0424	3.0226	1.12	194 ± 7
	x005	1.0290	3.0170	1.01	188 ± 7
	Ave.	*1.036 ± 0.005*	*3.019 ± 0.003*		*190 ± 12*
	RSD	*0.47 %*	*0.11 %*		*6.5 %*

Chemical Yield determination by measurement of ^{133}Ba tracer

Some loss of precipitate (and of radium) is to be expected in spite of all the efforts discussed. This can be compensated for by determining the chemical yield for barium (*i.e.* the fraction of the carrier recovered in the final precipitate), and by assuming that this value can be applied to the radium too.

Based on the theoretical considerations as discussed in detail in 2.13.13 the decision was made to use ^{133}Ba rather than ^{225}Ra as tracer, especially since the concentrations of ^{224}Ra and ^{223}Ra are estimated simultaneously with ^{226}Ra, and ^{225}Ra daughters occur in the same regions used for estimation. ^{133}Ba is a pure β emitter and does not interfere with the measurement of radium isotopes by alpha spectrometry. A known activity of ^{133}Ba tracer is added to the sample and the same precipitate is measured by GFPC. A correction is made for the

contribution from α-emitting radium isotopes to the gross alpha counts.

The yield determination is subject to error due to uncertainties in the calibration of the gross β-counter. It is therefore better to use a relative approach in which calibration of the counter is eliminated. Calibration samples, which are identical regarding their form and composition to the Ba(Ra) precipitates from the field samples, were prepared by adding the same amount of ^{133}Ba tracer solution (~50 Bq) to a known and relatively large (about 10 mg) amount of Ba^{2+}. Since the calibration samples are not counted by α-spectrometry the limitation on mass of precipitate is not applicable. The calibration sources can be used repeatedly and need only be replaced whenever a fresh labelled barium nitrate solution is prepared. Yield of field samples was determined by relative comparison of observed counting rates with the calibration samples.

Evaluation of historic QC data revealed some problems with this method during routine use. The yield was often overestimated and higher than 100%, resulting in a systematic negative error for the control sample (Table 4-13), as also observed in the results presented in Table 4-9. The possible cause of the overestimation was investigated. One possible explanation is that the final precipitate is not free from lead, and that radioactive lead isotopes (*e.g.* ^{210}Pb and ^{214}Pb) then contribute to the gross beta counting rate. The results of a number of field water samples to which no ^{133}Ba tracer was added showed traces of gross beta activity in some samples, which, when attributed to ^{133}Ba, will result in high yield. This only occurred in highly radioactive samples.

The use of gamma spectrometry to measure ^{133}Ba (as done by many authors – see 2.13.13) may eliminate overestimation of the yield and should be investigated in future work. Counting ^{133}Ba by gamma spectrometry will prevent activity from other nuclides to be erroneously attributed to ^{133}Ba, as in a gross technique. ^{133}Ba has an energy line at 356 keV with high intensity of 60%. Other nuclides occurring at the same energy line have a very short half life with low intensity of less than 0.00010% and will not interfere with the ^{133}Ba spectrum.

4.9 Sensitivity of measurement

When characterizing natural radionuclides in water, food and solids, the question should be: What level of precision and detection capability is required? In Table A2.1 of RG-002 the

NNR specifies suitable techniques and the required sensitivity to be used for analysis. Furthermore RG-002 paragraph 6.8 states that the analysis should be performed at a sensitivity level and accuracy acceptable to the NNR. The mentioned techniques are mostly applicable to solids. No specific LODs for water, as for example in the European council directive for drinking water (Table 2-5), are however mentioned.

To assess the total dose to the public from all sources at the level of 1 $mSv.a^{-1}$, the NNR sets a dose constraint of 0.25 $mSv.a^{-1}$, which requires evaluation of each individual nuclide at a level of 0.025 $mSv.a^{-1}$ (SA government, 1999). The sensitivity of the analytical technique used for measurement of the radioactivity in water and food should be good enough to measure at the level required for dose evaluation. Analytical data obtained with a technique not sensitive enough will have limited value and using a high LOD in dose calculations, as is often erroneously done, may result in an overestimation of the dose and impact. One should only rely on LOD-values for dose calculations, if it results in a "less-than" the acceptable dose.

When deciding on the most appropriate radiometric techniques to be used, it is always important to consider the purpose and application of the data. For example, our laboratory uses two different protocols for determination of gross alpha/beta activity. For analysis of bottled water and samples for the NRMP of the DWS, large volumes of samples are counted for five hours to reach detection limits low enough for the water to be evaluated using the DWS guidelines (DWS, 2007). For water samples from NORM industries gross alpha/beta is used only as complementary technique to control that the "sum-of-nuclides" concentration correlates with the gross value. Therefore the required LOD is not as low as for drinking water and smaller volumes of samples are counted for shorter periods. Typical LOD's are as in Table 4-22. In a study mentioned in 2.5.7 (Leshomo, 2011) it may well be that it was incorrectly concluded that the water from specific boreholes was not suitable for use, because the analytical technique used was not sensitive enough for the intended purpose of the study. The reported MDA's were 1-2 $Bq.L^{-1}$, whereas to comply with DWS guidelines, MDA's in the order of 0.1 $Bq.L^{-1}$ is required. Similarly, with solids the sensitivity requirements are different when evaluating for dose via intake of food than when evaluating against the 500 $Bq.kg^{-1}$ "presence-of- radioactivity" criteria.

4.9.1 Detection limits of radiometric techniques used

The theoretically obtainable detection limits of the various methods/techniques discussed in the previous sections and implemented for use were calculated using equation 2.19 and are summarized in Table 4-21. The theoretical LOD of the radiochemical separation techniques was calculated for a background reading of 4-10 counts, counting time of 24 hours, yield 60%, efficiency 20% and volume of 200 ml. The detection limit of 5-10 $mBq.L^{-1}$for alpha spectrometry was about a factor 50-100 higher than that of 0.1–0.2 $mBq.L^{-1}$ reported by Jia & Torri (2007). In their study a volume of 1 litre of sample was counted for 10 days. Since the MDA depends on parameters such as volume/mass of sample and yield, background counts and counting time, there is a variation in typical LODs mentioned in literature (Table A-4, Appendix A).

Certain assumptions are made when calculating theoretical LODs; therefore the MDA reported during analysis may often differ from the theoretically calculated value. Typical experimental MDA's obtained are shown in Table 4-22.

4.9.2 Sensitivity required for analysis of water samples for dose evaluation

Table 4-10 shows the calculated activity concentration of each individual nuclide that will result in an annual effective dose of 0.025 $mSv.a^{-1}$ using the DCFs listed in Table A-4 (Appendix A). For adults annual consumption of water was taken as 600 L per annum (NNR, 2013). This is the required sensitivity level to evaluate for ingestion of water at a dose of 0.25 $mSv.a^{-1}$.

When comparing the theoretical LODs (Table 4-21) with the required LODs in Table 4-23 it is clear that the instrumental methods are not sensitive enough to evaluate the dose at the required level in water. The estimated dose for intake of water will be overestimated if these methods are used for analysis of water samples, as shown in Table 4-10. From the theoretical evaluation of the sensitivity of the measurement techniques the following can be concluded for water:

— A screening method (gross counting) is not sensitive enough to compare water quality against NNR regulatory criteria for dose assessment.

— Although gamma spectrometry offers cost effective analysis of many radionuclides, poor sensitivities are specifically obtained for ^{232}Th and ^{210}Pb.

— Radiochemical separation; that is individual element separations, will be necessary to provide the required information for most nuclides, even though they are labour intensive.

Table 4-10: Estimated annual effective dose (µSv.a^{-1}) for water calculated with theoretical LODs

	Radiochemical		Instrumental	
Nuclide	**LOD**	**Calculated dose**	**LOD**	**Calculated dose**
^{238}U	0.005	0.135	6	162
^{234}U	0.005	0.147	6	176
^{230}Th	0.05	6.3		
^{226}Ra	0.01	1.68	2	336
^{210}Pb	0.005	2.07	10	4140
^{210}Po	0.005	3.6		
^{235}U	0.005	0.141	6	169
^{231}Pa	0.005	2.13		
^{227}Ac	0.01	6.6		
^{232}Th	0.01	1.38	6	828
^{228}Ra	0.01	4.14	2	828
^{228}Th	0.01	0.432	2	86.4
		28.8		**6730**

4.9.3 Sensitivity required for analysis of food samples for dose evaluation

Table 4-23 shows the calculated activity concentration of each individual nuclide that will result in an annual effective dose of 0.025 mSv, for the different food groups, based on consumption rates as in RG-002. For some nuclides one is faced with a required LOD of 0.1 to 0.5 Bq.kg^{-1} for some of the foodstuffs. Lower LODs are required for food with higher consumption rates (*e.g.* beetroot, cereal). It was observed that although some of the nuclides, specifically ^{238}U, ^{235}U and ^{232}Th can be determined conveniently by NAA, the direct instrumental techniques will be inadequate to provide useful data for the nuclides ^{230}Th, ^{210}Pb, ^{210}Po, ^{231}Pa and probably also for ^{227}Ac and ^{228}Ra without pre-concentration by drying or

ashing. Longer counting times and the application of high efficiency gamma-ray detectors can improve the overall sensitivity, but not easily to the required sensitivity.

The typical LOD for the broad energy detector is from 0.1 to 1 $Bq.kg^{-1}$ (Table 4-21). For dried foodstuffs one may not reach the required sensitivity for ^{210}Pb, ^{228}Ra and ^{232}Th. The sensitivity can be improved by ashing the samples. Depending on the ash/wet ratio the LOD can be decreased to as low as 0.01 $Bq.kg^{-1}$. The necessary sensitivity for most of the nuclides can therefore be obtained by analysing ashed samples on the broad energy detector. However, due to its volatility, pre-concentration by ashing at elevated temperatures is not possible for ^{210}Po, which is a very important nuclide for evaluation of dose via intake of food (5.2). Radiochemical separation after acid digestion is therefore usually required to provide the necessary information for this nuclide. The importance of using analytical techniques with good sensitivity was illustrated in the case studies in Chapter 5 where the use of non-sensitive low energy gamma spectrometry, with a high LOD for ^{210}Pb, resulted in an overestimation of the dose.

Whilst physical properties of the matrix (*i.e*. the actual fresh mass of the material analysed), limit sensitivity of instrumental techniques; radiochemical techniques are limited by the ability to dissolve an adequate amount of material to obtain the required sensitivity for dose evaluation (*e.g*. a maximum mass of three gram of dried fish can be digested using open-vessel microwave digestion).

4.9.4 Sensitivity required for analysis of solids

The legislative exemption level for natural radioactivity in solids is 500 $Bq.kg^{-1}$ (2.2.6). Policy at our laboratory is that the LOD of the radioanalytical technique should be at least a factor 10 lower than this; *i.e.* 50 $Bq.kg^{-1}$. The recommended sensitivity of the NNR is 10 $Bq.kg^{-1}$ for ^{238}U, 4 $Bq.kg^{-1}$ for ^{232}Th and 100 $Bq.kg^{-1}$ for ^{226}Ra, ^{228}Ra, ^{228}Th, ^{210}Pb and ^{40}K (NNR, 2013).

It is therefore not required to measure as sensitive as for foodstuffs and a counting period of a few hours should be adequate. As can be seen from the experimentally obtained MDAs in Table 4-22 all nuclides in solids were measured with the necessary sensitivity using the routine counting conditions (200-300g samples, counting for 2 hours), except for ^{210}Pb.

4.10 Reporting of results

RadioAnalysis routinely reports the activity value (X), the probable error on this value (s), and the minimum detectable activity (MDA). The following conventions are observed when reporting data:

- If $X \geq MDA$: Report the activity value as $(X \pm s)$;
- If $X < MDA$: Report the MDA as a "less than value";

In the tables in Appendix D containing the data used in the case studies in Chapter 5 only the activity concentration values are shown; uncertainty and MDA values are omitted for easier readability. Results for all the daughters of the Uranium-235 and Thorium-232 series are also not shown because the concentrations were mostly insignificantly low compared to those of the Uranium-238 series.

4.10.1 Calculation of activity and MDA

Following the sample analysis process, the activity concentration (in Becquerel, Bq) for each radionuclide is calculated using equation 2.15. The reported activity is corrected for decay using Bateman equations (Friedlander *et al.*, 1981). The detailed activity- and decay calculations are shown in Appendix B. Detection limits are calculated using equations 2.19 and 2.20 based on the Currie formula (Currie, 1968).

4.10.2 Calculation of uncertainty (probable error)

The probable error reported in the data used in the case studies in Chapter 5 is statistical error for individual measured activities (counting uncertainty or square root of counts observed) and not replicate measurements. Counting uncertainty was calculated using equation B1.6 (Appendix B) corresponding to coverage factor k=2.

International guides for expression of uncertainty recommends the use of a combined "all-sources" uncertainty (IAEA, 2004). The impact of each of the input parameters in the equations for calculation of final activity shown in Appendix B on the total measurement uncertainty has to be considered. A "warning" issued in a proficiency exercise is often the result of underestimated uncertainty. Underestimation can be caused when all sources of uncertainty are not considered or when uncertainty in one, major component of the method is decreased (*e.g.* longer counting times). Including the bias or repeatability of the method as

additional sources of uncertainty can result in overestimation. Repeatability (precision) as evaluated in the validation studies refers to the standard deviation of replicate measurements.

During validation of the radiochemical methods the probably error (or total propagated uncertainty, TPU) estimating all contributing factors, was calculated for each of the activity values using the propagation of errors approach. This took into account uncertainties associated with counting of sample and background, mass or volume of sample used, yield determination (tracer), and more indirect contributors such as detector efficiency, radioactive decay and half-life. As an example the uncertainty budget calculation for the determination of ^{210}Po is shown in Table 4-11. The associated uncertainty is the sum of all the uncertainties of all the parameters in the equation:

$$UNC = As\ x \sqrt{\left(\frac{u_{At}}{At}\right)^2 + \left(\frac{u_{It}}{It}\right)^2 + \left(\frac{u_{Is}}{Is}\right)^2 + \left(\frac{u_v}{V}\right)^2 + \left(\frac{u_m}{M}\right)^2 + \left(\frac{u_{\lambda 1}}{\lambda 1}\right)^2 + \left(\frac{u_{C1}}{C1}\right)^2 + \cdots}$$

The calculation includes uncertainty for all decay constants (λ) and ingrowth factors (C) as defined in the activity calculations *e.g.* for the Po method it included decay constants of ^{210}Pb, ^{210}Bi, ^{210}Po and ^{209}Po, as well as ingrowth factors C_1-C_4 (as defined in Appendix B5, and not all shown in this equation).

The calculation in Table 4-11 showed statistical error on counting to be the most significant contributor of error associated with the reported value (97.6%), with uncertainty from the tracer and decay of tracer contributing about 1% to the total. Uncertainty due to decay parameters, mass and volume was negligible. Uncertainty of the peak areas depends on its size – close to detection limits it is typically about 30% and it decrease to less than 1% for well defined peaks. For the example shown, the uncertainty on I_{s2} (with low counts) was 45% and that of I_{t1} (with high counts) 3.8%. Uncertainty of the tracer was 3.1%, volume 0.5% and mass 0.01%. For the efficiency calibration it was about 2%, only contributing in methods not using an internal standard, *e.g.* Ra method.

The presence of other contributors to the uncertainty are indicated when the RSD of replicate analysis (repeatability uncertainty) is constantly much higher than the reported probable error based on counting uncertainty (as shown for Ra in 4.8.5; RSD = 10%, S = 4%).

Table 4-11: Polonium -Typical uncertainty budget for a single measurement of a sample

Symbol	Description	Value	Uncertainty	Contribution %
T (s)	Counting time	86400		
I_{t1}	Nett peak area ^{209}Po, time t_1	706	26.6	0.49
I_{t2}	Nett peak area ^{209}Po, time t_2	556	23.6	0.62
I_{s1}	Nett peak area ^{210}Po, time t_1	12	3.46	28.7
I_{s2}	Nett peak area ^{210}Po, time t_2	5	2.24	68.9
V (L)	Sample volume	0.1	0.0005	0.01
M (g)	Tracer mass	1.0000	0.0001	Negligible
A_t (Bq/g)	Tracer activity	0.0705	0.0022	0.33
λ_1 (h)	Decay constant ^{210}Pb	3.56E-06	3.53E-08	0.03
λ_2 (h)	Decay constant ^{210}Bi	5.76E-03	5.75E-06	Negligible
λ_3 (h)	Decay constant ^{210}Po	2.09E-04	3.02E-09	Negligible
λ_4 (h)	Decay constant ^{209}Po	7.75E-07	3.80E-08	0.83
C_1	ingrowth of Po from Pb in time t_1-t_0	0.14	1.43E-03	0.03
C_2	decay of Po in time t_1-t_0	0.83	2.49E-09	Negligible
C_3	ingrowth of Po from Pb in time t_2-t_1	0.66	6.54E-03	0.03
C_4	decay of Po in time t_2-t_1	0.32	9.77E-1	Negligible
A_s (mBq.L^{-1})	Activity sample at time t_0	8.50		
μ_s(mBq.L^{-1})	Combined uncertainty	4.58		
	Expanded uncertainty (k=2)	9.16		

4.11 Quality Control and Statistical Analysis

Quality and reliability of analytical methods are of significance in the assessment of radioanalytical data (Betti & Aldave de las Heras, 2004). Internal QC is required mainly to check the consistency of results, whereas participation in proficiency testing (PT) is a means of detecting and initiating remediation of any problems arising in the laboratory. RA is an SANAS accredited laboratory, which means that adequate quality control procedures are adhered to. These include regular analyses of control samples where a known quantity of radioactive material is added to a blank sample, as well as participation in internationally organized proficiency exercises.

4.11.1 Statistical Process Control (SPC)

Statistical Process Control was done to evaluate the performance of the radiochemical methods with the objective to spot unhealthy trends, establish the validity of performance standards and propose corrective actions. The trend analysis of the quality control data of a period of 5 years is summarized in Tables 4-12 and 4-13.

Detector background

Background samples are counted every week to check for detector contamination. The specified limit is "*less than 24 counts in 24 hours over the total region*" and "*no more than 5 counts per region of interest*". For data reduction the background counts are subtracted from the sample counts.

Contamination of the alpha spectrometer could result from contamination inherent in the samples or contamination of the geometry rigs or spacer. Some types of samples that are counted on the PIPS detectors consist of loose powder on the filters, and there is some chance that the detector may become mechanically contaminated from these samples. Recoil contamination presents a potential serious problem, but can be minimized by keeping counting time for highly active samples as short as possible. The average detector background counts recorded in all ROIs over the period 2012-2017 was (2±1), which was within the specified limit of 5 counts per ROI, with a maximum of (3.5 ±3.1) recorded in ROI with energy 6.1-6.8 MeV (Table 4-12). Higher counts (up to 68) in this region were observed occasionally, most often for detectors used for counting of Th samples. Despite precautions, contamination of detectors due to recoil from ^{228}Th commonly occurred in the method. The background decreased after sufficient time was allowed for decay of the recoil nuclide ^{224}Ra (3.66 d). Since the recoil peaks do not interfere in the ROIs of Po and U samples, the contaminated detectors can still be used for counting of Po and U sources, while waiting for decay to counts less than 5. The recoil peaks do interfere in the Ra and Th procedures where the specific region is utilized for mathematical corrections.

Using the average background of all ROIs the MDA was calculated as 6.7 mBq.L^{-1} (sample volume 200 ml, efficiency 20%, chemical yield 40%, and counting time 86400s). By increasing the sample volume to 500 ml, and with an improved yield of 60%, the MDA can be lowered to 1.8 mBq.L^{-1}. To maintain this low MDA value, contamination of the detectors should be avoided at all times. Smaller sample volumes should be used to reduce the activity on the counting source, if known or suspected that a sample might contain high activities.

Results for blank samples

The average counts and activities (in mBq) for the method blank samples for the period 2012-2017 are shown in Table 4-12. The activity was calculated assuming a volume of 1, chemical

yield of 0.4 and efficiency of 0.2. The average counts for the method blanks of all nuclides were higher than the detector background, especially for ^{230}Th and ^{234}U. Possible contributors to the blank include detector contamination, added tracers, reagents, glassware and water used for preparing the blank. Another possible cause of contamination could be cross-contamination from field- or control samples during the analysis while samples are stirring, from beakers that are not properly soaked or filtering equipment. The source of the high blank could not always be explained.

Table 4-12: Quality control data for method blank 2012-2017

	N	Counts	mBq	Moving AVE (mBq)
Detector background	732	2.0 ± 1.0		
ROI 6.1-6.8 MeV		3.5 ± 3.1		
^{210}Po	301	9.4 ± 7.9	1.1 ± 1.2	1.83
^{234}U	371	32 ± 45	3.7 ± 2.8	4.89
^{238}U	371	17 ± 15	2.4 ± 2.2	4.59
^{226}Ra	311	5 ± 9	0.8 ± 1.3	0.31
^{232}Th	225	9 ± 9	1.0 ± 1.1	0.87
^{230}Th	225	36 ± 25	4.8 ± 3.4	2.42
^{228}Th	225	11 ± 16	1.1 ± 1.1	0.77

The variation in blank values over the period of evaluation for Th- and U- isotopes is shown as "moving average" graphs in Figures 4-31 and 4-32. The increase in blank for U towards the end of the reporting period as seen from the increase in moving average is of some concern. It is unlikely that the observed counts are caused by an interfering nuclide with an alpha energy similar to that of ^{234}U presenting in the same ROI, since none of the nuclides of interest in water presents in this region. Furthermore, the specificity of the chemical separation procedure has been proved in the validation. Due to the ubiquitous nature of U, it is frequently encountered in analytical reagents (MARLAP, 2004) and will be found everywhere, also in the water standing on the bench, contributing to the blank. The ratio of higher counts of ^{234}U compared to ^{238}U suggests that the blank contamination was not caused by natural U.

The blank for Th fluctuated with some individual high results recorded, but did not show specific periods with increased counts. The high blank values in the ^{230}Th peak can be contributed to tailing of the ^{229}Th peak, which has its main energy of 4.84 MeV rather close

to the peak of ^{230}Th at 4.69 MeV, and therefore interferes when the resolution of the spectrum is poor (Figure 4-25). Selection of the ROIs is critical (and operator dependent), since poor selection may result in a too high blank value for ^{230}Th. After an initial learning curve with a new technician the blank gradually decreased, indicating that experience with this method is essential in order to obtain good results.

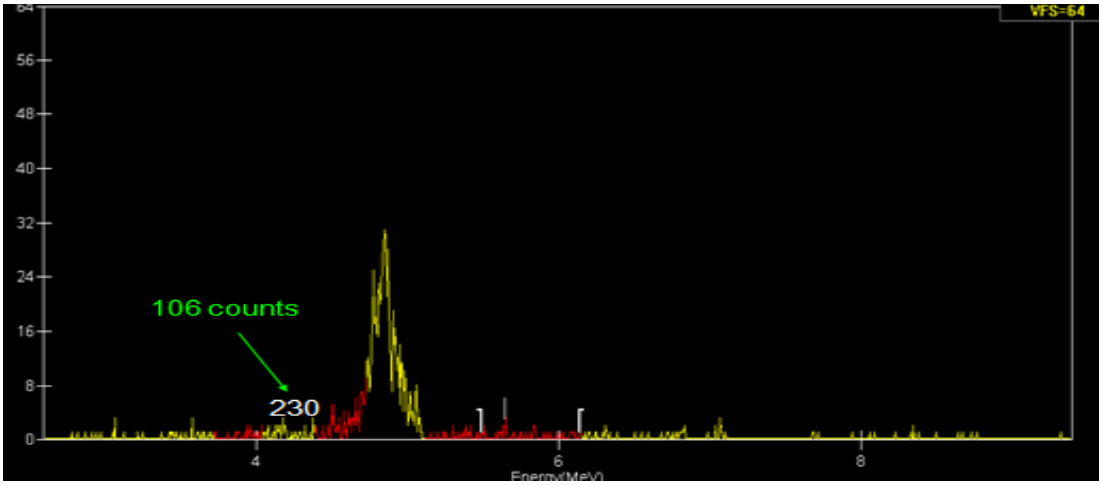


Figure 4-25: Spectrum showing high counts in ROI for ^{230}Th due to overlap from ^{229}Th peak

According to Jia & Jia (2012) the detection limit, or MDA, is mainly affected by the blank activity and not detector background. The reported MDA was calculated using background data. Using the average background in Table 4-12 the MDA was calculated as 6.7 mBq.L^{-1}; using the blank counts for ^{230}Th it can be as high as 22 mBq.L^{-1}.

Results for control samples

Statistics for the control sample analysed from 2012-2016 are summarized in Table 4-13. The RSD gives an indication of the reproducibility of the method over time and the bias is an average for all control samples over the period. Also shown is the percentage of values with deviation > 20% (k=2). The fluctuation of the control samples for U and Th are graphically presented in Figures 4-33 and 4-34 respectively.

The control data for Po showed a large variation. Reproducibility of the data was very dependent on analyst as well as the specific tracer solution used at the time. The method has regularly been out of control, as reflected by the large percentage of outlier values. The reason for this has not been resolved yet. The Ra method seems to be under control. The

average yield over the period was 0.90±0.17 with a maximum of 1.18. This overestimation was the cause of the observed negative bias. To resolve this problem, the use of an alternative radiometric technique for counting of the ^{133}Ba tracer is currently being investigated (4.8.5).

Table 4-13: Quality control data for control sample 2012-2016

Nuclide	N	RSD (%)	Bias (%)	% values > k=2
^{210}Po	266	18-25	-3.4 – +6.4	>30
^{234}U	190	9-16	-9.9 – -1.3	<15
^{238}U	190	7-11	-3.9 – +1.0	<5
^{226}Ra	174	11-14	-12.3 – -1.9	<10
^{232}Th	222	7-11	-11.7 – -3.0	>20

Based on RSD and bias the performance of the U and Th methods was good with precision better than 15%. The precision and accuracy for ^{238}U was slightly better than that for ^{234}U, which can be contributed to the larger variation in blank value for ^{234}U. Also, the expected activity concentration for ^{234}U is not known, but was estimated from historical data. For Th, although within specification, the results were negatively biased. The negative bias may be due to overestimation of the yield (too high counts in the ^{229}Th ROI), resulting in underestimation of activity in the sample. As explained for the blank samples this is caused by counts in the ROI of ^{230}Th erroneously attributed to ^{229}Th because of poor separation of the peaks. The negative bias may be also be due to a small systematic error in preparation of the control sample stock solution, which was prepared from a thorium nitrate salt.

In-house Stability Sample

Water samples received for analysis are usually filtered and acidified within a few days of receipt (4.3.1) and then stored at room temperature until analysed; sometimes being "in-process" for as long as nine months. A large volume "in-house" control sample was prepared in 2013 by combining left-over mine water samples with measurable uranium activity concentrations. This "stability" sample was used to investigate the effect of storage conditions on sample stability. The sample was split into two fractions of which sample A was kept in storage room (temperature 24.5 ^{0}C) and sample B was kept in a fridge (temperature 3 ^{0}C). Such a sample cannot prove the accuracy of the method (because the true concentration is not known), but it can at least demonstrate that there are no changes between batches stored under different conditions over time. The results of monthly analysis of the

sample using the radiochemical procedure for uranium (4.8.2) are shown in Figure 4-26 with averages in Table 4-14.

From Figure 4-26 and Table 4-14 is clear that there was no difference between the results obtained for the two samples and that the sample remained stable for a period of at least 8 months, whether stored at room temperature or in the fridge. The reproducibility for both samples was good with a RSD of less than 10%. Use of the t-test confirmed that there is no significant difference between the two sets of values at the 95% confidence interval. The results obtained for the samples after eight months were still consistent with the initial values, suggesting that the uranium concentration in the water remained stable and that there was no need to refrigerate the samples.

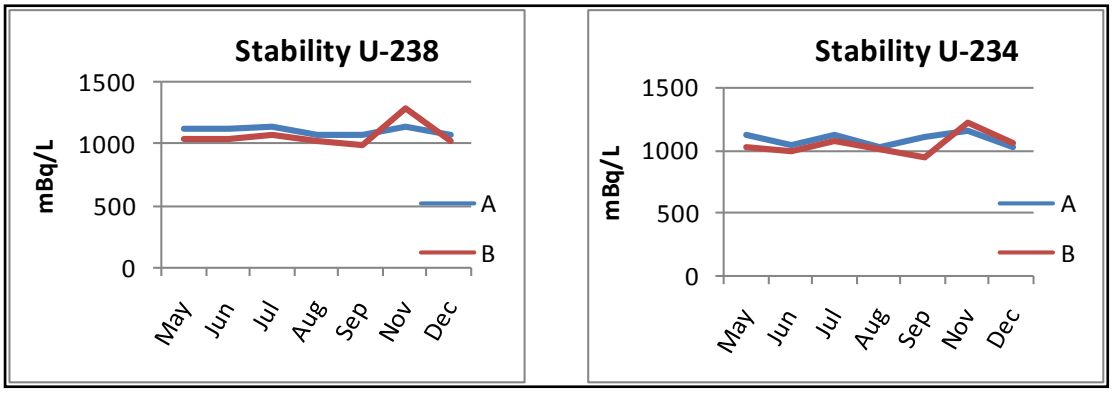


Figure 4-26: Uranium activity concentrations for stability sample fractions A and B

Table 4-14: Average Uranium activity concentrations in stability sample stored under different conditions for 8 months in 2013 (mBq.L^{-1})

Sample	^{238}U		^{234}U	
	A	**B**	**A**	**B**
Average	1100 ± 35 (3.2%)	1060 ± 100 (9.5%)	1090 ± 50 (4.8%)	1040 ± 90 (8.2%)
t calculated	1.51		1.43	
t critical	2.4		2.4	

The stability sample (B) was kept for future use as an in-house control sample, since the matrix is typical of samples received for analysis. The average concentrations obtained in 2013 was used as target value with the associated uncertainty based on the standard deviation of the result. Results obtained in 2014-2017, using UTEVA resin for separation, are shown in Table 4-15. For comparison the sample was also analysed by ICP-MS. The measured mass

concentration was converted to activity concentration using the specific activity of ^{238}U. Sample B was also used in a hands-on training course on determination of uranium; the average result obtained by six different groups showed good comparison with the target value, which was excellent proof of the robustness of the analytical method.

Table 4-15: Uranium concentration in the stability sample used as an in-house control sample (mBq.L^{-1})

		^{238}U		^{234}U	
		Value	**Bias**	**value**	**Bias**
2014	RA, UTEVA	1000 ± 30	-5.5	1130 ± 30	8.2
2014	RA, UTEVA	1200 ± 30	-12.8	1010 ± 27	-3.1
2017	RA, UTEVA	1080 ± 30	2.1	956 ± 25	-8.3
2017	RA, UTEVA	1060 ± 30	-0.24	1080 ± 30	3.6
2014	ICP-MS	1190	11.9	-	
2014	ICP-MS	1100	3.9	-	
2018	Training course	1070 ±210	+0.78	1070 ±170	+2.6

4.11.2 Proficiency Tests (PT)

The laboratory regularly participates in proficiency testing (PT) to maintain ISO-17025 accreditation. Some of the recent results obtained are presented in this section. Samples were supplied by different PT providers including the IAEA in Vienna, the Department of Energy (DOE) in the United States and the National Physics Laboratory (NPL) in the UK. Samples were analysed using the methods discussed in the preceding sections.

The proficiency results were evaluated using three different tests as prescribed in ISO-13528 (2015), *i.e.* relative bias, z-score and u-score or normalized z-score (E_n). Where bias just consider the difference between the two values, the u-score rating takes into account the expanded uncertainty of the reported value at the 95% confidence interval. The criteria for acceptance vary for different providers; the final result was accepted when two out of three tests were in, an outlier with two tests indicated a questionable result and the result was only discarded if all three tests were out.

Acceptance criteria:

Bias: -20 to + 20%

Z: <2 accepted; 2-3 questionable; >3 rejected

E_n: <1 accepted; >1 rejected

MAPEP

Figures 4-27 to 4-30 show the historical performance of the laboratory in the MAPEP PT programme. The graphs show performance for sessions 26-34 from left to right.

- Gross alpha/beta (Figure 4-27 and 4-28): The majority of the results were acceptable.
- U in water by KPA (Figure 4-29): The results for chemical uranium determined by KPA were mostly good with bias <15%, except for S32, which had a very large negative bias; S30 was not reported since the instrument was broken at the time.
- Radiochemical, ^{238}U and ^{234}U in water (Figure 4-30): Although the results were mostly accepted with bias < 20%, it was clearly negatively biased.
- ^{238}U in soil, radiochemical (Table 4-4): Good results were obtained for samples digested in a microwave (S28-29). The negative bias observed for later sessions was probably due to incomplete digestion of the soil samples, as the microwave was not available at the time.
- U in soil, elemental (Table 4-16): The score obtained in this PT depended very much on the isotopic ratio of the uranium present in the sample. Results of both DNC (based on ^{235}U) and NAA (based on ^{238}U) were accepted when the samples were spiked with natural uranium. When spiked with depleted uranium the NAA results were accepted, whereas the value determined by DNC was underestimated, because this technique assumes a natural isotopic ratio for conversion of the measured ^{235}U activity concentration to mass concentration units. U is routinely measured by both techniques even though a natural ratio in most solid samples is expected. If a discrepancy between the two results is observed, the isotopic ratio is determined.

#	Study	Ref Value	Ref Unc	Expt'l Result	Expt'l Unc	Bias (%)	Result Flag	Unc Flag	Notes	Units
1	MAPEP-16-GrW34	0.673	0.011	0.14	0.14	-79.2	N	N		(Bq/L)
2	MAPEP-15-GrW33	0.429	0.007	0.636	0.118	48.3	A	W		(Bq/L)
3	MAPEP-15-GrW32	1.066	0.016	0.908	0.120	-14.8	A	A		(Bq/L)
4	MAPEP-14-GrW31	1.40	0.02	0.817	0.165	-41.6	A	W		(Bq/L)
5	MAPEP-14-GrW30	0.849	0.013	0.824	0.107	-2.9	A	A		(Bq/L)
6	MAPEP-13-GrW29	0.701	0.011	1.43	0.12	104.0	N			(Bq/L)
7	MAPEP-13-GrW28	2.31	0.04	1.77	0.18	-23.4	A			(Bq/L)
8	MAPEP-12-GrW27	1.79	0.03	1.33	0.35	-25.7	A	H		(Bq/L)
9	MAPEP-12-GrW26	2.14	0.03	1.526	0.422	-28.7	A	H		(Bq/L)

Figure 4-27: MAPEP Results for Gross Alpha in water

#	Study	Ref Value	Ref Unc	Expt'l Result	Expt'l Unc	Bias (%)	Result Flag	Unc Flag	Notes	Units
1	MAPEP-16-GrW34	2.15	0.05	2.34	0.24	8.8	A	A		(Bq/L)
2	MAPEP-15-GrW33	3.52	0.16	3.35	0.25	-4.8	A	A		(Bq/L)
3	MAPEP-15-GrW32	2.79	0.15	2.44	0.23	-12.5	A	A		(Bq/L)
4	MAPEP-14-GrW31	6.50	0.19	6.02	0.33	-7.4	A	A		(Bq/L)
5	MAPEP-14-GrW30	4.19	0.16	4.31	0.19	2.9	A	A		(Bq/L)
6	MAPEP-13-GrW29	5.94	0.19	7.82	0.31	31.7	A			(Bq/L)
7	MAPEP-13-GrW28	13.0	0.3	13.9	0.7	6.9	A			(Bq/L)
8	MAPEP-12-GrW27	9.1	0.2	10.2	0.4	12.1	A			(Bq/L)
9	MAPEP-12-GrW26	6.36	0.15	7.274	0.521	14.4	A			(Bq/L)

Figure 4-28: MAPEP Results for Gross Beta in water

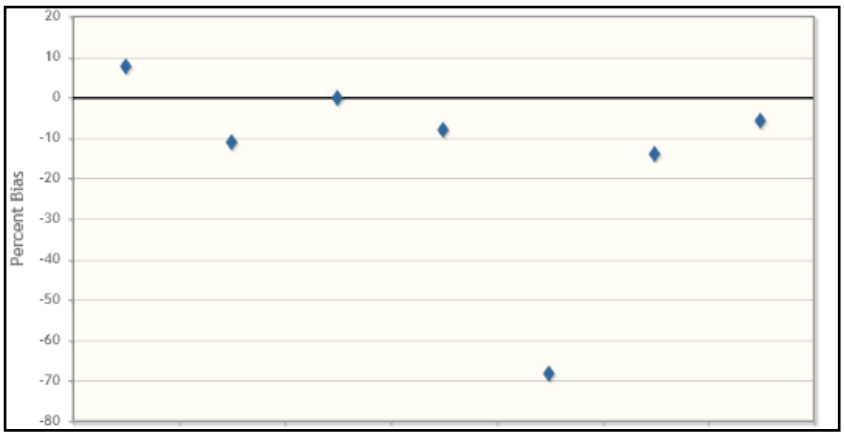


Figure 4-29: MAPEP Percentage bias for U in water by KPA (S27-34 from left to right, S30 not reported)

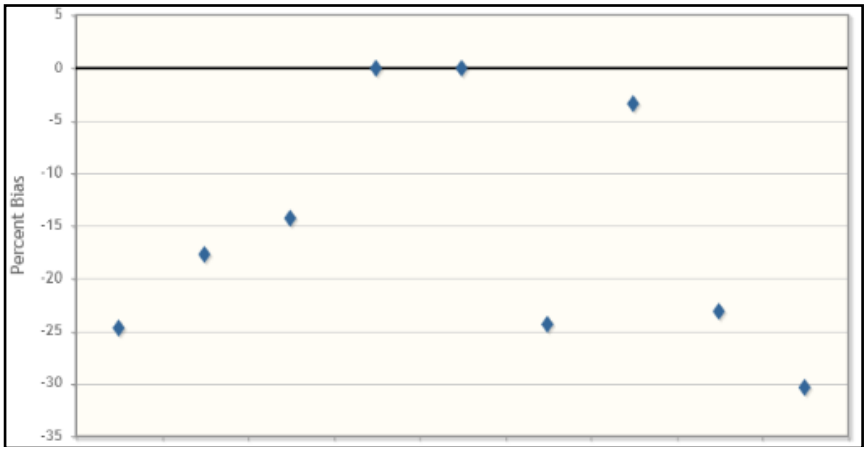


Figure 4-30: MAPEP Percentage bias for ^{234}U in water (S26-34 from left to right)

Table 4-16: MAPEP results for U in soil (µg.L^{-1})

S	Ratio	Method	Ref	Range	Measured	Bias	Evaluation
26	depleted	DNC	25.6	17.9-33.3	9.87±0.17	-61.4	N
		NAA			28.7±4.3	3.1	
27	depleted	DNC	21.2	14.8-27.6	8.72±0.11	-58.9	N
28	depleted	PRS	22.7	15.9-29.5	18.4±1.1	-18.9	A
29	natural	DNC	2.75	1.93-3.58	3.06±0.09	11.3	A
30	natural	DNC	6.7	4.7-8.7	6.30±0.29	-6.0	A
		NAA			7.04±0.39	5.1	
32	depleted	NAA	16.2	11.3-21.1	16.2±0.8	0.0	A
33	depleted	NAA	17.7	12.4-23.0	17.7±0.2	0.1	A
34	depleted	NAA	11.8	8.3-15.3	10.5±0.1	-11.0	A

IAEA and NPL

Tables 4-17 to 4-20 show the historical performance in the IAEA and NPL proficiency test programmes. For the NPL sample (Table 4-17) the results for ^{232}Th, ^{228}Th and ^{238}U were acceptable. The NPL sample is currently used as a CRM for the Th method, which is not often included in PT exercises.

Table 4-17: NPL proficiency test exercise 2015 (Bq.L^{-1})

			RadioAnalysis				
Year	**Nuclide**	**Target**	**Value**	**bias**	**U**	**Z**	**Final**
2015	^{232}Th	4.025 ± 0.076	3.56 ± 0.15	-11.6	-3.01	-1.98	W
2017	^{232}Th	4.025 ± 0.076	3.68 ± 0.16	-3.4	-0.7	-1.3	A
2015	^{228}Th	4.025 ± 0.076	3.53 ± 0.14	-12.3			W
2017	^{238}U	15.22 ± 0.52	15.9 ± 0.3	-5.0	1.2	1.5	A

**Mean of intercomparison (n=15) = 3.807±0.099*

IAEA solids by non-destructive techniques (Table 4-18): Unfortunately, not many results were available, since naturally occurring nuclides are not often included in the IAEA PT. In 2016 the result for ^{226}Ra was accepted but had a large negative bias (~20%). This was due to the fact that the sample was not sealed to prevent escape of radon from the sample, even though ^{226}Ra was reported using the ^{214}Bi peak assuming equilibrium. This was corrected in 2017 after which good results were obtained. Good results were obtained for U, which were analysed by both DNC and NAA. The results showed good correlation, since the samples were spiked with natural uranium.

Table 4-18 IAEA-proficiency test results for solids using non-destructive techniques 2011-2017 (Bq.kg^{-1} dry mass)

			RadioAnalysis				Evaluation		
Year	**Nuclide**	**Target**	**Value**	**bias**	**U**	**Z**	**True**	**Prec**	**Final**
Soil									
2016	^{226}Ra	782 ± 40	618 ± 14	-20.9	-3.87	-1.29	A	N	W
2016	^{234}U	741 ± 80	646 ± 15	-12.8	-1.17	-1.86	A	A	A
2016	^{238}U	708 ± 72	641 ± 15	-9.5	-0.91	-1.20	A	A	A
Carbonate									
2017	^{226}Ra	6970 ± 200	6850 ± 110	-5.6	-1.71	-0.48	A	A	A

Table 4-19: IAEA-proficiency test results for water and solids using radiochemical procedures 2011-2017 (Bq.kg^{-1} or Bq.L^{-1})

			RadioAnalysis				Evaluation		
Year	**Nuclide**	**Target**	**Value**	**bias**	**U**	**Z**	**True**	**Prec**	**Final**
Water									
2010	^{226}Ra	0.86 ± 0.02	0.70 ± 0.023	-18	-5.18	-7.90	N	A	W
2010	^{226}Ra	1.57 ± 0.04	1.29 ± 0.03	-18	-5.60	-7.00	N	A	W
2014	^{226}Ra	14.2 ± 0.06	15.3 ± 0.1	-7.67	9.35	0.61	A	N	W
2014	^{226}Ra	17.9 ± 0.1	16.5 ± 0.1	-7.8					
2017	^{226}Ra	0.86 ± 0.02	0.822 ±0.036	-4.5	-0.9	1.92	A		
2017	^{226}Ra	1.57 ± 0.04	1.61 ± 0.056	2.7	0.7	-1.06	A		
2010	^{234}U	1.3 ± 0.03	1.21 ± 0.03	-6.9	-2.12	-3.00	A	N	W
2010	^{234}U	0.47 ± 0.01	0.459 ±0.020	-2.3	-0.49	-1.10	A	A	A
2014	^{234}U	1.91 ± 0.01	1.99 ± 0.05	4.19	1.57	0.80	A	A	A
2014	^{234}U	2.69 ± 0.02	2.40 ± 0.04	-10.8					
2010	^{238}U	0.70 ± 0.02	0.75 ± 0.025	-6.6	1.44	2.30	A	A	A
2010	^{238}U	0.31 ± 0.01	0.30 ± 0.016	-3.6	-0.58	-1.10	A	A	A
2014	^{238}U	1.98 ± 0.01	2.38 ± 0.05	20.2	7.84	2.67	N	N	N
2014	^{238}U	2.70 ± 0.02	2.64 ± 0.05	-5.4					
Soil									
2011	^{210}Po	42.6 ± 2.2	43.6 ± 4.3	2.3	2.83	0.45	A	A	A
2012	^{210}Po	573 ± 25	460 ± 12	-19	4.07	4.52	A	N	W
2015	^{234}U	46.2 ± 2.5	43.2 ± 1.7	-6.49	-1.05	-0.77	A	A	A
2015	^{234}U	26.4 ± 2	22.2 ± 1.3	-15.9	-1.76	-0.78	A	A	A
2012	^{238}U	23.6 ± 0.7	24.6 ± 1.8	4.2	4.97	9.86	A	A	A
2015	^{238}U	46.4 ± 2.5	41.7 ± 1.7	-10.1	-1.55	-1.07	A	A	A
2015	^{238}U	27 ± 1.4	19.5 ± 1.3	-27.8	-3.93	-1.44	N	N	N

IAEA solids by radiochemical techniques (Table 4-19): Most of the results were accepted. The chemical recovery for all nuclides was better than 40%, which indicates efficient sample preparation. Samples were digested by microwave. One result for ^{238}U was rejected due to a large negative bias indicating some losses during digestion.

IAEA water samples (Table 4-19): For most samples the accuracy was accepted. A warning was issued for some of the final results due to failure of the u-test, indicating either over- of underestimation of the reported uncertainty.

IAEA gross alpha/beta (Table 4-20): Gross alpha/beta values were not formally evaluated by the organizer, but based on the z-score the results were acceptable. Gross beta results in 2017 had a z-score >2, but improved in 2017.The technique of gross alpha/ beta analysis faces many sources of uncertainties leading to a large spread of results (up to two orders of magnitude), in inter-laboratory exercises (Jobbagy *et al.*, 2015).

Table 4-20: IAEA-proficiency test results gross alpha/beta 2016-2017 ($Bq.L^{-1}$)

Year	Nuclide	Target	RadioAnalysis Value	Z	Final
2016	Gross α	58 ± 15	59.0 ± 2.5	0.07	A
2017	Gross α	42.3 ± 6.5	26.6 ± 2.9	-2.42	W
2017	Gross α	10.0 ± 3.2	14.2 ± 1.1	1.31	A
2017	Gross α	13.8 ± 4.3	13.7 ± 1.6	-0.02	A
2016	Gross β	106 ± 20	165 ± 6	2.95	W
2016	Gross β	76 ± 20	134 ± 5	2.90	W
2017	Gross β	38.1 ± 10	40.4 ± 2.5	0.23	A
2017	Gross β	106 ± 19	105 ± 2	-0.05	A
2017	Gross β	28.9 ± 5.7	25.0 ± 1.4	-0.68	A

4.12 Summary of radio-analytical techniques used in the study

In summary - for the case studies presented in Chapter 5 the following protocols were followed to conduct a "full-nuclide" analysis.

4.12.1 Analysis of Solids

After appropriate sample preparation solid samples were routinely analysed for the following:

— Gross alpha/beta analysis

— Uranium and Thorium by neutron activation analysis
— ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K by gamma analysis
— ^{210}Pb by low energy gamma analysis

Gross alpha/beta measurement was used for screening of radioactivity in the samples. Approximately 1-3 g of each milled sample was weighed, pressed into a tarred 47mm planchette and counted for three hours on a gas flow proportional counter. Samples with high activity were counted for a shorter period to avoid contamination of the detector.

For determination of the U and Th element concentrations, sub-samples of approximately 200 mg each were weighed out in specially designed irradiation capsules and irradiated in the SAFARI-1 research reactor for 20 seconds each, together with a thorium and uranium standard (~ 50 µg). The uranium (^{235}U) concentration (µg.g^{-1}) was determined by DNC. For NAA the same samples were cooled for seven days and counted with a 25% relative efficiency well-type HPGe detector. ^{238}U was measured on the 228 keV of ^{239}Np and ^{232}Th on the 312 keV ^{233}Pa gamma line for determination of the thorium concentration (µg.g^{-1}).

For gamma spectrometry a sub-sample of approximately 20-50 grams was analysed on a low-background high energy HPGe detector system with a 20 % relative efficiency. Samples were counted for between 5 to 18 hours each. The spectral data was analysed for the radionuclides ^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K. Samples were sealed and stored for three weeks before counting to allow for radium and its short-lived progeny to reach equilibrium. ^{226}Ra activity concentration was determined through its daughter nuclides ^{214}Pb and ^{214}Bi.

For ^{210}Pb analyses, samples were adjusted to a specific counting geometry for analysis on a 10% relative efficiency coaxial, p-type HPGe gamma detector system with an ultra-thin beryllium window for low energy counting. Sample masses typically ranged from 11-20 g and were counted for eight hours. Absorption corrections were made for each sample by counting a collimated absorption source.

A low-background coaxial, p-type broad energy germanium detector with 50% relative efficiency, and much better sensitivity than the low and high energy counting systems, was used for the analysis of food samples. Ashed samples of approximately 50-70 g were counted for two hours; dried samples were counted for 5-18 hours depending on the mass of sample available. The spectral data was analysed for the radionuclides in the uranium and thorium

decay series (^{238}U, ^{226}Ra, ^{210}Pb, ^{235}U, ^{232}Th, ^{228}Ra and ^{228}Th). For samples where the LOD of gamma spectrometry was not low enough for the intended purpose (*e.g.* when the dose via food intake has to be evaluated), ^{210}Po (and ^{210}Pb) was determined by alpha spectrometry after suitable digestion of the sample.

4.12.2 Analysis of Liquids (Water and solids after digestion)

A "full-nuclide" or "nuclide specific" analysis for water samples entailed the following:

- Gross alpha/beta analysis
- Uranium isotopes by radiochemical separation and alpha spectrometry
- Thorium isotopes by radiochemical separation and alpha spectrometry
- Radium isotopes by radiochemical separation and alpha spectrometry
- ^{210}Po and ^{210}Pb by radiochemical separation and alpha spectrometry

Gross alpha/beta screening was done on most water samples. An appropriate aliquot of the sample was evaporated onto a planchette and counted on a GFPC. For samples received from NORM industries, an aliquot of 25-50 ml was used and the samples counted for 20 minutes; for screening for compliance to WHO regulations (*e.g.* bottled water and DWS samples) a larger aliquot of up to 300 ml was used and the samples were counted for at least five hours.

The Uranium elemental concentration was determined by KPA (Chemcheck Instruments Inc, model KPA-11 instrument). For direct measurement a one ml sample aliquot was mixed with enhancing agent and injected into the KPA cell. Light emitted by uranium when excited by a laser was measured and converted to uranium concentration. Samples with high uranium concentrations were diluted before analysis. Samples containing high levels of interfering substances were either diluted or pre-treated with concentrated nitric acid and peroxide before analysis.

The individual nuclides were measured by alpha spectrometry after radiochemical separation. An appropriate tracer was added to determine chemical yield. For determination of polonium ^{209}Po was added, for uranium ^{232}U, for thorium ^{229}Th and for radium ^{133}Ba. The activity on the prepared sources were measured by counting for 24 hours on a Canberra Alpha Analyst spectrometer equipped with passivated implanted planar silicon (PIPS) detectors with an active area of 450 mm^2.

Polonium was separated by spontaneous deposition onto a silver disc. A silver disc was added to a 200 ml sample aliquot, acidified with hydrochloric acid. After addition of hydroxyl ammonium chloride the sample was heated and stirred for 3-4 hours to allow for spontaneous deposition. The disc was removed and the alpha activities of ^{209}Po and ^{210}Po were measured with α-spectrometry. The plating and counting were repeated after 3-4 months of storage of the solution to measure the ingrowth of ^{210}Po from ^{210}Pb and calculate the ^{210}Pb concentration in the original sample.

Radium was separated by a method of $BaSO_4$ co-precipitation. Radium was separated from bulk material, together with barium as a sulphate. A 500 ml aliquot of sample was used. The precipitate was counted by alpha spectrometry and by gross beta counting to determine the chemical yield of the separation procedure. Thorium and Uranium were separated from interfering nuclides on a solid-phase extraction column (Eichrom TruResin), followed by a cation exchange separation; recently changed to separation using UTEVA (for U) and TEVA (for Th). A 200 ml aliquot of sample was pre-concentrated by evaporating to a small volume. Two separate aliquots were used for U and Th analysis. The final eluate was deposited onto a filter paper using LaF_3 precipitation and then counted with alpha spectrometry.

The same procedure as for the water samples was followed for solids such as foodstuff and building material, after suitable digestion and filtration.

4.12.3 Equilibrium assumptions

The following equilibria were assumed for solid samples (actual measured nuclide in bold):

Uranium-238 Series

- **^{238}U** is in equilibrium with its daughters up to ^{230}Th (the last may be questionable)
- ^{226}Ra is in equilibrium with all its short-lived daughters (**^{214}Pb,^{214}Bi)**
- ^{210}Bi and ^{210}Po in equilibrium with **^{210}Pb**.

Uranium-235 Series

- **^{235}U** is in equilibrium with its daughters up to ^{231}Pa
- ^{223}Ra is the equilibrium activity of ^{227}Ac and its daughters

Thorium-232 Series

- **^{232}Th**

— ^{228}Ra is in equilibrium with its daughter **^{228}Ac**

— ^{224}Ra is the equilibrium activity for ^{228}Th and its daughters (**^{212}Pb,^{212}Bi)**

4.13 Conclusions

In this section, the experimental development and implementation of radiometric techniques for the measurement of natural radioactivity at the radio-analytical laboratory at NECSA was presented. Both non-destructive and radiochemical methods were included, although the focus of development was primarily the radiochemical methods. Attention was paid to the required sensitivity of the measurement to obtain meaningful results. Through the analysis one should be able to evaluate exposure, not to exceed a lifetime average exposure to the general public of one milli-Sievert per year

Although the primary application for the radiochemical methods was analysis of water samples, applications for some other matrices have been evaluated. The radiochemical methods were adequate for determination of individual nuclides of interest at a level of 0.005-0.01 Bq.L^{-1} with a precision and accuracy of better than 20%. Analyses at low levels were however limited by the high counts obtained for the blank samples. Long-term performance of the methods was evaluated by reviewing the QC results and performance in PT exercises.

The focus of the next chapter (Chapter 5) is on the implementation of these methods for analysis of samples from various NORM industries.

Table 4-21: Radio-analytical techniques implemented for routine analysis of NORMs

Description	Nuclides		*LOD ($Bq.kg^{-1}$)
DESTRUCTIVE TECHNIQUES			
Radium in water and urine samples: — Radiochemical separation using $BaSO_4$ co-precipitation — Alpha spectrometry — 500 ml sample, 24 hours counting	^{226}Ra, ^{224}Ra, ^{223}Ra	α	0.002
Polonium-210 in water: — Radiochemical separation using spontaneous deposition on Ag discs. — For ^{210}Pb: Second deposition after in-growth period of > 3 months — Alpha spectrometry — 200 ml sample, 24 hours counting	^{210}Pb, ^{210}Po	α	0.005
Polonium-210 in vegetation: Microwave digestion of solid samples is required. — Radiochemical separation using Ag discs — Alpha spectrometry — 2 g sample, 24 hours counting	^{210}Pb, ^{210}Po	α	5
Thorium isotopes in water : — Radiochemical separation using TEVA resin — Alpha spectrometry — 200 ml sample, 24 hours counting	^{232}Th, ^{228}Th, ^{227}Th(^{227}Ac), ^{230Th}	α	0.005 0.005 0.050 (^{230}Th)
Uranium isotopes in water : — Radiochemical separation using UTEVA resin — Alpha spectrometry — 200 ml sample, 24 hours counting	^{238}U, ^{235}U, ^{234}U	α	0.005
Uranium in water by Kinetic Phosphorescence Analysis.	U		0.05 $\mu g.L^{-1}$
Uranium in urine by Kinetic Phosphorescence Analysis.	U		0.1 $\mu g.L^{-1}$
Gross alpha/beta analysis			
Gross alpha/beta solids (3.5 g)	α/β		1000/100

Description	Nuclides	*LOD ($Bq.kg^{-1}$)
Gross alpha/beta water (V=50 ml, t=30 min)		1.4/2.2
Low gross alpha/beta environmental samples (V=300 ml, t=300 min)		0.1
NON-DESTRUCTIVE TECHNIQUES		
Measurement of the gamma-activity of a sample using a solid state detector in the Genie-PC system.	^{226}Ra, ^{228}Ra, ^{228}Th (and ^{40}K)	ϒ 2
— High energy gamma spectrometry		
— Presence of U may interfere with direct determination of ^{226}Ra.		
— ^{226}Ra is determined indirectly by measuring the progeny (^{214}Pb, ^{214}Bi) after 3 weeks gas-tight sealing to ensure equilibrium.		
— LOD obtained with well shielded, high resolution detectors and counting time of a few hours		
— 200-300 g sample, 2 hour counting		
Lead-210	^{210}Pb	ϒ 10-100
— Low energy gamma spectrometry (25g sample)		
— Self-absorption corrections required.		
Gamma emitters		ϒ 0.1-1
— Broad energy gamma spectrometry (on dried or ashed sample)		
Determination of Uranium and Thorium by Neutron Activation Analysis.		α
INAA	U-238	6
Direct measurement	Th-232	4
200 mg sample		

**LOD indicated in the table was obtained from the RA service portfolio and is an approximate value only. In radiometric techniques the LOD is a function of the method and can be tailored (lowered or increased) by adjusting parameters such as sample size and counting time if required. LODs reported during analysis may therefore vary from this. The average measured LODs obtained during the analysis of samples in the case studies are shown in Table 4-22.*

Table 4-22: Typical experimental MDAs reported for routine jobs

	Solids (Bq.kg^{-1}) – soil etc.	**Solids (Bq.kg^{-1}) –phosphates**	**Food (Bq.kg^{-1}) wet weight**	**Water (Bq.L^{-1}) DWS nuclide specific**	**Water (Bq.L^{-1}) Bottled water screening**
Radiometric technique	High energy gamma, NAA	High energy gamma, NAA	Broad energy gamma, NAA, alpha (^{210}Po)	Alpha spec	Gross alpha/beta
Conditions	NAA: 200 mg ϒ: 300g, 2h Low: 25 g	NAA: 200 mg ϒ: 300g, 2h Low: 25 g		200ml, 24 h counting	50-300ml, 300 min counting
N	140	70	50	308	289
^{238}U	0.55 ± 0.23	0.52 ± 0.18	1.75 ± 2.17 [0.01-9.8]	0.0029 ± 0.0075	-
^{234}U	0.55 ± 0.23	0.52 ± 0.18	1.75 ± 2.17 [0.01- 9.8]	0.0033 ± 0.0099	-
^{230}Th	-	-	-	0.0178 ± 0.0159	-
^{226}Ra	30.1 ± 19.6	19.7 ± 10.5	1.90 ± 3.02 [0.086- 16]	0.0025 ± 0.0019	-
^{210}Pb	123 ± 52	110 ± 21	0.64 ± 1.02 [0.009- 4.8]	-	-
^{210}Po	-	-	0.30 ± 0.37 [0.010- 1.9]	0.0034 ± 0.0033	-
^{235}U	0.025 ± 0.010	0.023 ± 0.008	0.20 ± 0.35 [0.0004- 1.6]	0.00038 ± 0.00074	-
^{227}Th	-	-	-	0.0061 ± 0.0049	-
^{232}Th	3.27 ± 2.78	5.18 ± 1.98	1.27 ± 1.92 [0.007- 8.6]	0.0032 ± 0.0037	-
^{228}Ra	49.1 ± 34.3	31.6 ± 20.9	1.87 ± 2.59 [0.010- 9.6]	-	-
^{228}Th	84.4 ± 57.9	27.2 ± 25.8	1.44 ± 2.16 [0.014- 7.6]	0.0042 ± 0.0037	-
^{40}K	209 ± 148	120 ± 104	-	-	-
Gross α	1172 ± 861	364 ± 258		0.407 ± 0.233	0.072 ± 0.035
Gross β	115 ± 79	37 ± 15		0.616 ± 0.292	0.162 ± 0.255

Table 4-23: Nuclide specific water (Bq.L^{-1}) and food concentrations (Bq.kg^{-1}), which will result in a dose of 0.025 mSv.a^{-1} based on consumption rates and dose conversion factors as indicated

Nuclide	DCF adult (Sv.Bq^{-1})	Root veg	Leafy veg	Fruit	Cereal	Fish	Chicken	Meat	Water
Consumption (kg.a^{-1})		170	55	75	250	25	50	75	600
U-238	4.50E-08	3.27	10.1	7.41	2.22	22.2	11.1	7.41	0.926
U-234	4.90E-08	3.00	9.28	6.80	2.04	20.4	10.2	6.80	0.850
Th-230	2.10E-07	**0.70**	2.16	1.59	**0.48**	4.76	2.38	1.59	0.198
Ra-226	2.80E-07	**0.53**	1.62	1.19	**0.36**	3.57	1.79	1.19	0.149
Pb-210	6.90E-07	**0.21**	**0.66**	**0.48**	**0.14**	1.45	**0.72**	**0.48**	0.060
Po-210	1.20E-06	**0.12**	**0.38**	**0.28**	**0.08**	**0.83**	**0.42**	**0.28**	0.035
U-2 35	4.70E-08	3.13	9.67	7.09	2.13	21.3	10.6	7.09	0.887
Pa-231	7.10E-07	**0.21**	**0.64**	**0.47**	**0.14**	1.41	**0.70**	**0.47**	0.059
Ac-227	1.10E-06	**0.13**	**0.41**	**0.30**	**0.09**	**0.91**	**0.45**	**0.30**	0.038
Th-232	2.30E-07	**0.64**	1.98	1.45	**0.43**	4.35	2.17	1.45	0.181
Ra-228	6.90E-07	**0.21**	**0.66**	**0.48**	**0.14**	1.45	**0.72**	**0.48**	0.060
Th-228	7.20E-08	2.04	6.31	4.63	1.39	13.9	6.94	4.63	0.579

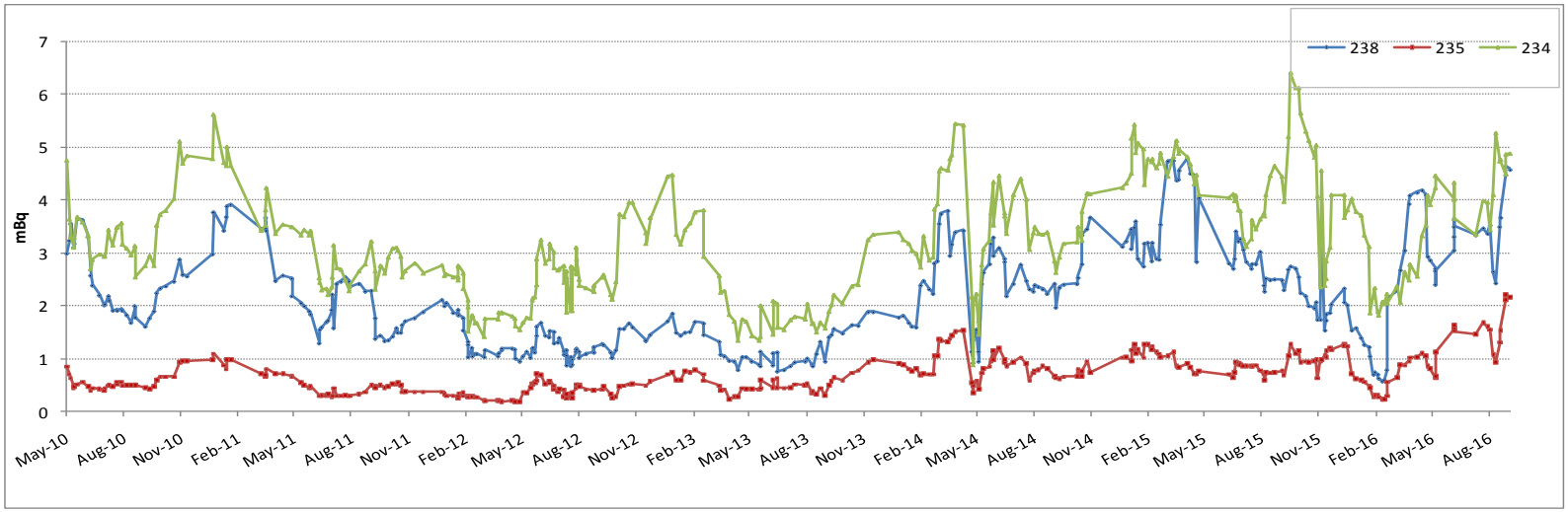


Figure 4-31: Moving average of U blank from 2010-2016 (mBq)

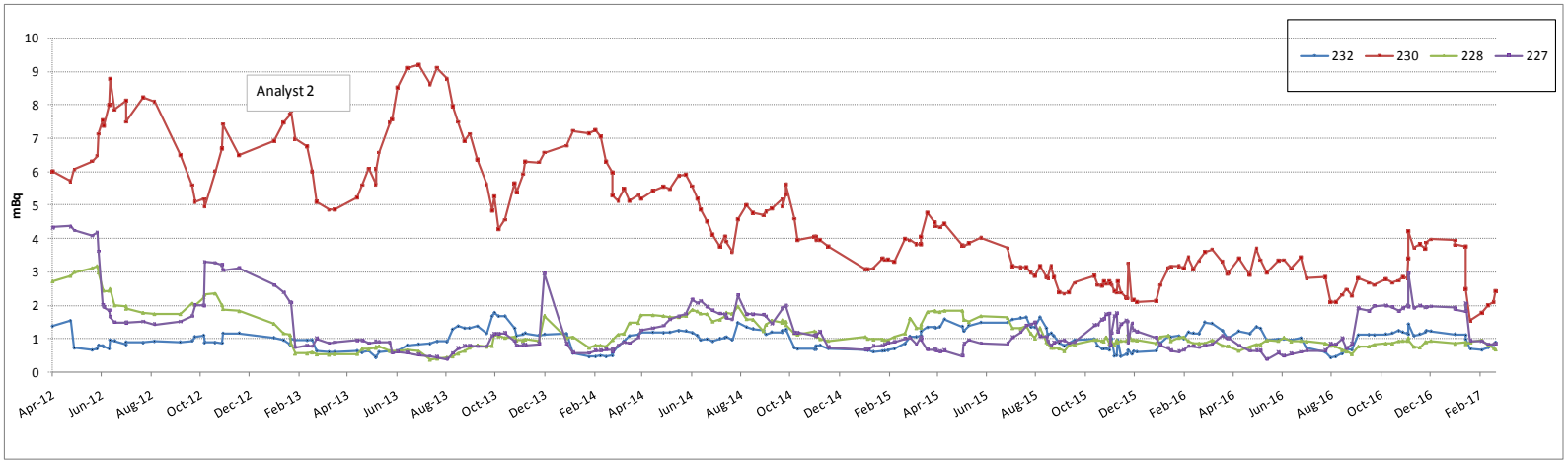


Figure 4-32: Moving average of Th blank from 2012-2017 (mBq)

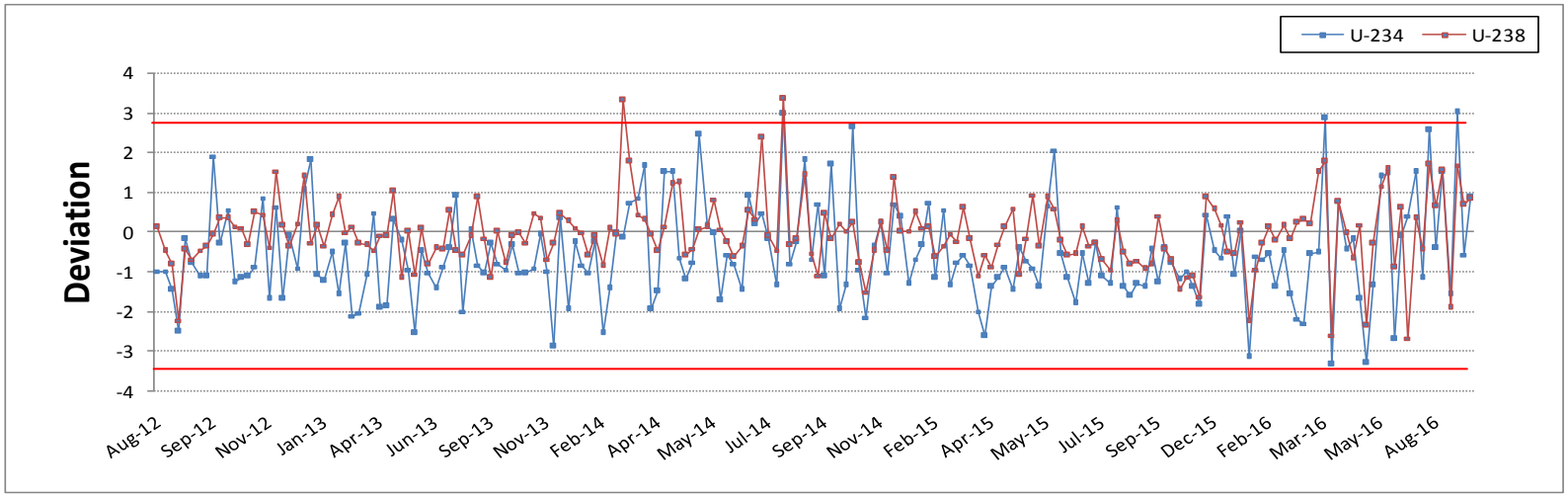


Figure 4-33: Quality control chart ^{238}U and ^{234}U control sample 2012-2016

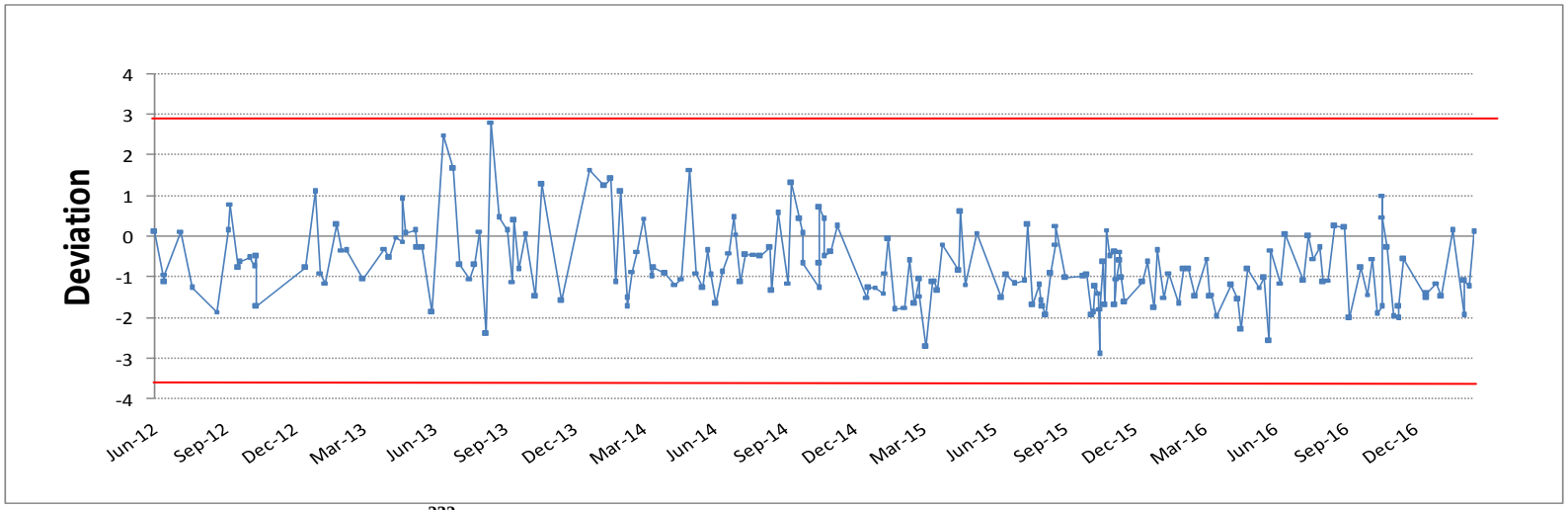


Figure 4-34: Quality control chart ^{232}Th control sample 2012-2016

Chapter 5 CASE STUDIES FROM THE NORM INDUSTRY

Most NORM industries in South Africa have monitoring programmes to ensure compliance with all applicable legislation, standards, guidelines and licence conditions. The main aim of Chapter 5 is to present the results of samples submitted for analysis by various NORM industries over a period of 5-10 years as part of these monitoring programmes. The results are used in case studies to assess the radiological impact on humans and non-human biota that may be exposed to radiation from mining- and mineral processing activities, as well as consumption of contaminated water and foodstuffs.

The analytical techniques discussed in Chapter 4 were used for analysis. The focus of this thesis is to demonstrate how analytical techniques can be applied for radiological evaluations in the NORM industry, and not necessarily on the radiological impact assessment itself. In most of the presented case studies the origin of the samples could not be disclosed due to client confidentially; results are therefore presented in a general manner except where samples were received from independent entities.

5.1 Natural radioactivity in water

5.1.1 Introduction

Water intake, as an essential part of the human diet, may contribute to natural radioactivity exposure, although the contribution is typically very small and can be controlled and restricted by safety regulations. Human industrial activities may increase the radiation contribution from water, therefore radiometric investigation of drinking water and the associated dose estimation are important in environmental studies. Radioactive discharges from mining- and mineral operations, which can affect water quality, should be controlled and monitored to ensure that exposure of any individual using the water does not exceed the allowable dose limit. The risk from consumption must be evaluated against the average natural background exposure of 2.4 $mSv.a^{-1}$.

The WHO, US EPA and EU had issued regulations on drinking water (2.2.7). Many countries worldwide have adopted the WHO guidelines and implemented radioactivity monitoring

programmes to check the quality of drinking water. Countries belonging to the EU will be expected to follow the regulations set out by the directive of 2013 (EU, 2013a). In SA no official regulations enforcing monitoring of radioactivity in drinking water existed at the time of this study although limits based on international guidelines were set by South African institutions *e.g.* SANS (see Table 2-7). The South African Department of Water and Sanitation (DWS) controls water quality in SA. A national monitoring programme for radioactivity (NRMP) has been established in identified catchment areas to assess the radiological quality and impact on the public using these water sources as part of their dietary intake (DWS, 2006). The NRMP has been continued, of which some of the latest data are presented in this case study. With the exception of the NRMP survey, which is limited to specific catchments, monitoring of the radioactivity of all sources of drinking water in SA on a national level is not done routinely.

In this work the results of the radioactivity analysis of water samples submitted for assessment of radiological quality, are presented. The focus was on three types of water, *i.e*. bottled (mineral) water, groundwater and surface water. The main aim of the studies reported on in this section was (1) to ascertain the radiological quality of different sources of water in South Africa, specifically with regard to human use (2) to determine the potential dose from the water sources (3) to demonstrate the use of the radio-analytical techniques developed and implemented (Chapter 4) for the accurate determination of uranium, thorium, radium, and polonium isotopes in water. For this purpose, the concentrations of the most important α-emitters, *e.g*. ^{234}U, ^{238}U, ^{230}Th, ^{223}Ra, ^{224}Ra, ^{226}Ra, ^{210}Po and ^{210}Pb were measured by alpha spectrometry, and the dose contribution estimated. The data may contribute for establishment of natural radioactivity baseline levels for water sources in South Africa.

5.1.2 Experimental

Sampling and sample preparation

Samples were received from bottling water companies, water suppliers and various NORM industries. Samples volumes of 2 L were collected in high density polyethylene bottles and preferably transferred to the laboratory on the same day of collection for filtration within 24 hours. Samples were filtered using both 8 and 0.45 µm membrane filters, and then acidified to pH < 2. The filtered samples were returned to the container. The suspended solids (retained on the 0.45 µm filter) were kept for analysis of gross alpha/beta activity when required.

Radioactivity Analysis

The radio-analytical techniques, as discussed in Chapter 4, were used. For gross alpha/beta determination an aliquot of the sample was evaporated and the residue counted on a low-background GFPC for 0.5 to 5 hours per sample, depending on the required detection limit. The Uranium elemental concentration of some samples was determined by Kinetic Phosphorescence Analysis (KPA). Analyses of the individual nuclides of U, Th, Po and Ra were performed by radiochemical procedures summarized in 4.12.2. A very specific protocol was developed for drinking water and analysis of samples for the DWS-NRMP (4.4.1).

The TDS content was determined during preparation of the water samples for gross alpha/beta analysis. It gives some indication of the water quality and is used to determine the appropriate volume of water to evaporate (4.4.1). TDS was measured using a conductivity metre as well as gravimetrically, using the dry residue value (Eaton *et al.*, 1999).

Interpretation of results

In the case studies presented in this section screening results as well as results for full nuclide analysis, where applicable, are presented.

The same approach as suggested in international regulations was followed. Water sources were screened by analysing for gross beta (GB) and gross alpha (GA) activity. Because these concentrations are often extremely low, the analysis results carry a significant margin of error, which has to be taken into account. The criterion for passing the screening test was that "Result+Uncertainty" should not exceed either of the recommended screening levels for beta (1 $Bq.L^{-1}$) or alpha (0.5 $Bq.L^{-1}$) activity. If this was the case, the water was radiologically acceptable, no further analyses were required and it conformed to specification. Only those sources that exceeded the screening levels had to be examined in more detail for an accurate dose evaluation based on the specific radionuclide levels found.

The measured individual radioactivity concentrations were used to calculate the annual ingestion dose using the lifetime age-weighted approach equation 2-1, also showing the dose values for the adult and infant groups (2.3.5). All nuclides in the series were used in the dose calculation, assuming equilibrium for those not specifically measured. The dose conversion factors recommended by the ICRP (1996) was used (Table A-5, Appendix A). Water

consumption was based on annual intake as in RG-002 (NNR, 2013) (see Table A-8, Appendix A). The lifetime average annual dose is the sum of all doses with proportional contribution for the different age groups. The most popular approach is to use the lifetime age-weighted dose, while also showing the dose for all age groups. More conservatively only the dose to the most sensitive user (infants younger than a year) can be used.

A combination of NNR, DWS and international guidance documents was used to assess the concentrations of natural nuclides in terms of their potential radiological hazard. The water was categorized based on the DWS Guidelines (DWS, 2007), and was also evaluated using the guidance provided in WHO, EPA and EU regulations (2.2.7). According to these guidelines, water which may result in exposure of more than 0.1 mSv per annum should be investigated. The NNR required a single facility/source dose constraint of 0.25 mSv per year for evaluation. Where applicable, concentrations were compared to guidance levels provided by WHO (Table 2-4) and the EU (Table 2-5).

Uranium is a special case, since it also operates as a heavy metal in the body and needs to be limited in drinking water, mainly due to its chronic effects on the kidneys at a lower level than its radioactivity would require. The SANS limit of 30 $\mu g.L^{-1}$ for uranium was used for evaluation. Using the specific activity of U and assuming a global average ratio for $^{234}U/^{238}U$ (typically ~2), ^{234}U was calculated from the chemical U concentration when not specifically measured.

5.1.3 Bottled water

In many countries worldwide radiological surveys have been done by the relevant government agency, such as the food standard agency, to determine concentrations of uranium and natural radioactivity in bottled-, mineral- and spring water. As mentioned in the literature review (2.5) no published radiometric data on bottled water in South Africa could be found.

A monitoring program was designed by a SA bottling company to assess the radiological quality of samples of bottling plants in compliance with international standards. The program covered more than 150 bottling plants in Africa. Although no formal legislation existed in SA at the time of this study, beverage producers interested to export to Europe will probably be forced to comply with international regulations in future. There had been an attempt over the

last few years to document legal requirements in SA. A draft document specifying limits for radioactivity to be used by SANBWA members has been drawn up but has not been issued to date (SANBWA, 2012).

Samples

Batches of 6-8 samples were submitted for analyses at two monthly intervals. For operational bottling plants a number of bottles from a typical batch were send for analysis. Samples included treated water as well as packaged water from the different plants; both final products and water from the source of bottling were analysed. Mineral and spring waters bottled by the SA producer were obtained directly from the distributor. Due to client confidentiality no specifics as to origin of the samples can be disclosed.

Assessment

In the absence of specific SA legislation, legislation applicable for European countries was used. The assessment was done as follows: (1) Initial screening for gross alpha/beta activity; (2) analysis of individual nuclides in samples exceeding screening levels, for dose evaluation. This is similar to the process followed by most European Countries.

For gross alpha/beta analysis an aliquot of sample was evaporated and the residue measured by GFPC. The routine gross alpha/beta technique was adapted to reach low enough detection limits for screening (4.4.1). The experimentally obtained MDA was 0.072 ± 0.035 and 0.162 ± 0.255 $Bq.L^{-1}$ for gross alpha and beta determination respectively (see Table 4-22). These low levels were achieved by using a large volume of sample (300 ml) and counting the sample for five hours. The values are an order 10 lower than the required screening limit and the analytical method can thus be considered as suitable for use.

Results and discussion

The dry residue value ($mg.L^{-1}$) of the water samples is shown in Figure 5-1. The majority belong to the high-mineral class (50-500 $mg.L^{-1}$), while only some were classified as low-mineral (< 50 $mg.L^{-1}$). All values were below the SANS acceptance limit of 1200 $mg.L^{-1}$ (SANS, 2015).

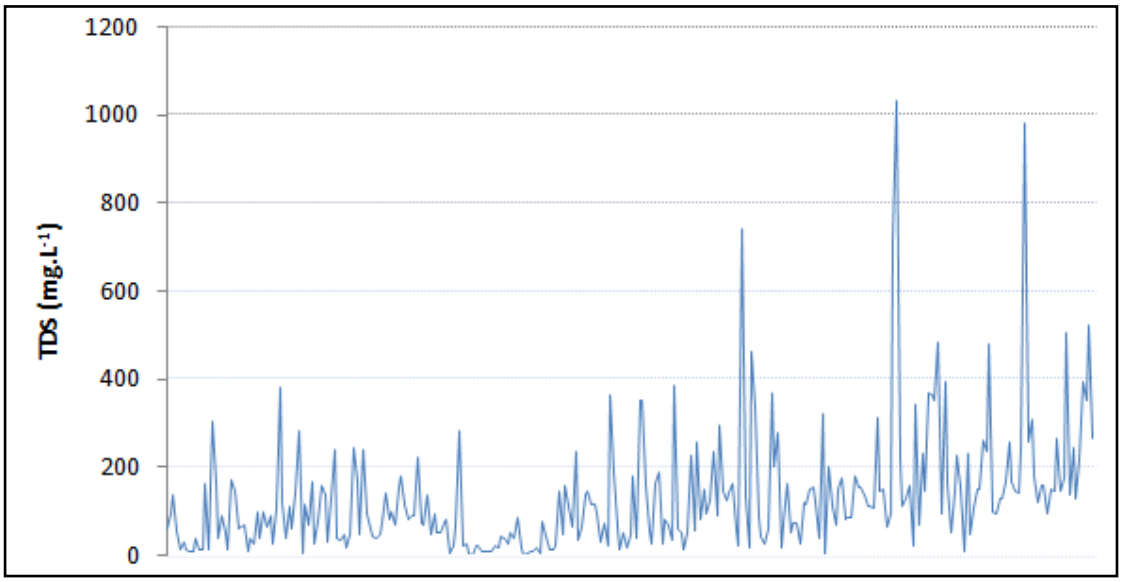


Figure 5-1: Total Dissolved Solids (TDS) for bottled water (mg.L^{-1})

The GA activities (in Bq.L^{-1}) are graphically presented in Figure 5-2. The GA activities include uranium and radium isotopes, but exclude radon and its short-lived progeny. GA activity in the sample ranged from below the LOD to 0.446 Bq.L^{-1}. Of the 290 samples analysed only one sample (not shown on the graph) exceeded the screening limit of 0.5 Bq.L^{-1} and was analysed for uranium as prescribed by the protocol. The measured activity of 1.24 ± 0.07 Bq.L^{-1} was confirmed to be due to uranium (KPA measurement = 58.8 ± 9.6 µg.L^{-1}, which is the equivalent of 1.49 ± 0.24 Bq.L^{-1} ^{238}U). This concentration is less than the reference level of 3 Bq.L^{-1} set by the EU to comply with a dose of less than 0.1 mSv.a^{-1} (Table 2-5).

The GB activities measured are shown in Figure 5-3. GB activity includes ^{40}K, and tritium was also not analysed for separately. GB activity in the samples ranged from below the LOD to 0.94 Bq.L^{-1}. Only two of 290 samples (not shown on the graph) exceeded the screening limit of 1 Bq.L^{-1}, but no further radionuclide analysis was performed. For high beta values a first step should have been to undertake a separate determination of potassium (by a chemical laboratory) and correct the gross beta result for the contribution from ^{40}K as discussed in 4.4.1.

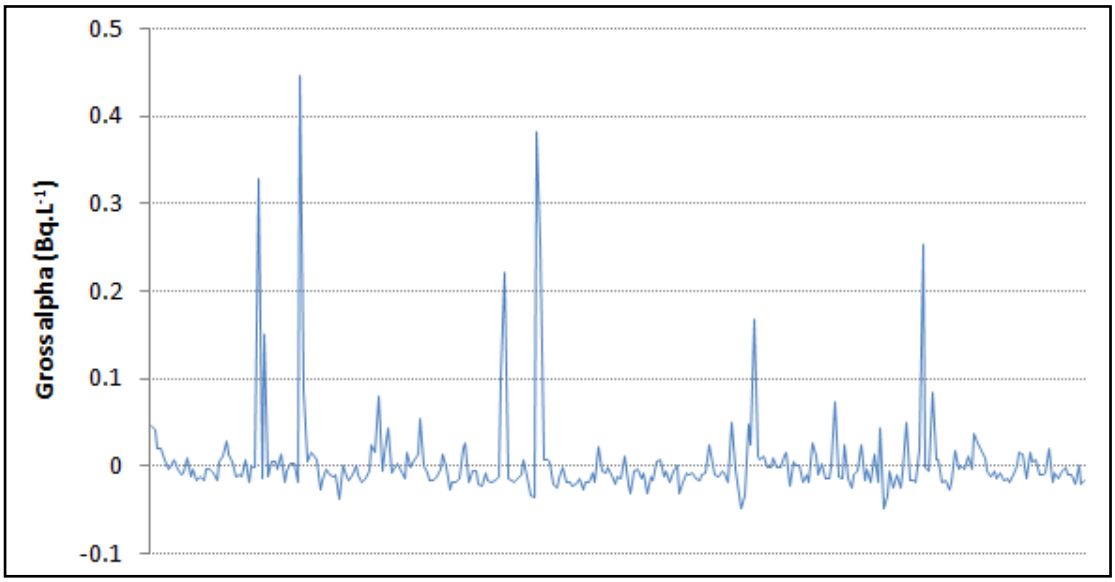


Figure 5-2: Gross alpha activity of bottled water (Bq.L^{-1})

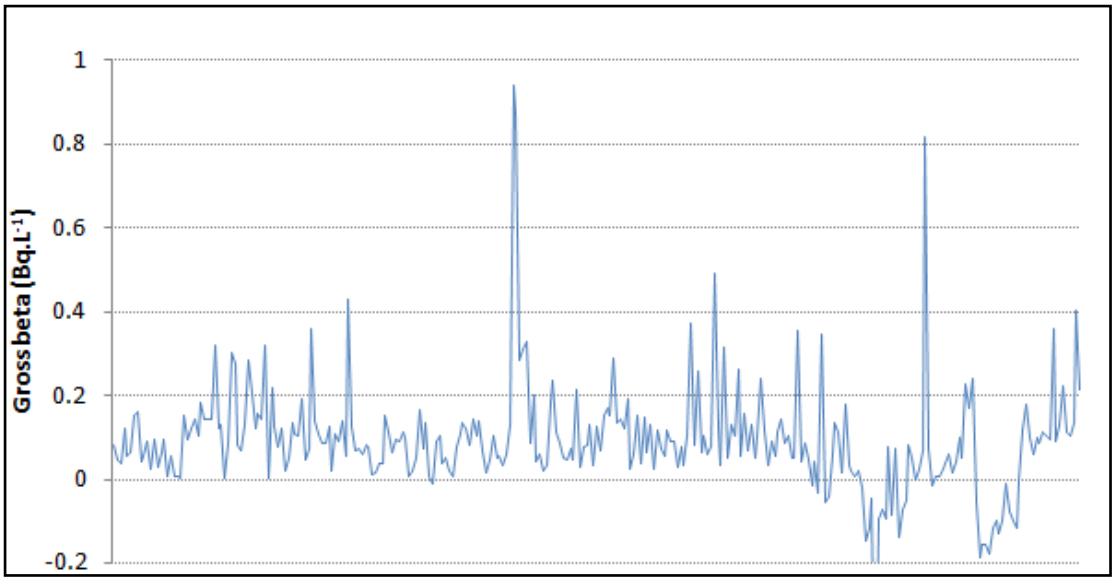


Figure 5-3: Gross beta activity of bottled water (Bq.L^{-1})

Conclusions

With the exception of three measurements, none of the bottled products analysed exceeded screening limits. The expected exposure to radiation due to consumption of these bottled water products is expected to be less than 0.1 mSv.a^{-1} and the water can be considered safe for intake by the consumer.

5.1.4 DWS water monitoring program in South Africa

Chapter 14 of the National Water Act (SA government, 1998b) requires for the quality of water resources in South Africa to be monitored. In response to the water act requirements, national water quality programmes, including the NRMP was initiated. The NRMP aims to report on the radiological quality of the water resources of South Africa (DWS, 2006). A DWS guideline document provides information on the approach to the analysis of radioactivity at three different water quality tiers and interpretation of the results for assessment of radiological quality (DWS, 2007). Screening measurements are performed with the aim to get an overview of the distribution of natural radioactivity in water bodies.

In this section results for samples analysed as part of the NRMP are presented. This section focus on the following: (1) To report on the radioactivity in surface-and groundwater submitted as part of the NRMP, and (2) to give an estimation of the dose from drinking this water. Where the emphasis in previous studies were only on the aqueous fraction of the water *i.e*. radioactivity in solution, some results for the radioactivity present on the suspended component (filters) are also presented.

Assessment

The advanced screening method as discussed in the DWS guideline was used to assess the water quality (DWS, 2007). The general NRMP protocol requires initials screening by gross αβ measurement, followed by a detailed analysis for samples where high levels of radioactivity have been observed (see Table 4-1). Full nuclide analysis was done only for selected sampling points that showed transient and elevated radioactivity.

Dose calculations were performed to determine the dose received by members of the public from this possible source of ingestion. Determination of radon was excluded, since it normally does not contribute significantly to dose from drinking water. It is only of concern where high concentrations are associated with conditions promoting dissolution and release of radon gas into an enclosed space with poor ventilation (UNSCEAR, 2000). The dose was calculated using the lifetime age-weighted approach equation 2-1, also showing dose for the adult and infant age groups.

SANS criteria, based on WHO guidelines, was also used to evaluate the quality of the water. For screening for compliance with WHO regulations a larger aliquot of up to 300 ml

(depending on the TDS value) was used and the samples were counted for at least five hours in order to obtain lower detection limits. Using this method with lower sensitivity will prevent overestimation and thereby concluding incorrectly that water is not suitable for use whereas it well may be.

When evaluating the impact of a NORM industry on the radiological quality of water the increase in dose caused by the industry has to be considered. In order to do this a reliable estimation of the natural background is required. In case of gold mining, a "true" background level could not be established, due to the fact that mines have been operating in the area for many years before any measurements of radioactivity was done. The natural background dose in drinking water in the Klip- and Mooi River catchments was estimated at about 0.03 and 0.02 $mSv.a^{-1}$ respectively (DWS, 1999). A value of 0.03 $mSv.a^{-1}$ was also assumed for the purpose of this study.

Due to seasonal variations in water quality, it is more accurate to use a median value as indication of the suitability for use, than individual observations. If the data are equally spaced over the time period they represent, the median implies that while users were subjected to a higher concentration for 50% of the time, they also enjoyed a lower concentration for the other 50%. If the variability of the concentrations is not excessive, the median can be compared with the guideline values to determine the quality of the water and suitability for use.

Selection of Monitoring Sites

Sampling sites for the NRMP were chosen for two purposes, namely to provide information of the radiological quality of water resources to water quality managers, and also to provide enhanced monitoring in "hot-spot" areas known to be at risk for increased levels of natural radioactivity from human activities.

With the development of the NRMP (DWS, 2006), 114 sampling sites were selected for monitoring of surface water. For groundwater analysis 380 monitoring points, which cover the whole country and are representative of the major aquifers of South Africa, were selected. Because of the costs involved in the analysis the original plan was scaled down and fewer samples than originally planned for in the NRMP were sent for radioactivity analysis. The results for some of the selected sites are presented in this study. These include:

— Groundwater samples (15 boreholes from Region A)
— Groundwater samples (13 boreholes from Region B)
— Surface water samples (18 sampling points from Region C)
— Full nuclide analysis (14 sampling points from Region C)

Unfortunately the exact sampling site information and location of the sites cannot be disclosed.

Sampling frequency and duration

In order to achieve the required accuracy and also to detect trends, it was planned for surface water quality monitoring sites to be sampled every two weeks, and boreholes twice per year. In general, quality of groundwater is expected to be more stable than surface water, and can be sampled less frequently. More frequent samples are required from rivers and streams more susceptible to a change in water quality. Due to financial and analytical constraints, sampling frequency was not consistent and this lead to some sites not being sampled as often as planned.

Groundwater samples were sampled every 1-3 months; a total of 206 samples were analysed. For surface water 1200 samples from 18 sampling points were analysed from 2007 to 2017. Samples were analyses for elemental uranium and gross alpha/beta activity only. The radioactivity in the suspended solids on the filters of 90 of these samples was also determined. Nuclide specific analysis was done for 210 samples from Region C, which was selected for the following reasons:

— Several gold mines operate in the region discharging process water into the aquatic environment. Potential pollution of ground- and surface water in the region is therefore a strong possibility.
— Mine residue deposits and abandoned mines are present.
— Informal settlements occur in the area, possibly consuming untreated water.
— Formal townships occur in the region. Municipalities abstract some water for domestic use from boreholes and dams in the region.

Results and Discussion

TDS, gross alpha/beta activity and U concentrations of the ground- and surface water samples analysed for screening only are shown in Tables 5-24 and 5-25. Nuclide specific analysis results for samples from the Gauteng region are shown in Table 5-1 (raw data in Table C-11, Appendix C). Also shown in the tables is the DWS water classification.

TDS Measurement

The measured TDS varied between 73 and 2910 $mg.L^{-1}$ for groundwater and from 150 to 5831 $mg.L^{-1}$ for surface water. This is the typical range as expected for water in contact with sedimentary rock formations (4.3.1). Only a few TDS values were higher than the South African water quality guideline of 1200 $mg.L^{-1}$ (SANS, 2015). To minimize self-absorption the precipitate weight was maintained below 100 mg (2.13.3). A reduced volume of sample was evaporated when the mass exceeded this limit. A volume of 300 ml was suitable for about 95 % of the samples.

A correlation was observed between TDS and radioactivity - in most cases the samples with high TDS were also associated with high alpha/beta and uranium concentrations. For groundwater from Catchment B there were no sampling points with high TDS; for groundwater from Catchment A four sampling points (SP 3, 4, 5, 8) had an average TDS value exceeding 1200 $mg.L^{-1}$ of which all had higher U concentrations compared to other sources. For surface water this relation was even more pronounced with the two sampling points with the highest TDS values (SP 7, 8) also having high alpha activity and U concentrations. The relationship between TDS and uranium concentration for surface water is shown in Figure 5-4. The linear correlation showed good agreement ($R^2 = 0.990$) confirming correlation of high uranium concentrations with salinity in water from the specific catchment.

For the majority of samples the alpha activity was less than 1 $Bq.L^{-1}$ in water with TDS lower than the SANS-241 limit of 1200 $mg.L^{-1}$ One must however be careful not to generalize and assume that no samples with low salinity contain any radioactivity (*e.g.* SP 4,16 were exceptions).

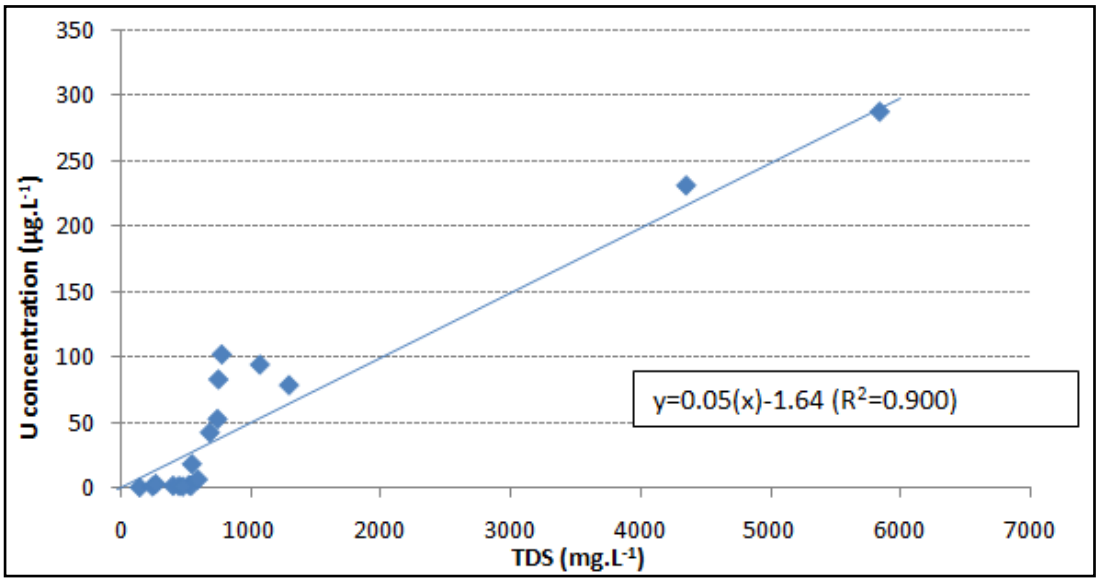


Figure 5-4: Correlation between TDS and uranium concentration for DWS surface water samples

Activity of Suspended Solids

One of the main points of criticism after completion of the Mooi River study (DWS, 1999) was that the published values in the study are not a true reflection of the radioactive contamination of the water sources, since the radioactivity may be present on particles in the water and not in the water itself (Pretoria News, 1999). Since filtering of the samples is done prior to measurement, the radioactivity in the sample may thereby effectively be removed *e.g.* Th isotope concentrations might be low in the filtered samples, since it is generally transported with particulate matter and therefore removed by filtration. The concern is valid since the practise at our laboratory is to do acidification only after filtration, thereby capturing any activity that might be present in the suspended solids. Acidification of the sample prior to filtration will dissolve most of the particles and release the radioactivity into the water thereby contributing to the measured radioactivity in the aqueous phase (which is closer to the real-life scenario where a consumer taking water directly from the source will ingest water with suspended particles).

In the work presented here the filters (suspended solids/colloids) of 90 surface water samples were counted by GFPC to determine the radioactivity of the suspended solids and to get an indication of possible contribution of radioactivity in the suspended solids to dose when untreated water is consumed. The alpha and beta activity on the filters were low and

insignificant compared to that in the water; less than 5% of the activity remained on the filter; with for all analysed samples an average of 2.1±2.6 % of alpha and 2.6±3.1% of beta activity remaining. This data show that the activity (mostly uranium) in the surface water is present in solution and not adsorbed to colloids. This implies that uranium is not transported as mineral particles or colloids but it is dissolved, possibly forming complexes with other complexing agents (2.1.2).

The results confirmed the preliminary indications found in the Mooi River study that radiation dose from the ingestion of the suspended solids can be ignored. Since the results clearly indicated that most of the activity is present in the water and not in the suspended solids, it was decided that no further analyses of filters of the samples received for analysis was required.

Screening results: Groundwater

Groundwater samples were analysed for chemical uranium and gross alpha/beta only. The average U concentration and gross alpha/beta activity per sampling point are presented graphically in Figures 5-5 and 5-6 and summarized in Table 5-25. Results exceeding the SANS 241 limits (Beta > 1 $Bq.L^{-1}$; Alpha > 0.5 $Bq.L^{-1}$ and U > 30 $\mu g.L^{-1}$) are indicated in red in the tables.

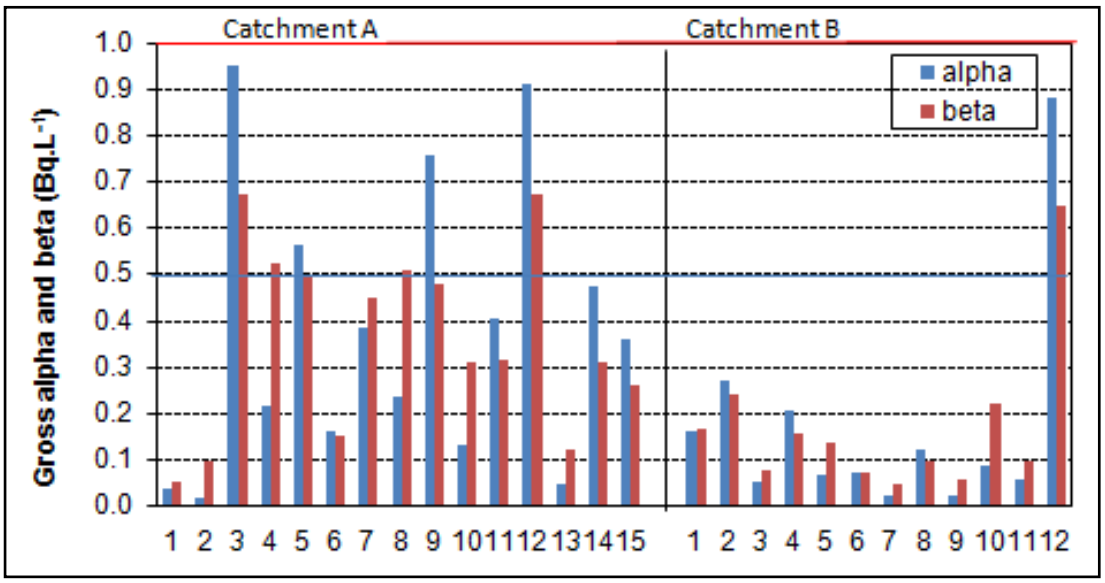


Figure 5-5: GA and GB in DWS groundwater samples ($Bq.L^{-1}$)

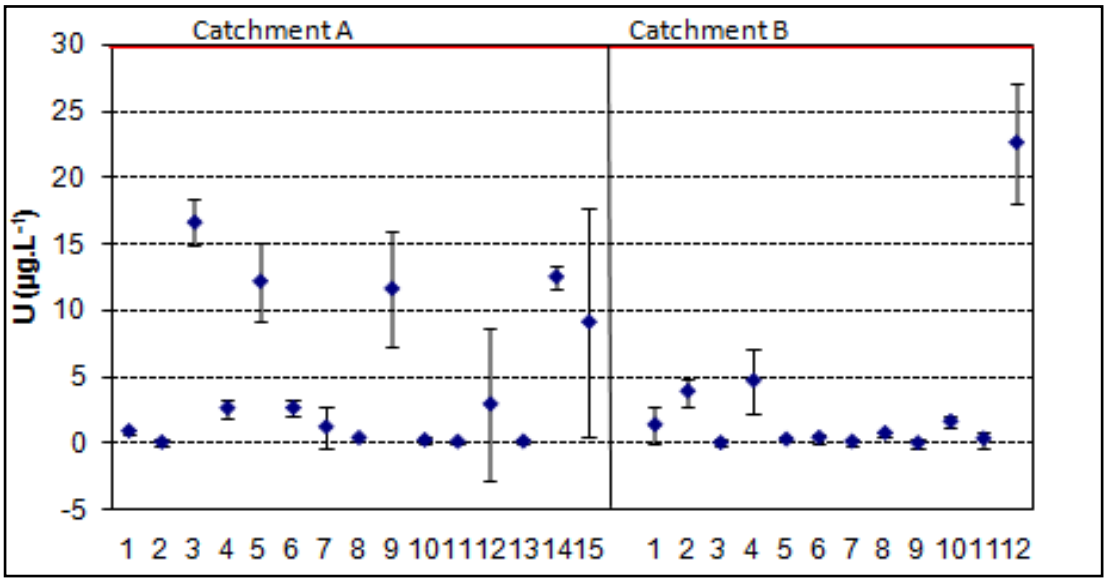


Figure 5-6: Uranium concentration (µg.L^{-1}) in DWS groundwater samples

In catchment area A a total of 46 samples from 15 sampling points (SP) were analysed. Of these, four sampling points had GA activity > 0.5 Bq.L^{-1}, with no samples exceeding the GB limit of 1 Bq.L^{-1}. The highest alpha activity of 0.95 Bq.L^{-1} was measured at SP 3. This was the also the sampling point with highest measured U concentration (16.6 µg.L^{-1}). Using the DWS screening classification (DWS, 2007) the water from all the sources were of either ideal (blue, class 0) or good (green, class 1) quality. Consumption of water with green classification may results in a dose of 0.1–1 mSv.a^{-1}, which is the typical dose range expected for natural water sources such as groundwater and wells.

In catchment area B a total of 160 samples from 13 sampling points were analysed. The measured activity at most of the sampling points was very low (< 0.2 Bq.L^{-1}). Only two sampling points had GA activity > 0.5 Bq.L^{-1}, with the water from only SP 13 having significantly high GA, GB and uranium concentrations. The measured uranium concentration for this point (not shown on graph) varied significantly for the 11 samples analysed over the one year period with a range of 60 to 455 µg.L^{-1}. Using the DWS screening classification (DWS, 2007) the water from all the sources, except one (SP 13), were of either good (green) or ideal (blue) water quality. The water from SP 13 was classified as marginal quality (yellow, class 2), meaning that consumption of untreated water may result in a dose of 1-10 mSv.a^{-1}. Based on the analysis protocol in Table 4-1, samples from this site require further nuclide specific analysis. This sample point is a mining shaft discharge point and the

probability of it being used for public consumption is low. Intervention will be required for improvement of the water quality if is to be used for public consumption.

The measured GA activity concentrations were compared with the estimated GA activity as calculated from the ^{238}U concentration measured by KPA (assuming a natural isotopic ratio). The correlation was poor with the "true" measured activity higher than the estimated value for all the samples, with a range in ratios (estimated/measured) from 0.22 to 0.67. Data points with measured U concentrations < 1 µg.L^{-1} was excluded due to limitations of the analytical technique at levels close to the detection limit, especially for groundwater where interferences may cause problems with the KPA technique (4.8.3).

As discussed in 2.1.2 the ^{234}U activity in groundwater is often enhanced due to the increased solubility and mobility of ^{234}U and ratios above one are commonly observed in groundwater. Because of this disequilibrium use of the measured ^{238}U concentration to calculate total uranium activity assuming a natural isotopic ratio can result in underestimation of activity. This is illustrated in Figure 5-7 where the correlation between measured and estimated concentrations was better where a 3:1 ratio for $^{234}U/^{238}U$ was assumed. The experimental data suggest a mass-to-activity ratio conversion factor of about 53.5 mBq per µg applicable to groundwater from this region, which is markedly different from that based on the natural abundance of uranium of 25.4 mBq per µg.

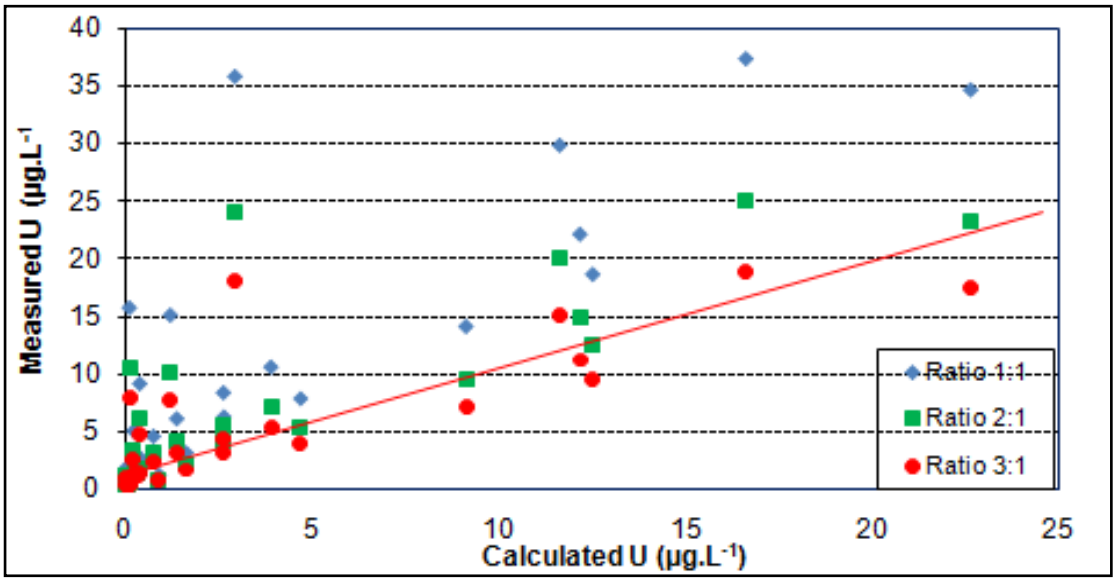


Figure 5-7: DWS Groundwater: Comparison of measured (KPA) to expected uranium concentrations (from gross alpha)

Screening results: Surface water

As planned in the NRMP basic screening was continued for various sampling points with analysis of samples for gross alpha/beta and chemical uranium content only. The average and median U concentration and gross alpha/beta activity per sampling point are presented graphically in Figures 5-8 and 5-9 and summarized in Table 5-24. Results exceeding the SANS-241 limits (Alpha > 0.5 $Bq.L^{-1}$; Beta > 1 $Bq.L^{-1}$ and U > 30 $\mu g.L^{-1}$) are indicated in red. A total of 1200 samples from 18 sampling points were analysed over a period of ten years. The uranium concentration of eight of these sampling points was > 30 $\mu g.L^{-1}$ with four (SP 4, 7, 8, 10) being higher than the previous DWS limit of 70 $\mu g.L^{-1}$. These sites may require further investigation, specifically with regard to chemical toxicity.

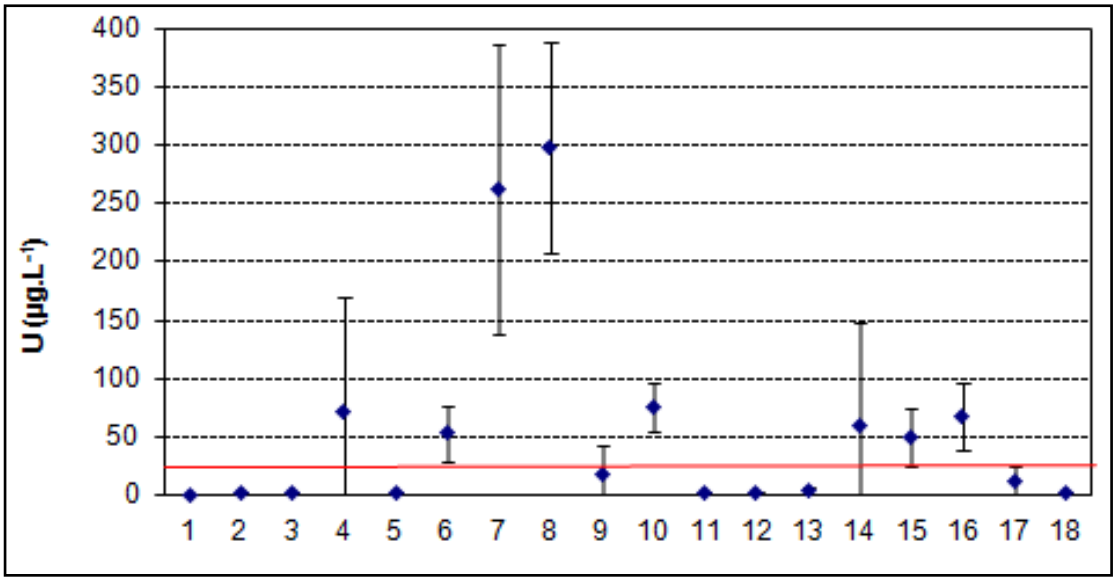


Figure 5-8: Uranium concentration in DWS surface water samples ($\mu g.L^{-1}$)

The GA activity of the eight sites with high measured U was greater than 0.5 $Bq.L^{-1}$ and was classified to be of marginal (yellow) quality. The water quality of these sources is obviously of some concern. These sites may involve the discharge of mine process water that had been pumped to the surface. Mine authorities should investigate options to control the quality and release of the water and to quantify impact on the water environment. Based on the analysis protocol in Table 4-1, samples from SP 7 and SP 8 required further nuclide specific analysis.

The concentrations at some sampling points (SP 4, 9, 14) varied significantly over the monitoring period. A large discrepancy between the mean and median was found indicating

that the dataset is not evenly distributed. The median is less influenced by outliers and is preferred for a highly skewed distribution. As shown in Figure 5-10 for the U concentration of SP 4, the variance appears to be due to incidences of transient high levels of radioactivity, which were not sustained over time. Monitoring of the points showing transient and elevated radioactivity should continue in the future.

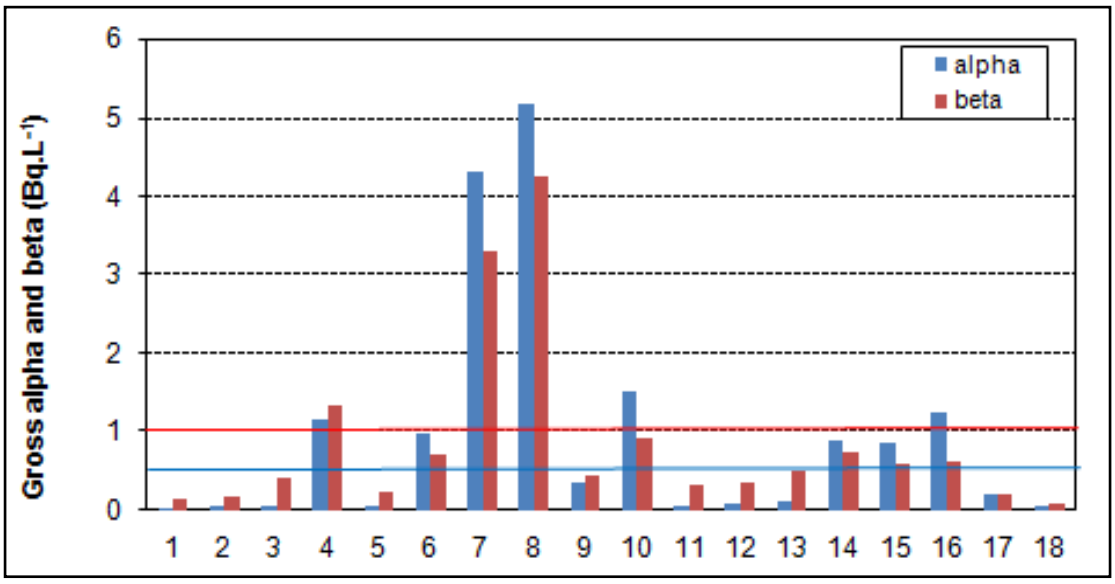


Figure 5-9: GA and GB activity in DWS surface water (Bq.L^{-1})

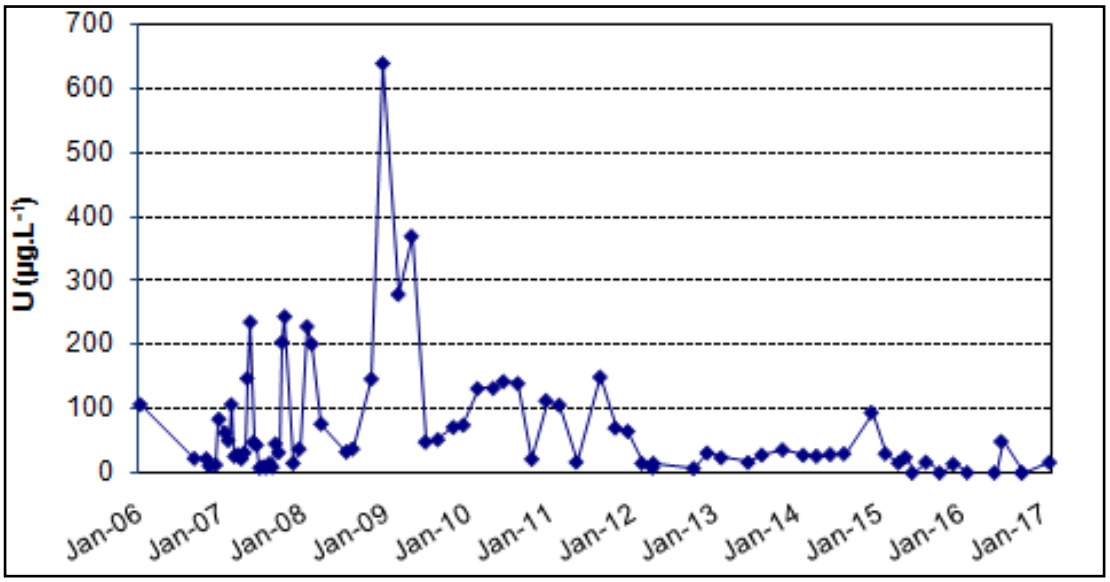


Figure 5-10: Variation in U concentration at sampling point 4 of DWS surface water

A scatter plot of measured U versus U estimated from alpha radioactivity (Figure 5-11) gave R^2=0.997, confirming correlation and suggesting that the observed GA activity is largely due to U present. The good correlation also indicates radioactive equilibrium of the uranium isotopes in surface water. The experimental data suggest a mass-to-activity ratio conversion factor of about 25.9 mBq per µg applicable to surface water from this region, which is similar to the conversion based on the natural abundance of uranium of 25.4 mBq per µg. It is important to note that since one typically expects a ratio of > 1:1 in natural water due to the selective mobilization of ^{234}U by alpha recoil, a ratio of 1:1 is usually indicative of contamination of the water source from other sources such as mining activities. The observed ratios confirm that many of the surface water sources are possibly contaminated by discharges from gold mining activities.

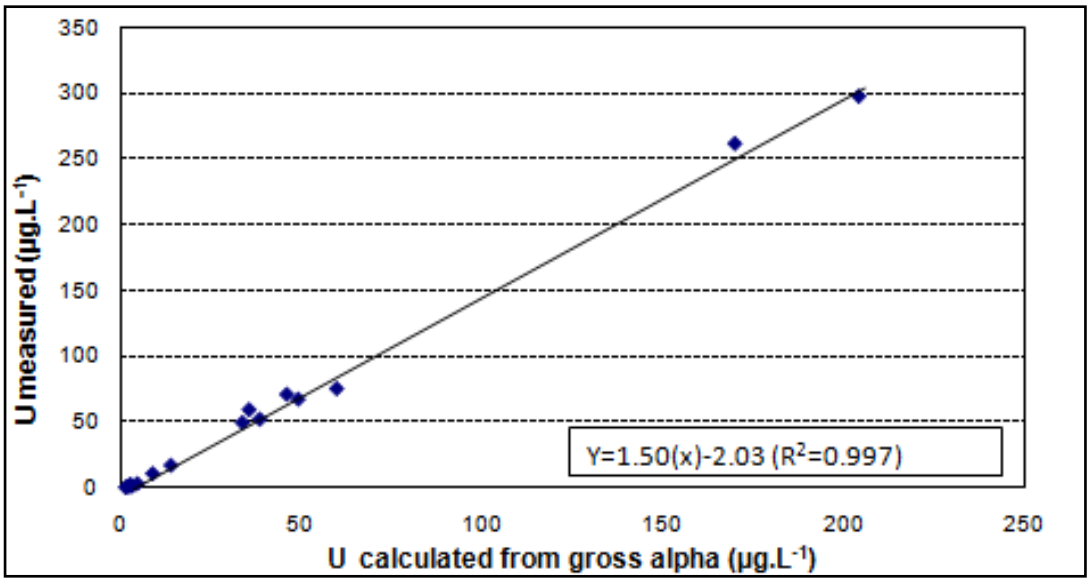


Figure 5-11: DWS Surface water - Comparison of measured (KPA) to expected uranium concentrations (from gross alpha)

Although GA activity constitutes a sum of all alpha emitting isotopes, it is clear from the fairly good correlation of the gross alpha activities and the uranium chemical concentration, the activity in the water can be mostly attributed to uranium and to a much lesser degree to other radionuclides such as radium and polonium. In the case of these surface water samples it seems possible to measure only the uranium elemental concentration and, assuming radioactive equilibrium, calculate the ^{238}U (=^{234}U) activity concentrations.

Uranium results obtained with different analytical techniques: KPA and ICP-MS

For QC purposes in the DWS study split sample inter-comparisons were done by measurement of uranium by two independent analytical techniques. 44 Surface water samples with concentrations ranging from 0.34 to 336 µg.L^{-1} and 190 ground water samples with concentrations ranging from 0 to 178 µg.L^{-1} was analysed with both KPA and ICP-MS. Even though the data were scattered there was very good comparison between the two techniques (Figure 5-12), especially at higher concentration with R^2 = 0.968.

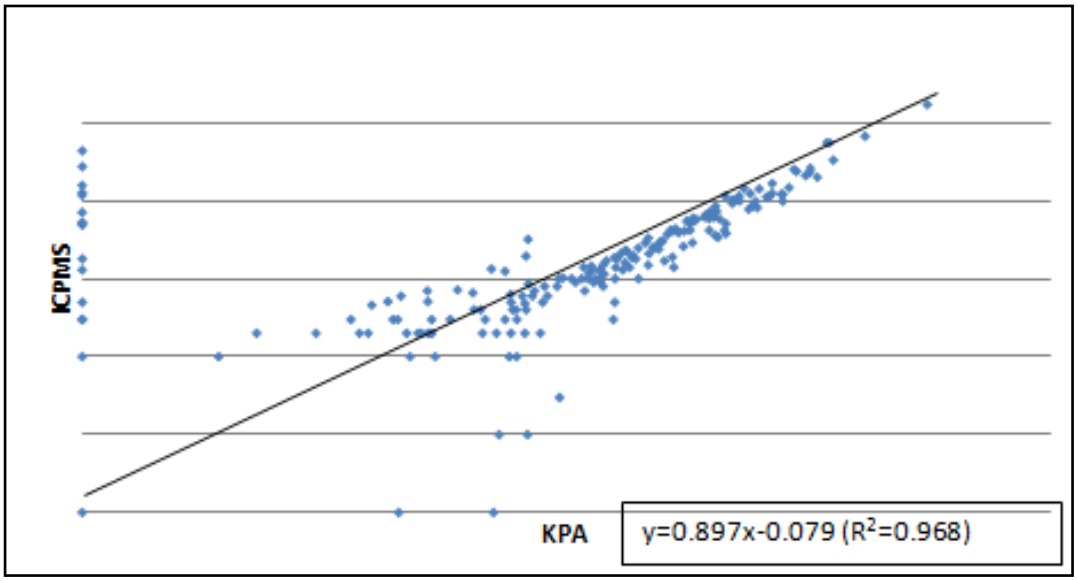


Figure 5-12: Comparison of KPA and ICPMS values for U measured in DWS groundwater samples

Nuclide Specific Analysis: Activity Concentrations and activity ratios

Samples from selected sampling points in catchment C, which were identified during the initial screening in 1997 and 1999 to be of radiological concern, were submitted for full-nuclide analysis; 210 samples from 14 sampling points were analysed.

The measured activity concentrations of the individual nuclides, as well as isotopic ratios of interest, are shown in Table C-11 (Appendix C). High individual data points (marked with * in Table C-11) were rejected as outliers in the calculation of averages when occurring only once per sampling point or if not confirmed by a correlation with either a high uranium activity concentration or a high gross activity value. This occurred mostly for ^{230}Th due to overlap of the ^{230}Th and ^{229}Th peaks in spectra with poor resolution, as mentioned in 4.8.4.

The annual doses from the water ingestion pathway, calculated using equation 2.1, for the infant- and adult age groups are also shown.

The radiological data for some sampling points varied significantly over the monitoring period *e.g*. for SP 9 high uranium concentrations were measured in two samples taken in Feb/Mar 2011 (5250; 1610 $mBq.L^{-1}$). The data from the same sampling point showed an improvement in quality with further measurement during the monitoring period. The single high values may therefore be an indication of a single release incident of contaminated water at the specific time only, and illustrates the importance of frequent monitoring of sites where the possibility of contamination exists. For the purpose of this study the average water quality over the monitoring period was considered and no seasonal trend analysis was done.

For most of the samples uranium represent the main radioactivity in the water. The range for ^{238}U and ^{234}U was 5.1 to 2070 (excluding single high value at SP 9) and 13.7 to 1960 $mBq.L^{-1}$, respectively. Figure 5-13 shows the average ^{238}U activity concentration per sampling point. The water from SP 5 exceeded the TWQR of 0.890 $Bq.L^{-1}$ for radioactivity in water intended for domestic use set by DWS (DWS, 1996a), with SP 10 also close to this limit. With the exception of one measurement at SP 9, the ^{238}U and ^{234}U activities of all the samples were less than the EU reference value for contribution of individual nuclides set at 3 and 2.8 $Bq.L^{-1}$respectively (EU, 2013a).

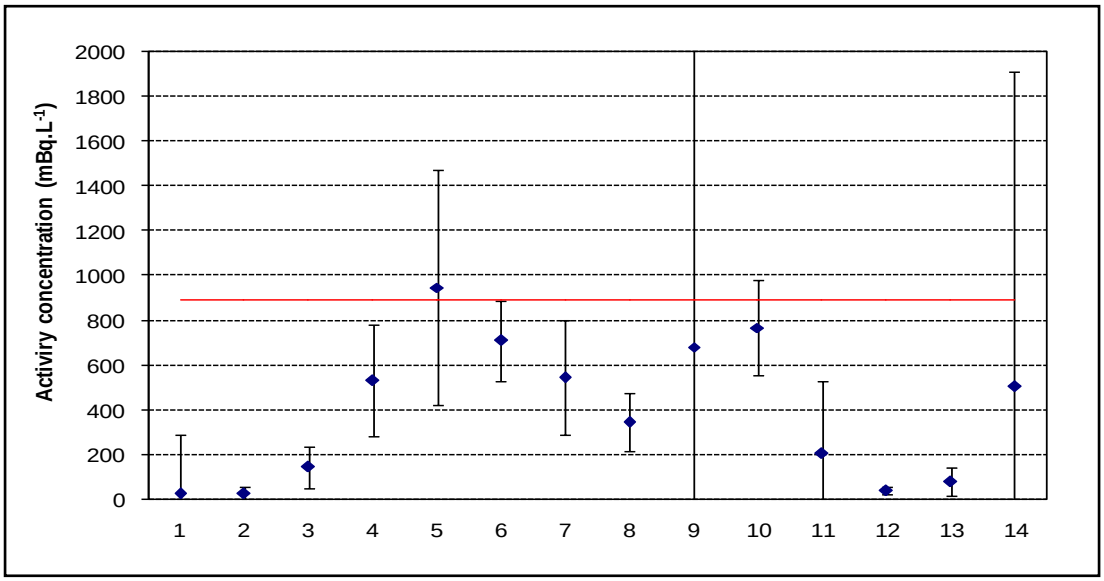


Figure 5-13: DWS region C - Uranium-238 activity concentration in water samples ($mBq.L^{-1}$)

Table 5-1 shows the mean isotopic ratio for $^{234}U/^{238}U$ for each sampling point. Equilibrium was observed for most sampling points. This is similar to the findings in the Klip-and Mooi River studies indicating that equilibrium can be assumed at relatively high concentrations of U. As already mentioned a ratio of 1:1 is usually indicative of contamination of the water source from other sources such as mining activities. Disequilibrium between ^{234}U and ^{234}U was observed for SP 1 and SP 2 with a ratio > 2; and also to a lesser degree for SP 12 and SP 13 with a ratio of ~ 1.5, which is as expected for natural water. These were also the sampling points with lower U concentrations.

Table 5-1: Quality of water from DWS sampling points based on full nuclide analysis

SP	U-238 mBq.L^{-1}	Ratio 234:238	> 17 a		< 1 a	
			Dose µSv.a^{-1}	Quality	Dose µSv.a^{-1}	Quality
1	21.3 ± 24.7	2.3 ± 1.0	30.1 ± 17.3	blue	193 ± 116	green
2	23.4 ± 27.3	2.6 ± 1.3	18.4 ± 12.3	blue	83.0 ± 7.4	blue
3	142 ± 94	1.2 ± 0.3	34.9 ± 12.6	blue	187 ± 68.6	green
4	531 ± 249	1.0 ± 0.1	64.8 ± 22.6	blue	251 ± 84	green
5	946 ± 525	1.0 ± 0.1	121 ± 43	green	456 ± 169	green
6	707 ± 180	1.1 ± 0.1	92.9 ± 20.6	blue	335 ± 96	green
7	542 ± 257	1.0 ± 0.1	60.6 ± 19.7	blue	237 ± 79	green
8	344 ± 130	1.1 ± 0.1	53.9 ± 17.8	blue	243 ± 99	green
9	351 ± 583	1.1 ± 0.1	110 ± 146	green	507 ± 571	green
10	766 ± 211	1.2 ± 0.2	92.5 ± 11.3	blue	316 ± 79.5	green
11	202 ± 327	1.2 ± 0.3	32.3 ± 10.1	blue	179 ± 68.8	green
12	36.5 ± 17.6	1.6 ± 0.4	28.8 ± 15.0	blue	189 ± 119	green
13	76.8 ± 65.2	1.5 ± 0.4	32.6 ± 15.6	blue	192 ± 108	green
14	501 ± 273	1.0± 0.1	60.2 ± 22.2	blue	277 ± 116	green

The ^{226}Ra concentrations ranged from -0.9 to 207 mBq.L^{-1} and did not exceed the DWS TWQR of 0.42 Bq.L^{-1} or the EU reference value of 0.5 Bq.L^{-1}. Higher concentrations were measured at SP 5 compared to the other sampling points. The ^{228}Ra concentrations were not measured, but assumed to be in equilibrium with ^{228}Th with lower concentrations than for ^{226}Ra in water from this area. Since this may not be true, due to the difference in mobility of Ra and Th, actual measurement of ^{228}Ra via its direct beta-emitting daughter ^{228}Ac by counting with either GFPC or LSC after chemical separation of Ac, is recommended.

The activity concentration for ^{210}Pb in the analysed water ranged from 0.14 to 29.6 mBq.L^{-1} and for ^{210}Po the range was -1.2 to 31.8 mBq.L^{-1}. The ^{210}Pb activity concentration was lower

than that of ^{226}Ra for most of the samples indicating disequilibria (median=0.16 for ^{210}Pb/^{226}Ra ratio). Although ^{238}U, ^{226}Ra and ^{210}Po are from the same decay series, there was poor correlation between the measured concentrations. The nuclide ratios for the different sampling points also vary, which is why nuclide specific analysis is advisable if a detailed study of the behaviour of the nuclides at a specific site is required. The activities for ^{210}Pb and ^{210}Po were lower than EU reference levels of 0.2 and 0.1 Bq.L^{-1} respectively.

Activity concentrations for the thorium isotopes ^{232}Th (range -1.5 to 34.1 mBq.L^{-1}) and ^{228}Th (range 0.026 to 35 mBq.L^{-1}) were of the same order, but were very low compared to that of uranium. This is expected due to the low solubility of Th in water. ^{228}Th seems to be slightly enriched compared to ^{232}Th (median = 1.76 for ^{228}Th:^{232}Th ratio). The concentration of ^{230}Th, a decay product in the Uranium-238 series, was however higher (range -1.1 to 175 mBq.L^{-1}) than the other thorium isotopes (median = 7.6 for ^{230}Th:^{232}Th ratio), but still much lower than the activity concentrations of its precursors ^{238}U and ^{234}U. As mentioned in 2.1.3 elevated ^{230}Th activity concentrations have been found in some waters in the South Africa mining industry and measurement of the nuclide is advisable. One should however be careful when evaluating high ^{230}Th concentrations, due to the already mentioned high uncertainty with measurement of the nuclide. The activities for thorium isotopes were lower than reference levels [DWS:0.228 Bq.L^{-1}; EU:0.6 Bq.L^{-1}].

On average the activity concentrations of ^{238}U at some of the sampling points were higher than in water elsewhere in the world (see Table A-17, Appendix A), except for some sources in Finland and the USA. The concentrations of ^{226}Ra were lower, and that of ^{210}Po, ^{210}Pb and ^{232}Th comparable.

Correlation between Gross Alpha Activity and uranium activity concentration

From the raw data there seems to be a correlation between the uranium activity concentration values and high gross alpha values. This correlation was assessed to establish if alternative analysis protocols can be applied for future mapping or investigation purposes (Figure 5-14). The coefficient of correlation (R^2) was 0.709. The data shows reasonable correlation suggesting that uranium is primarily responsible for the measured alpha activity. It can be concluded that the measurement of only ^{238}U as an indication of the total activity in the sample may be a reliable means for screening for radioactivity in water. The measured gross activity concentration exceeded the WHO screening level of 0.5 Bq.L^{-1} for 40% of the

samples. Comparison of the measured gross alpha activity concentration with the total alpha activity calculated from individual nuclide concentrations (the sum of all nuclides in the U-series, assuming radiological equilibrium) gave a reasonable linear correlation (see Figure 5-15) but with strongly scattered individual data (R^2=0.758). This confirms that gross measurement is suitable to be used as a screening tool to identify samples with high radioactivity, but that decisions on the acceptable quality of water should not be based on it. The total alpha activity was higher than the measured gross alpha activity for most of the samples. Using the gross results can therefore result in an underestimation of the radiological impact of the water.

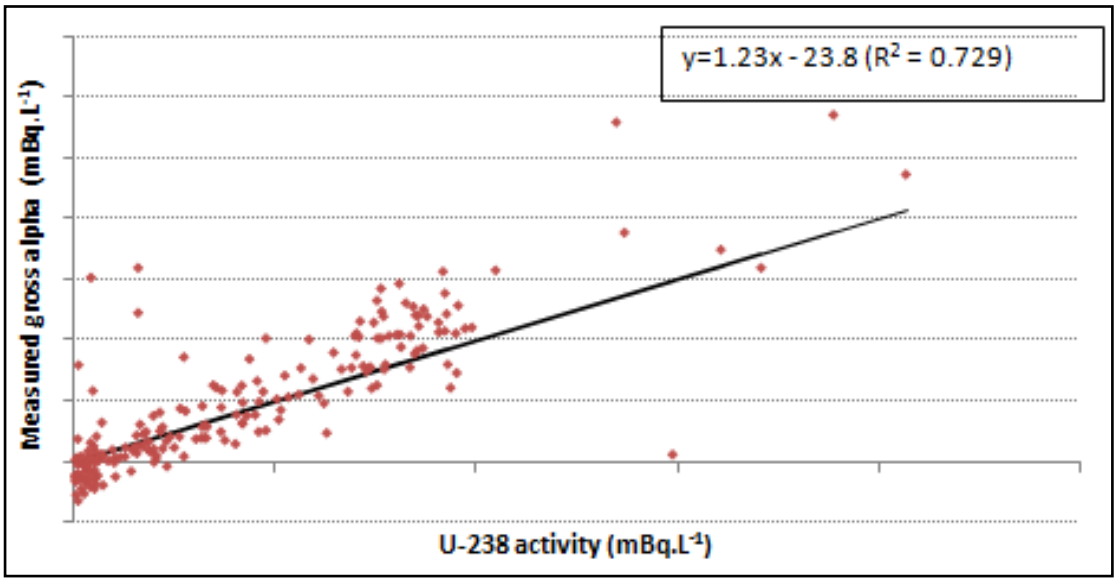


Figure 5-14: DWS region C - Correlation between gross alpha activity and ^{238}U activity

Dose and Radiological Quality

The dose ranged from 0.0088 to 0.51 mSv.a^{-1} (Table C-11, Appendix C). For the majority of the samples (85% of the 210 samples analysed) consumption of the water will result in a dose of well below the WHO reference level (0.1 mSv.a^{-1}). The average dose of the analysed water for each sampling point for the adult age group (>17a) and infant age group (<1a) is shown in Figure 5-16. For the adult age group a dose of > 0.1 mSv.a^{-1} was observed only for SP 5 and SP 9. As already mentioned the higher dose for SP 9 was due to only two individual high measurements. None of the sampling points had a dose higher than the NNR dose constraint of 0.25 mSv.a^{-1}. The dose was small compared to the world-wide average dose from natural sources (2.4 mSv.a^{-1}) and compared to the typical dose from ingestion of 0.12 mSv.a^{-1}

(UNSCEAR, 2000). Considering the (most conservative) dose to infants, water from SP 5, 6, 9, 10 and 14 exceeded the NNR dose constraint.

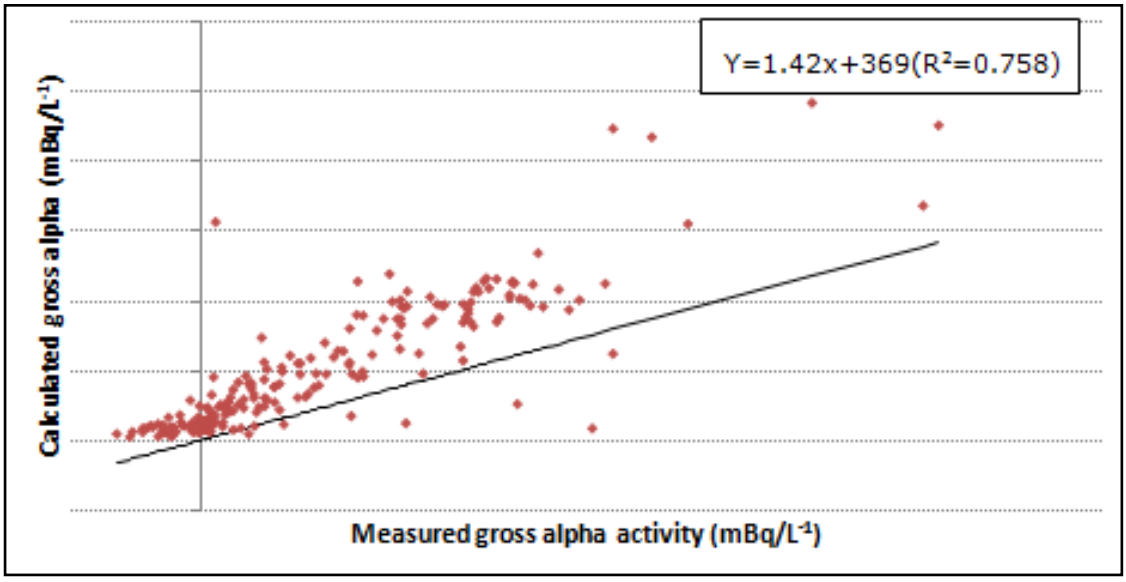


Figure 5-15: DWS region C - Comparison of calculated gross activity with measured gross activity

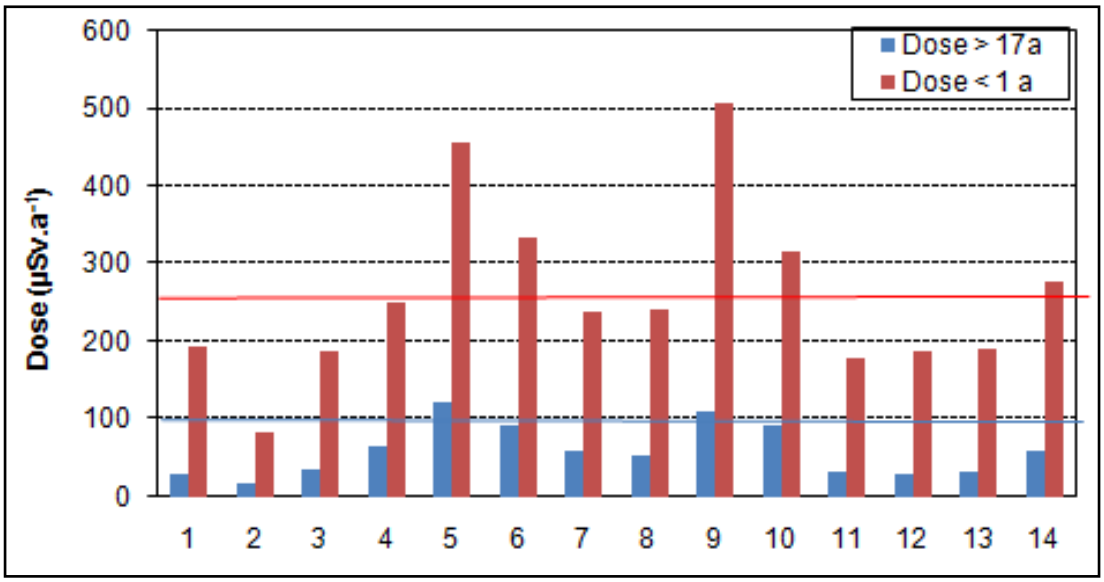


Figure 5-16: DWS region C - Average annual effective dose per sampling point (µSv.a^{-1})

The radiological quality of all the water was good or ideal based on DWS (2007), as shown in Table 5-1. It is often the case that the water quality at a specific sampling point is classified a marginal or poor only for the most sensitive age group (*i.e.* 0-1 years), whereas it will be good for all other age groups. It was decided to consider only the adult age group in this

thesis, since this constitutes 75% of the lifetime average dose. From the results in Table 5-1 the following can be concluded regarding the radiological quality of the sampling points for which nuclide specific analysis has been performed:

- The majority of sites were classified from the radiological point of view for drinking water in the ideal (blue) class (dose 0 to 0.1 $mSv.a^{-1}$) indicating no radiological risk.
- Two sites were in the good (green) class (dose 0.1 to 1 $mSv.a^{-1}$), acceptable for lifetime use despite a slight increase above natural background.
- There were no sites in the marginal (yellow) class or higher (>1 to 10 $mSv.a^{-1}$) implying that there is no indication that intervention is required.
- If the most sensitive age group (0-1 years) is considered, the radiological quality of all sampling points was still within the ideal to good classes, with one site classified as ideal whereas the rest were considered good quality. There were still no sites in the marginal class.

Even though the radiological quality of the water based on dose criteria as set in the latest DWS guidelines (DWS, 2007) were ideal, the chemical quality of the water is of some concern with the average uranium concentration of 9 of the 14 sampling points higher than the SANS limit of 30 $\mu g.L^{-1}$ (~ 373 $mBq.L^{-1}$ ^{238}U); 60% of the samples exceeded this limit.

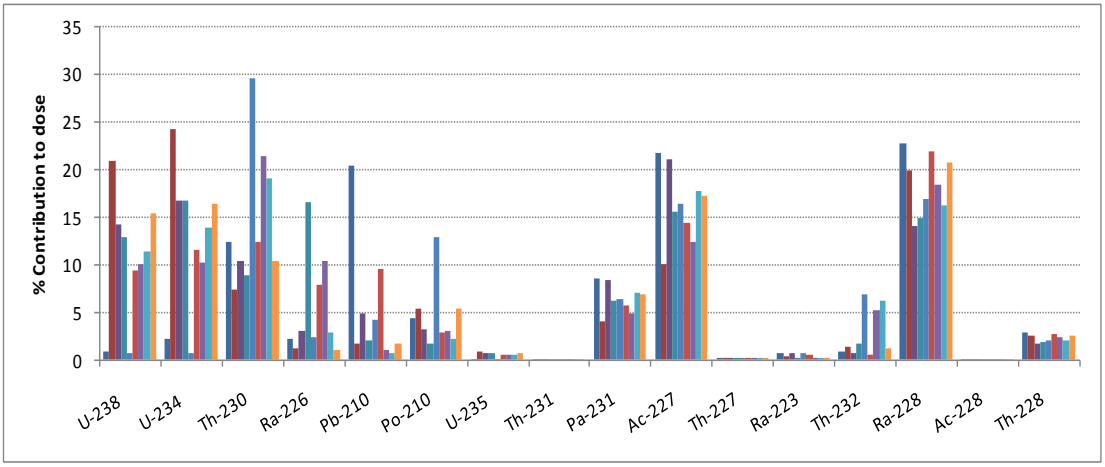


Figure 5-17: DWS region C - Relative contribution of individual nuclides to dose

Figure 5-17 shows the relative contribution of individual nuclides to the mean estimated dose for a selection of samples. The contribution varies from sample to sample but is typically less than 10% for ^{210}Po and ^{210} Pb. Although U dominates in the sample, it contributes less than

20% of the dose. ^{228}Ra, ^{227}Ac and ^{230}Th seem to contribute significantly, which is due to higher DCFs for these nuclides. The concentrations of ^{228}Ra and ^{227}Ac were not measured but were derived from that of ^{228}Th and ^{227}Th, respectively, assuming equilibrium (Table 2-2).

Correlation between uranium concentration and the annual dose

As can be seen from Figure 5-18 there was a fairly good linear correlation between annual effective dose for consumption of water calculated from all radionuclides and the ^{238}U activity concentration in the water (R^2=0.712), even though other nuclides may also contribute significantly to the dose as shown in Figure 5-17. The implication of this correlation is that for this specific region the dose can be estimated from the ^{238}U concentration.

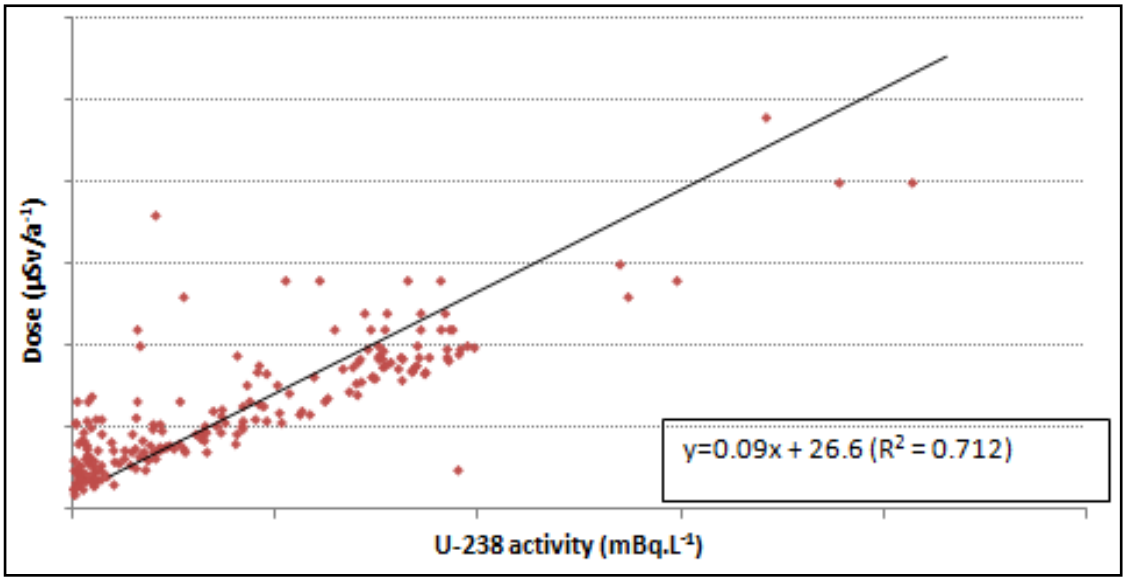


Figure 5-18: DWS region C - Correlation between dose and ^{238}U activity concentration

To illustrate the accuracy when making this assumption a comparison of the dose calculated from the full nuclide analysis (dose A; from Table 5-1) as compared to the doses estimated from the uranium activity concentration (C_U in mBq.L^{-1}) (dose B; calculated using the linear regression *Dose in µSv.a^{-1}= 0.09 C_U +26.*6) is shown in Table 5-2. The ratio of estimated versus measured dose varied from 0.80 to 1.56 with a tendency to be overestimated. Note that ^{238}U in this study refers to activity concentration as measured with alpha spectrometry, but where a natural isotopic ratio for uranium can be assumed for the sample (as has been proven for many of the sampling sites from this study - see Table 5-1) U can also be measured by the

elemental technique KPA. Converted to $mSv.a^{-1}$ and U chemical concentration in $\mu g.L^{-1}$ the relation is given by $Dose=0.0011C_U+0.0266$, which correlates very well with the correlation established for a different set of data in the previous DWS survey: $Dose(mSv.a^{-1})=0.00129C_U(\mu g.L^{-1})+0.0213$ (DWS, 1999). Although this correlation is not necessarily applicable to all different catchments, the results validate the protocol decided on in previous studies to use only the uranium concentration for routine monitoring within the catchment. The validation of the correlation between dose and uranium concentration should be checked periodically

Table 5-2: Annual dose ($\mu Sv.a^{-1}$) calculated for water from sites from region C

Site no	Dose A	Dose B	Ratio	Site no	Dose A	Dose B	Ratio
1	30.1	28.5	0.95	8	53.9	57.7	1.07
2	18.4	28.7	1.56	9	110	87.6	0.79
3	34.9	39.4	1.13	10	92.5	95.6	1.03
4	64.8	74.3	1.15	11	32.3	44.8	1.39
5	121	112	0.92	12	28.8	29.9	1.04
6	92.9	90.2	0.97	13	32.6	33.5	1.03
7	60.6	75.3	1.24	14	60.2	71.7	1.19

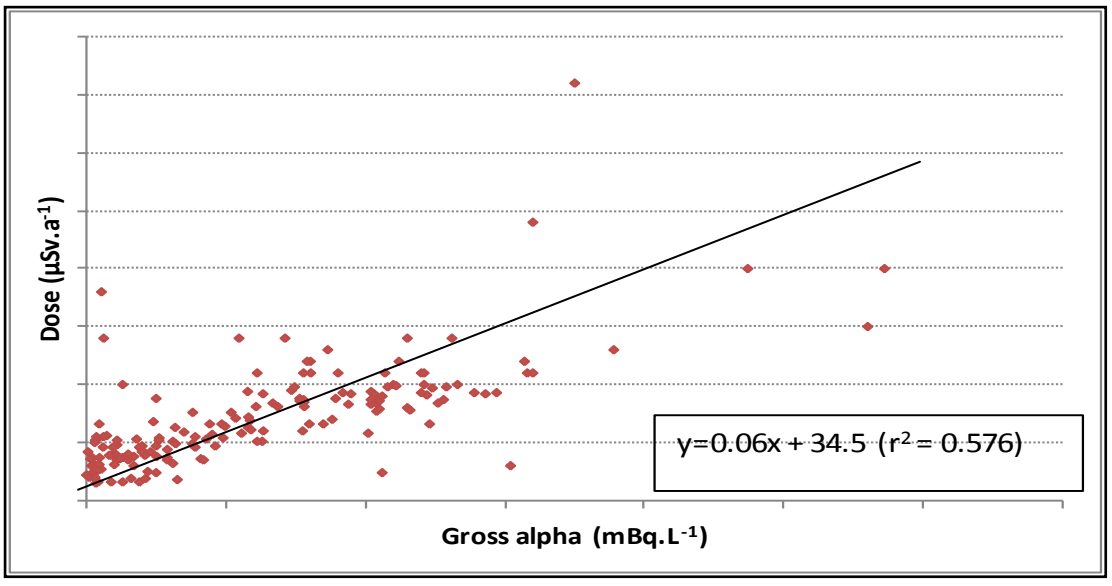


Figure 5-19: DWS region C - Correlation between annual radiation dose and gross alpha activity

There is reasonably good correlation between alpha activity and total radiation dose (Figure 5-19), but worse than the correlation between measured U and dose (Figure 5-18). This can

be expected due to the large uncertainty associated with gross alpha measurements. Therefore, whereas GA activity can successfully be used for initial screening to estimate the quality of the water sources, it cannot be used for accurate dose assessment.

Conclusions and recommendations

The data presented provide the public and other interested parties with information on the radiological quality of the water resources in South Africa and can be used to establish baseline data and trends. The radiological quality of the majority of the water sources was assessed to be fit for use based on the radiation dose received from life-time consumption of the water. Screening should continue for sites of concern classified in the marginal (yellow) class, with dose exceeding 1 $mSv.a^{-1}$. Even though no immediate action was necessary for intervention, discussions should be held with the relevant regulatory authority to determine the frequency of ongoing monitoring. A once-off nuclide specific analysis should be done to confirm the water quality of the samples concerned, where no data exists.

GA activity was more useful than that of GB, due to contribution of ^{40}K in the beta activity, which was not corrected for. Nevertheless, GB activity was also included in the results. It was shown that gross alpha activity gives an estimate of the dose, but is not sufficient to accurately calculate the dose. The alpha and beta activities in the 45 µm filter were low, indicating insignificant contribution to dose from ingestion of the suspended solids in the water.

Although 40% of samples from region C exceeded WHO GA screening limits, dose calculations based on nuclide specific analysis showed water from these sites to be of blue or green quality, and it is not expected to contribute significantly to the average annual background dose received by people living in SA. The majority of the samples complied with national and international regulation limits for individual nuclides. Water from only one site exceeded the limits for uranium isotopes, whereas another site was on the borderline of national limits. Care should be taken not to use water from these sites for infants due to the higher incurred dose.

The main radioactive element present was uranium. Though not of radiological concern, the chemical quality of the water was of some concern with the average uranium concentration of several sampling points higher than the SANS-241 limit of 30 $\mu g.L^{-1}$. Monitoring of chemical

uranium concentrations at sites associated with doses higher than 0.1 $mSv.a^{-1}$ should continue. The correlation between uranium and annual dose can be useful for monitoring, with more detailed analysis required only when reference levels are exceeded. In the case of water samples where the $^{234}U/^{238}U$ ratio is close to unity it is in principle possible to measure only the uranium chemical concentration and, assuming radioactive equilibrium, calculate the ^{238}U (=^{234}U) activities. In case of disequilibrium as found in groundwater where ^{234}U activity is often enhanced, the total uranium activity will be underestimated if calculated from the ^{238}U concentration.

It was found the radionuclide concentrations at a specific site may vary considerably with time. Hence a single measurement showing high activities does not imply that the water is unsuitable for consumption, but should be regarded as indication that further investigation may be required.

5.1.5 Water from Mining- and other NORM industries

Introduction

According to the legislation mentioned in 2.2.4 mining companies in SA have the obligation to supply adequate quality drinking water to all its employees. They therefore have to implement a water quality monitoring programme of which the results have to be reported to the regulator at predefined frequencies. Consequently water samples are submitted for radioactivity analysis. Typically about 1300-1700 samples are analysed annually. Figure 5-20 gives a breakdown of the origin of samples analysed in one year (2014), showing that about 57% of water samples were received from the gold industry. A summary of the typical ranges of radioactivity found in different types of water samples are presented in this section.

Sampling

Samples were collected from different areas in SA. Depending on the water quality monitoring programme of the specific industry, samples were analysed on a monthly, quarterly, semi-annual or annual basis. Water samples were collected from surface water bodies and boreholes and fissure water, process water, drinking water and treated water were supplied by mines. Unfortunately, due to client confidentiality the exact origin of the samples cannot be disclosed.

Potable water refers to any water, regardless of source, which meets the water quality standards; Fissure water constitutes natural groundwater pumped from dolomite rock to prevent mine flooding and which has not been in contact with mining activities; Process water constitutes water that has been in contact with mining processes and which is usually not suitable for consumption; Drinking water refers to water supplied by local municipalities; Treated water has been treated by in-house water treatment processes at the mine before being discharged and is now a source of drinking water; Surface water is water from rivers and dams from the surrounding area, used for drinking or irrigation.

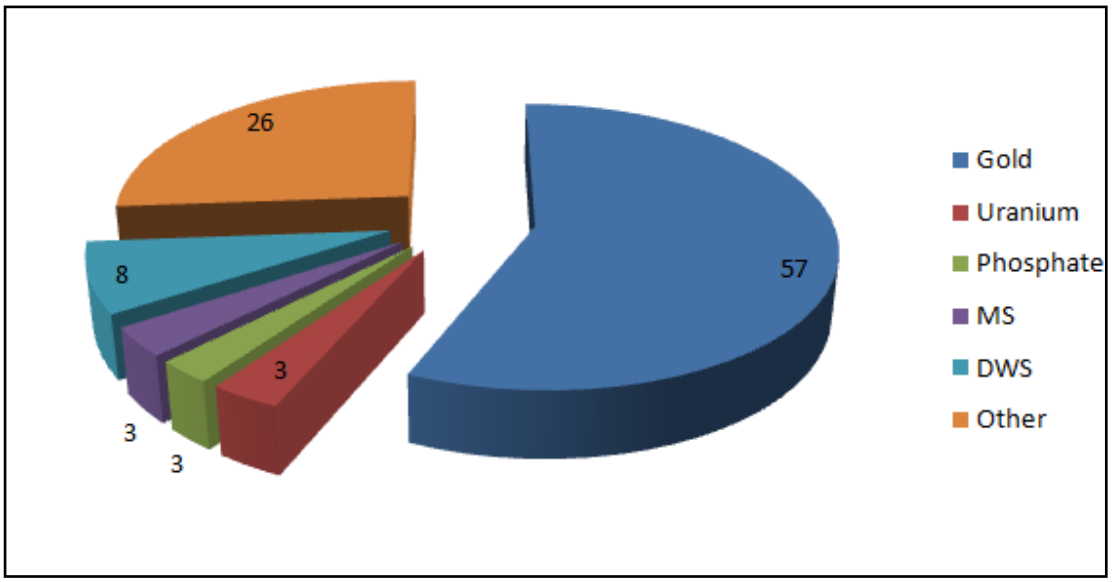


Figure 5-20: Water from NORM industries analysed in 2014 (% of total samples)

Radioactivity analysis and assessment

The water samples were all analysed for gross activity, as well as nuclide specific using the radiochemical methods summarized in 4.12.2. The quality of the water was evaluated based on dose for the adult age group. The methodology employed used dose coefficients to estimate dose from internal exposure, as discussed in 2.3.5. Results were also evaluated using DWS classification, or WHO and EU criteria (2.2.7), where applicable.

Results and discussion

Of 1365 water samples analysed in 2014 the gross alpha activity of 75% was less than 1 $Bq.L^{-1}$, which is green quality according to DWS classification (DWS, 2007) resulting in a

dose of less than 1 $mSv.a^{-1}$ if consumed; for 59% the gross alpha was less than 0.5 $Bq.L^{-1}$, which is blue quality resulting in a dose of less than 0.1 $mSv.a^{-1}$ (Figure 5-21). Although gross α-activity should be used for screening purposes only, it nevertheless gives a good indication of the radiological quality of the water.

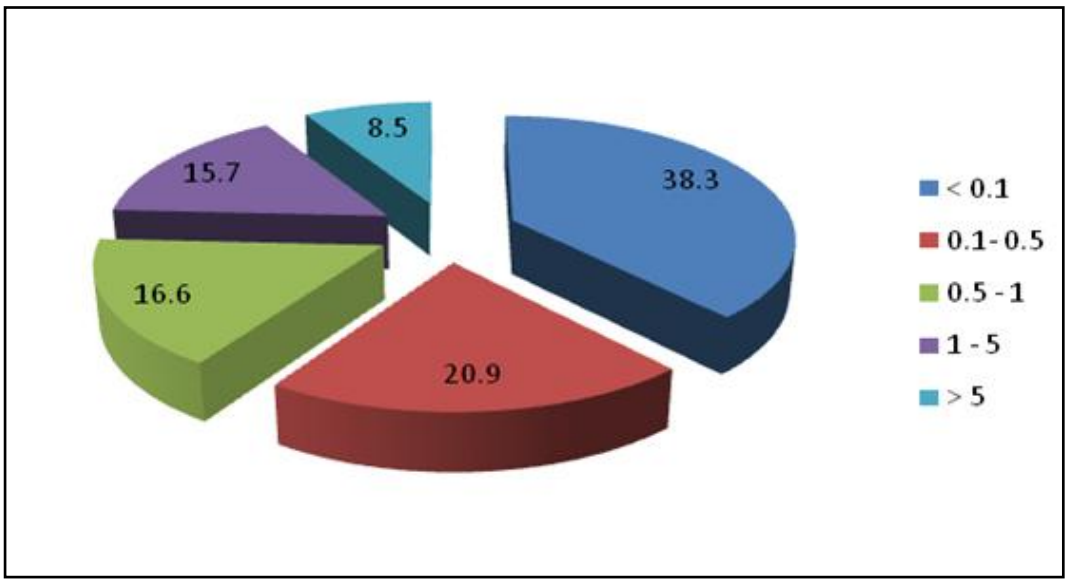


Figure 5-21: Gross alpha screening results of water samples from NORM industries analysed in 2014 ($Bq.L^{-1}$)

The activity concentrations of the individual nuclides for a selection (n=192) of the more than 1000 water samples analysed annually are shown in Tables D-9 and D-10. The results for water from a background area and areas impacted by mineral sands mining, fertilizer production and gold mining are shown. A summary of the results are presented in Tables 5-26 and 5-27.

Activity Concentrations

The majority of the samples had low concentrations for Th-series nuclides compared to that of the U-series nuclides. This can be attributed to higher solubility of U compared to Th. For most of the samples there does not seem to be secular equilibrium of the natural uranium series, although the situation was closer to equilibrium in affected areas.

As expected, ^{232}Th concentrations in water from all areas were relatively low, due to low mobility of Th under all environmental conditions. The higher ^{230}Th concentrations relative to all the other U-series nuclide concentrations in the background water samples (21±11 and

22±8 mBq.L^{-1}) are questionable and probably overestimated, due to overlap of the ^{229}Th and ^{230}Th peaks in spectra with poor resolution. The activity concentrations for ^{226}Ra in water from all areas were relatively low compared to literature data and much lower than the U isotope activity concentrations. In many countries worldwide ^{226}Ra is the nuclide of concern, especially in groundwater, in which concentrations vary from 20 to 930 mBq.L^{-1} (IAEA, 2014a). The highest concentrations were measured in groundwater from the mineral sands area (485 mBq.L^{-1}) and in surface water from the gold mines (370 mBq.L^{-1}). Only two samples exceeded the national regulation limit of 420 mBq.L^{-1} set for ^{226}Ra (DWS, 1996a), and all were lower than the EU reference value of 500 mBq.L^{-1} (Table 2-5). ^{210}Pb and ^{210}Po concentrations were lower than that of other nuclides, with ^{210}Po supported by ^{210}Pb.

Of the total of 192 samples analysed 38% exceeded the WHO proposed standard of 30 µg.L^{-1} (373 mBq.L^{-1} ^{238}U) for chemical uranium, of which 36 % were process and surface water samples from the gold mine area.

Background area (B): Activity concentrations in the background samples were low and comparable with world averages. For ^{238}U a concentration of 5 mBq.L^{-1} is considered as a global freshwater average with a range of 0.124 to 12.4 mBq.L^{-1} in unpolluted streams (Winde, 2013).

Phosphate area (P): The measured concentrations in ground- and surface water from this area were higher than in the background water but comparable to values reported by other authors for surface water (see Table A-17, Appendix A), and within the range of typical levels reported for tap water in South Africa, 16-323 mBq.L^{-1} (Winde, 2013). The average ^{238}U concentration of about 50 mBq.L^{-1} (4 µg.L^{-1}) found in these sources were insignificant from both a radiological and chemical toxicity point of view. As expected, very high concentrations were measured in water from the impounding dam or retention pond. Nuclides from the Th series dominated in this waste water as seen by the large ^{228}Ra/^{226}Ra ratio. Large volumes of water are recycled during mineral processing activities. The use of recycling ponds may contribute to accumulation of NORM in the environment surrounding the processing plant if care is not taken in the design of these ponds to prevent release of water into the environment.

Mineral sands area (MS): No surface water features are located at the site. Groundwater from this area had slightly enhanced activity concentrations compared to water from background

areas. The concentrations of ^{238}U, ^{234}U and ^{226}Ra were higher than in the phosphate water. The ^{238}U concentration (366±183 mBq.L^{-1}) found in these sources were insignificant from a radiological point of view, but may present problems based on its toxicity. Concentrations of ^{226}Ra in the area ranged from 2.4-485 mBq.L^{-1}, which were lower than for well water from similar areas in Brazil where values as high as 3790 mBq.L^{-1} have been reported (Godoy & Godoy, 2006). Thorium deposits are present in the area, but thorium series nuclides, being less soluble in neutral pH waters, were not observed in the well water.

Gold mining (GM): In general higher concentrations were observed in water from the gold mining area than from other areas, especially in process- and surface water, with concentrations in groundwater lower and similar to what has been found in water from the phosphate area. The groundwater can be used for domestic purposes without further treatment. Uranium is prevalent in the area and high concentrations of both ^{238}U and ^{234}U were measured in process water (^{238}U =204-13290 mBq.L^{-1}). Similar high concentrations were measured in most of the surface water samples (^{238}U =13.6 to 11410 mBq.L^{-1}), which shows that surface water in this area seems to be affected by process water from an operational site. Water from sampling points GS6 and GS8 (see Table 5-26) had U concentrations higher than the derived EU value of 3000 mBq.L^{-1}, exceeding radioactivity limits. The highest ^{238}U concentration of 7460 mBq.L^{-1} corresponds to about 600 µg.L^{-1} U (assuming natural isotopic ratio). The activity concentrations at GS1, GS5 and GS7 were lower and acceptable also when considering chemical toxicity of U. Water from some other sampling points exceeded the WHO limit of 30 µg.L^{-1} considering chemical toxicity (*e.g.* GS2: 956 mBq.L^{-1} =77 µg.L^{-1}), although not exceeding radioactivity limits.

Concentrations in surface water from gold mine areas were an order lower than the maximum values for ^{238}U reported by Njinga *et al*. (2016) and Tutu *et al*. (2009) (see 2.5.7), measured by ICP-MS. Winde (2013) reported typical levels for polluted surface water of 360-5659 mBq.L^{-1} (max=51 Bq.L^{-1}). For fissure (underground) water and treated water the concentrations of 4.46 and 9.22 Bq.L^{-1} respectively, as reported by Tutu *et al.,* (2009) for water from a mine in Gauteng, was much higher than what was found in this case study.

Isotopic ratios

It is well known, and has been discussed in 2.1.2 that the $^{234}U/^{238}U$ activity ratio in natural waters can differ from unity, due to environmental processes and human activities. The

average $^{234}U/^{238}U$ activity ratio for analysed waters from most areas was greater than two showing disequilibrium, with a ratio as high as 10.3 observed for groundwater from the gold mines (Figure 5-22). These activity ratios are consistent with what is expected from water originating from a natural background area not (or minimally) affected by NORM industrial operations.

In surface- and process water from the gold mines the observed average $^{234}U/^{238}U$ ratios were 1.10 ± 0.33 and 0.92 ± 0.09 respectively. Water sources from this area were clearly impacted by mining activities. A breakdown of the ratios for the individual sampling points (Table 5-26) showed that the $^{234}U/^{238}U$ ratios for SPs with higher U concentrations [GS2, GS6, GS8] was lower than those of SPs with lower U concentrations [GS1, GS5, GS7] confirming higher impact of mining activities at these sources.

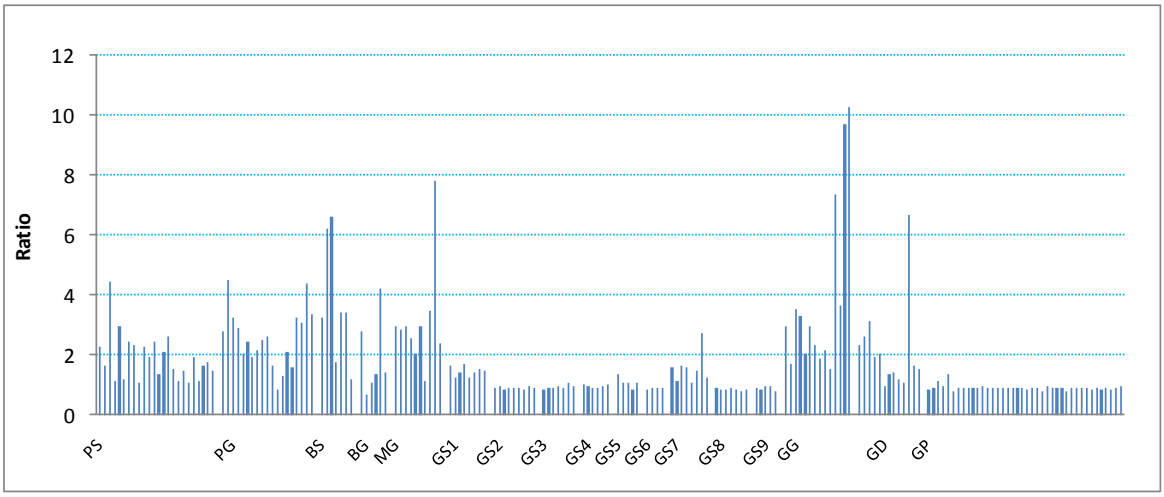


Figure 5-22: $^{234}U/^{238}U$ ratios observed in water samples from NORM industries

Correlation Analysis

To better understand the origin of the nuclides, correlation analysis can be used. The following correlation coefficients were plotted for the mine surface water data in Table 5-26 (n=59) – see Figure 5.23:

GA measured and ^{238}U: GA=0.914[^{238}U]+317 (R^2=0.929). The data shows a strong correlation and confirms that the measured activity in the water comes mostly from U. The ratio of the total GA (calculated by summation of the measured activity concentrations of all the individual nuclides) compared to the measured GA was 2.36 confirming that the activity

might be underestimated by a factor two if only GA is used.

^{238}U and ^{226}Ra: ^{238}U =18.4[^{226}Ra] +427 (R^2=0.432). The correlation analysis data show some correlation between the two nuclides although there is no equilibrium and ^{238}U dominates (average ratio ^{238}U/^{226}Ra is 60±85). It confirms differences in the behaviour of U and Ra in water. The ^{234}U/^{230}Th ratio was also much higher than unity (45±78), which can be explained by the fact that the solubility of ^{234}U in the U(VI) oxidation state exceeds that of ^{230}Th(IV) in water.

^{226}Ra and ^{210}Pb: ^{226}Ra=0.221[^{210}Pb]+78.1 (R^2=0.006). Although ^{210}Pb is the progeny of ^{226}Ra no correlation was observed. The concentration of ^{226}Ra was on average higher with a ratio of ^{226}Ra/^{210}Pb of 11.8±20.0.

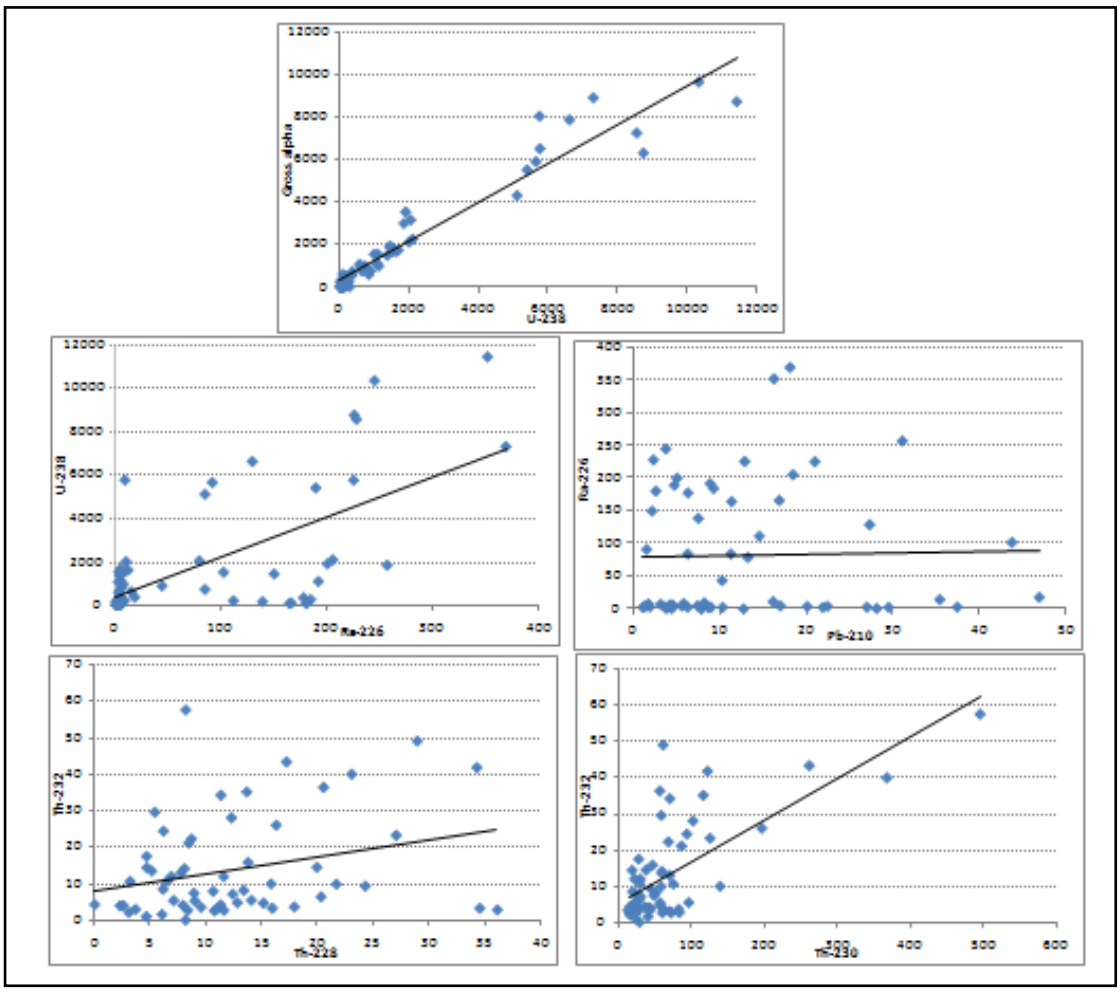


Figure 5-23: Correlation plots for surface mine water

^{232}Th and ^{228}Th: ^{232}Th=0.48[^{228}Th]+7.79 (R^2=0.084). The correlation analysis shows no correlation between the two nuclides even though ^{228}Th is the indirect daughter of ^{232}Th. The higher concentration of ^{228}Th compared to ^{232}Th (ratio 1.92±2.36) is probably coming from its parent ^{228}Ra (which was unfortunately not measured). In a natural environment the solubility of Ra is much higher than that of Th, especially with high concentrations of carbonate in the water.

^{232}Th and ^{230}Th: ^{232}Th=0.115[^{230}Th]+5.303 (R^2=0.473). Although ^{230}Th is the daughter of ^{238}U and not of ^{232}Th, some correlation was found between the two nuclides, indicating similar mobility behaviour.

Dose Evaluation

The annual dose calculated for the adult age group, as well as the most sensitive infant age group, is shown in Table 5-27 and graphically presented in Figure 5-24. For the adult age group the international dose limit of 1 mSv.a^{-1} was not exceeded for any of the samples. For more than 70% of samples the calculated dose from the full-spectrum analysis was less than the NNR dose constraint of 0.25 mSv.a^{-1}. Of the 30% exceeding this limit, 22% was mine process water. Since the water is not available for public use, no intervention other than routine monitoring is required for these sites. If age group classification is considered the most exposed group (infants less than 1 year of age) will receive a dose exceeding the NNR limit of 0.25 mSv.a^{-1} with 70% of samples, while 27% of the data exceeded the 1 mSv.a^{-1} dose limit, mostly for mine process water samples. The dose in process water ranged from 0.42 to 5.37 mSv.a^{-1}. Of more concern is the dose from surface water from GS8, which had a maximum dose of 2.2 mSv.a^{-1}.

When considering infants even some samples from the background area exceeded the NNR dose limit suggesting that the value of 0.25 mSv.a^{-1} is perhaps too conservative. The higher doses for infants are due to the large DCF for this group and the conservative assumption that infants consume 200 litre of water per annum from the contaminated source. It must be kept in mind that exceeding the dose constraint does not represent non-compliance with regulatory requirements, but only implies follow-up actions if so required by the regulator. Furthermore, evaluation of the water quality should never be based on a single measurement, but results obtained over a period of a few months should preferably be used.

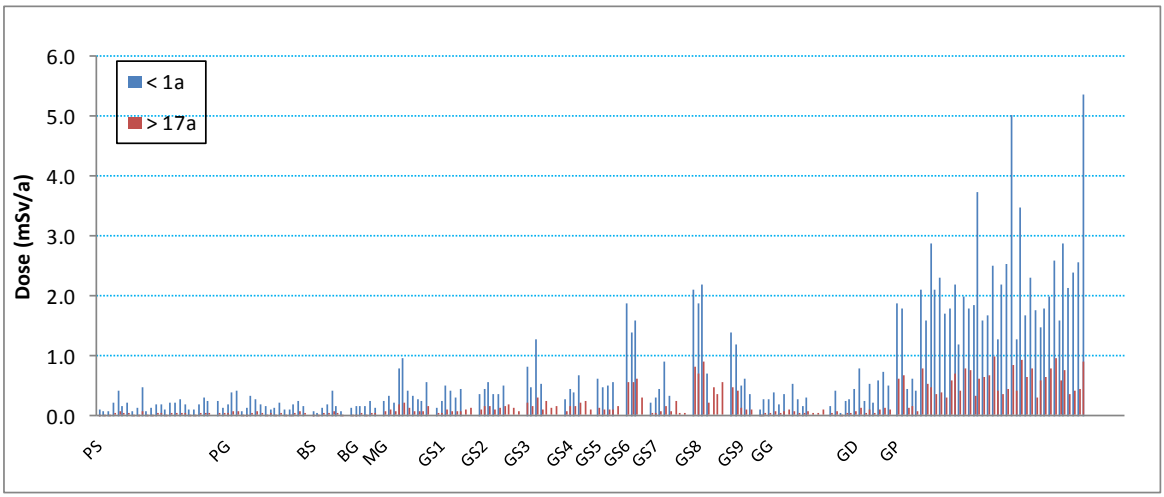


Figure 5-24: Annual ingestion dose for adult and infant age groups for all water sources from NORM industries

A more realistic determination of potential exposure from a source is the approach suggested by the DWS (2.3.5) where the average life-time consumption of the water is taken into consideration. When calculating the lifetime average dose from mine surface water using equation 2.1 and it was found that the adult dose contributed about 90 % to the lifetime dose (see Table 5-26). It must be emphasized that this would translate in a potential exposure, if this water would have been the sole source of drinking water for life-time consumption, which is seldom expected to be the case.

No dose evaluation was done for water from the impounding dams, because there is usually restricted access to these areas and it is therefore not assessable to the public to be used as drinking water. These dams collect all process water and storm water that leaves the site. The recovered water is returned to the plant via pipelines for re-use. Care is also taken in the design of these ponds to prevent release of water into the environment.

When looking at the contribution of individual nuclides to the total ingestion dose, high variations were found in the different types of water. As seen from Figure 5-25 the contribution to dose of both ^{234}U and ^{238}U was low in most samples, due to relatively low radio toxicity of uranium isotopes compared to other radionuclides. The exception was the gold mine process water sample with U concentration greater than 10 $Bq.L^{-1}$ where more than 80% of the dose was attributable to U (Figure 5-25F).

The examples shown in Figure 5-25 are for the sample from each source, which had the

maximum calculated dose for infants. The main contributor to dose was as follows:

- A: Phosphate surface water: dose =0.48 mSv.a^{-1}. Main contributor was ^{230}Th (42%).
- B: Phosphate groundwater: dose=0.44 mSv.a^{-1}. Main contributor was ^{228}Ra (50%).
- C: Monazite groundwater: dose=0.96 mSv.a^{-1}. Main contributor was ^{226}Ra (34%).
- D: Gold surface water from SP4, high U concentrations (~2 Bq.L^{-1}): dose=0.69 mSv.a^{-1}. Main contributor was ^{210}Po (26%).
- E: Gold surface water from SP5, low U concentrations (~0.1 Bq.L^{-1}): dose=0.64 mSv.a^{-1}. Main contributor was ^{227}Ac (40%) with ^{226}Ra contributing 27%.
- F: Gold process water, very high U concentrations (> 10 Bq.L^{-1}): dose=5.4 mSv.a^{-1}. Main contributor was ^{234}U (42%).

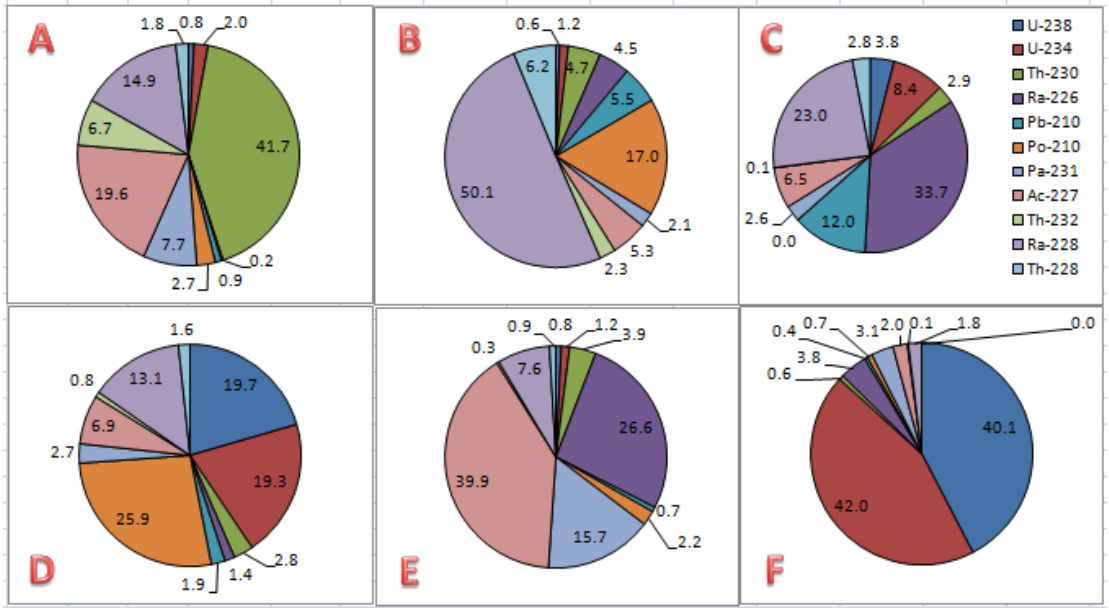


Figure 5-25: Contribution of individual nuclides to ingestion dose for water from different sources
(A: Phosphate surface; B: Phosphate ground; C: Monazite; D: Gold surface GS4; E: Gold surface GS5; F: Gold process

As can be seen from these examples the contributing nuclides differed for every type of sample, making it difficult to make general conclusions about the contribution of different nuclide to effective dose. On average the lowest portion of the dose was found for ^{238}U and ^{234}U despite the high concentrations, followed by ^{232}Th and ^{228}Th. Due to the very high DCF, ^{228}Ra and ^{227}Ac was found to contribute high dose proportions.

The two mine surface water from different sampling points (GS4 and GS5) is shown to

illustrate the importance of full nuclide analysis for dose assessment. A similar dose for both was observed even though the U concentration at GS4 was much higher than that of GS5. The ^{226}Ra concentration at the latter was however high, contributing to a higher dose.

Conclusions

With the exception of the process water and some of the surface water from the gold mine areas, all the water sources analysed had relatively low levels of natural radioactivity and can be used for drinking and domestic purposes. The highest activities in most of the water came from uranium isotopes. The ^{234}U/^{238}U ratios varied indicating both unaffected and affected water.

It was concluded that water from the gold mine areas may present a chemical hazard, with 36% of samples exceeding the WHO limit of 30 µg.L^{-1}. A maximum concentration of 600 µg.L^{-1}, twenty times higher than the WHO limit, was measured in some surface water samples. This corresponds to findings by Winde who have reported high uranium concentrations in water impacted by mining activities in several publications (see 2.5.7).

The lifetime average dose from most sources was lower than the NNR dose constraint of 0.25 mSv.a^{-1}; however, if age groups are considered, infants were exposed to higher dose. The highest ingestion dose was for process water with the maximum exposure estimated to be about five times higher than the international limit for members of the public. This water is not routinely released to the environment. Of concern were some individual surface water samples, which may result in a dose more than twice the international limit. The contribution of ^{234}U and ^{238}U to dose was relatively low, despite high concentrations present in water. The dose estimation done in the study was very conservative assuming that no water treatment has been done and that water has been used as is (direct consumption from the source).

This study showed a large variation in radionuclide concentrations, and thus estimated effective doses, from different sources. To get a more complete picture of the radiological impact due to consumption from water sources impacted by NORM industries in South Africa, additional studies are required.

The results obtained compared well with data from studies conducted in other countries (Table A-17, Appendix A). The baseline data can be used as reference for future studies for

evaluation of potential environmental contamination due to NORM activities.

5.1.6 Treated water

Quantity and quality of effluent discharge from mines to the environment are usually controlled. Impounding dams (or settling ponds) are used to improve water quality before discharge. Fissure water in mainly clean good quality water with low radioactivity and only slightly contaminated with salts (Table 5-27). In the mine water circuit fissure water is channelled to water settling ponds where it is mixed with mine process water pumped from underground. The blended water is then re-circulated in mining operations, discharged or, depending on the improvement of water quality, made available for domestic use.

Treatment may be required for mine process water contaminated with natural radioactivity before it can be released to the environment. Water treatment technologies have been described in 2.5.5. U and Ra are present in ionic form and can be removed by ion exchange method. Pb and Po exists mainly as particles and the primary method for removal is therefore flocculation and filtration.

The aim of water treatment in SA is mostly to reduce the levels of uranium, as main contaminant, to the WHO drinking water standard of 30 $\mu g.L^{-1}$ (370 $mBq.L^{-1}$ ^{238}U). Treatment plants employ ion exchange technology, addition of lime and dilution as preferred water treatment processes. Water after treatment should show a significant improvement in quality relative to pre-cleaning conditions, resulting in a reduced potential radiological impact to humans and the environment.

A typical full-nuclide radiological analysis for one water sample before and after treatment is shown in Table 5-3. The results show a 95% reduction in radionuclide concentrations for uranium and other radionuclides. The effectiveness of the treatment procedure in reducing the dose was clear- the lifetime average annual effective dose from ingestion of the water decreased from 1.20 to 0.062 $mSv.a^{-1}$, which is well below the dose constraint of 0.25 $mSv.a^{-1}$. It can thus be concluded that the treated water would be suitable for general household purpose and as a source of drinking water.

There are ongoing studies investigating treatment of contaminated mine water, specifically AMD (DWS, 2013). As seen from the presented results water treatment can be very effective; however the disposal or use of residues from waste treatment such as sludge, ion

exchange resin and other waste products may be a serious challenge.

Table 5-3: Radio-analytical results of mine water before and after treatment ($mBq.L^{-1}$)

Nuclide	Mine process	Treated water	WHO, 2011
^{238}U	3.53E+03	1.67E+02	1E+04
^{234}U	5.78E+03	1.90E+02	1E+04
^{230}Th	3.71E+02	1.23E+01	1E+03
^{226}Ra	3.77E+02	1.08E+02	1E+03
^{210}Po	7.14E+01	2.75E+00	1E+02
^{235}U	2.37E+02	7.67E+00	1E+03
^{227}Th	2.57E+02	4.94E+00	1E+04
^{223}Ra	1.03E+02	2.98E+00	1E+03
^{232}Th	2.94E+01	1.68E+00	1E+03
^{228}Th	7.72E+01	4.83E+00	1E+03
^{224}Ra	3.17E+01	2.32E+00	
Sum of all nuclides	1.99E+04	1.08E+03	
Lifetime average dose ($mSv.a^{-1}$)	1.20	0.062	1

5.1.7 Final conclusions

In this case study the results of the radioactivity analysis of various water sources were presented and the water quality evaluated with reference to South African national standards and international limits. The results presented are important since data on radioactivity in drinking water in SA is relatively scarce. The presented study is the first providing information on radioactivity in bottled water, and water from industries from different regions in the country. Although internal water standards for mines states that water quality results shall be communicated to end-users by publications, these reports are not accessible. This should be rectified - even if not published in conventional scientific literature, data should be made public and be available in a database on the internet for general access by the public.

The technique of gross alpha/ beta analysis, which has been used for screening of all water samples, is not radionuclide specific and has many sources of interferences resulting in high uncertainties of typically around 20% to 30%. Screening results can only give an indication of the radiological quality of water, but measurement of all the nuclides is required for accurate dose assessment. The implemented radiochemical methods proved to be sensitive

and accurate enough for determination of the radionuclides of interest in water samples and to assess the radiological quality of the drinking water. Since these methods are complex, time-consuming and costly, and therefore not applicable to a large number of samples, measurement of gross alpha/beta activities is recommended for screening purposes.

A LOD of 0.05 and 0.10 $Bq.L^{-1}$ for gross alpha and beta activity is proposed internationally (from WHO and EU), while that achieved by the analytical protocol adopted in our laboratory was 0.072±0.035 and 0.162±0.255 $Bq.L^{-1}$ respectively, only slightly higher than the proposed LODs. For ^{234}U and ^{238}U the proposed LOD is 0.02 $Bq.L^{-1}$; that achieved by the radiochemical method described in 4.8.2 was 0.003 $Bq.L^{-1}$. The LOD of the technique implemented for chemical analysis of uranium and used for this study was 0.05 $\mu g.L^{-1}$; well below the SANS 241:2015 limit of 30 $\mu g.L^{-1}$. These parameters indicate that the implemented methods were suitable for quantification at levels well below internationally accepted limits.

For bottled water the recommended WHO guideline activity concentrations was not exceeded for any sample. It was concluded that this water is radiologically safe and poses no significant hazard to the consumer.

The radioactive screening of the DWS water sources indicated some radioactive "hot spots" for surface water samples, which exceeded the WHO screening limit of 0.5 $Bq.L^{-1}$. To determine the dose impact from consumption of these water sources, future monitoring should include nuclide specific analysis. For the majority of sources the screening results indicated good or ideal quality water resulting in a dose of less than 0.1 $mSv.a^{-1}$. The data of the nuclide specific analysis of environmental surface- and groundwater analysed as part of the DWS NRMP showed that the radiological quality of most of the sources was good resulting in a dose of less than 1 $mSv.a^{-1}$ if consumed. These results were based assuming conservatively consumption of 2 litres per day (730 litres per annum) from the surface water. Water from six sites exceeded the NNR dose constraint of 0.25 $mSv.a^{-1}$ and might have health effects to the most sensitive age group (infant) if used for domestic purposes. Based on the correlation between the U concentration and gross activity it was concluded that measurement of only the chemical concentration of uranium may be sufficient for future radiological assessment of water from the specific catchment. It was also concluded that the concentration of U in water from the specific catchment correlated with TDS.

The quality of water from mining- and other NORM industries varied. Depending on the area

from which the water originated fairly high activities were measured in some samples, indicating a possible radiological health risk from ingestion of this water. However, for the majority of sources the results indicate insignificant levels of public exposure and suggest low radiological impact of industrial activities on communities in the area. As regards ^{238}U it was shown the chemical toxicity rather than the radioactivity was the limiting factor for classification of the quality of the water. The WHO chemical toxicity reference level of 30 $\mu g.L^{-1}$ (373 $mBq.L^{-1}$) was exceeded for many samples, whereas only a few samples exceeded the EU reference value for radio-toxicity for ^{238}U, 3000 $mBq.L^{-1}$.

The present study has pointed out needs for further studies, to better quantify the levels of natural radioactivity in water in South Africa. Even if no intervention is required, in terms of the ALARA principle, of keeping dose to the public "as low as reasonably achievable", mines and other industries should continue to limit the discharge of water containing unacceptable levels of radioactivity. Trend analysis of routine monitoring programmes should be used as an early warning mechanism to limit exposure.

It is currently not compulsory for all the water resources in SA to be monitored for radioactivity as per international regulations. It is recommended that the DWS guidelines are implemented and that all water resources used for domestic water supplies are regularly monitored to ensure that the water is safe to drink. Screening investigations should be conducted at all main waterworks or collection points that supply water to the public to characterise the radiological quality. In-depth investigations should be carried out in regions know to have above average background levels of radioactivity and for those sites exceeding the screening levels. Once the radiological quality has been established sampling frequency can be reduced. It should be kept in mind that no final conclusion regarding the radiological quality of a water resource in any area should be based on a single measurement and that long term trends should be considered.

5.2 Natural radioactivity in food

5.2.1 Introduction

National Food Monitoring Programmes for determination of natural radioactivity in diets exist in several countries worldwide, with the main objective to determine the annual intake and radiation dose due to consumption of food. No official monitoring program exists in

South Africa; therefore data of natural activity concentrations in food is scarce. For the public, it is important to know that the radioactivity levels in food do not exceed allowable limits.

In this case study the potential radiological impact of foodstuffs grown in areas in proximity to NORM industries in South Africa, was investigated. Results for food analysed as part of a baseline study for new industrial activities are also included. The dose for the adult age group, resulting from consumption of these foodstuffs, was estimated.

5.2.2 Experimental

Sampling and sample preparation

Food samples from the six categories defined by WHO (1988) *i.e.* fruit, roots and tubers, vegetables, cereals and grains, meat and seafood/fish, were analyzed. Samples were collected in the vicinity of industries of interest including the gold mining, phosphate- and mineral sands processing industries ("exposure sites"). Fish were sampled at different locations. Samples for a baseline study ("reference site") were also collected. Samples were conserved by freezing.

Samples were prepared as required for human consumption described in 4.3.2. Samples were dried and then ashed. Dried samples were digested in an open vessel microwave for ^{210}Po analysis (see 4.8.1). The digested sample was filtered and converted to chloride form by addition of hydrochloric acid and evaporating to dryness.

Radioactivity analysis

Radio-analytical techniques summarized in 4.12 were used for analysis of the food samples. NAA was used for determination of U and Th element concentrations. Initially high energy gamma spectrometry was used for analysis of ^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K and low energy gamma spectrometry for ^{210}Pb analyses. More recently use of a broad energy detector has been implemented due to the much better sensitivity of this detector (4.9.3). Sensitivity has been further improved by ashing the samples. Polonium was determined using the described radiochemical method in 4.8.1 and alpha spectrometry.

5.2.3 Results and discussion

Activity concentrations in food samples

Activity concentrations for naturally occurring nuclides in the analysed food samples are shown in Table C-1 in Appendix C. The reported data show a wide range in concentrations for different food categories. Concentrations within the same type of food varied depending on the area from where it was collected. Generally, the measured concentrations in South African food were within the range of worldwide values (Table A-18, Appendix A) but higher than UNSCEAR reference concentrations (Table 2-3). The high activity concentrations observed in some samples (indicated in bold in Table C-1, Appendix C) should be investigated.

Gold Mining Industry

The averages for the different food groups for samples received from gold mine areas are shown in Table 5-4. The measured concentrations for ^{210}Pb and the nuclides from the thorium series were mostly below the LOD of the analytical method used.

Table 5-4: Average activity concentration (Bq.kg^{-1}) for food from gold mine industry

Nuclide	Fish	Meat	Leafy	Root	Cereal
	G1-G11	G15-G25	G30-G41	G42-G53	G50-G65
^{238}U	1.42± 1.63	0.03± 0.01	0.11± 0.11	0.24± 0.20	0.03± 0.03
^{226}Ra	1.71± 1.57	0.33± 0.01	0.66± 0.26	0.76± 0.24	<LOD
^{210}Pb	<LOD	<LOD	1.00± 0.63	0.45± 0.22	2.11± 1.28
^{210}Po	0.56± 0.31	1.25± 1.49	0.31± 0.40	0.79± 0.77	1.28± 0.82
^{232}Th	<LOD	<LOD	0.21± 0.13	0.10± 0.07	0.13± 0.12
^{228}Ra	<LOD	<LOD	0.54± 0.27	0.43± 0.37	<LOD
^{228}Th	0.29± 0.27	<LOD	0.09± 0.06	0.17± 0.12	<LOD
Dose	0.09± 0.14	0.30± 0.22	0.12± 0.13	0.22± 0.32	1.11± 0.50

^{238}U concentrations in fish were higher than in fish from other regions with an average of 1.42±1.63 Bq.kg^{-1}, and also higher than literature and UNSCEAR values. This may indicate some intake of uranium by fish in these areas, which are known to contain elevated concentrations of uranium in water sources (see 5.1.5). ^{210}Po is known to accumulate in fish (2.1.5); therefore higher concentrations are to be expected. This accumulation is pronounced in the fish intestine and bone samples (G12-G13: 4-19 Bq.kg^{-1}). Since intestines and bone of

a fish are usually not consumed the dose will be overestimated if it is included in the dose calculation. High LODs of up to 10 Bq.kg^{-1} were obtained for ^{226}Ra, ^{228}Ra and ^{228}Th for samples not measured with broad energy gamma spectrometry (G10-G13).

The activity concentration of most of the nuclides in meat was low. High ^{210}Po concentrations were observed in the chicken (G13-14: 1.6-4 Bq.kg^{-1}) and some of the meat samples (G23-25:1.1-3.9 Bq.kg^{-1}), with even higher concentrations in the liver and kidney samples (3.9-13.1 Bq.kg^{-1}). This is as expected since internal organs are known to accumulate ^{210}Po (2.1.6). The reported LOD for ^{238}U for meat samples (G16-G21: 2.7-3.8 Bq.kg^{-1}) and the one chicken sample (G14: 21 Bq.kg^{-1}) was very high. The high ^{238}U concentrations in chicken and meat referenced by Winde (2013) were not actual measured activities but based on (overestimated) LOD values. A similar high LOD for ^{238}U (and for ^{232}Th) was observed for other samples from the same batch *i.e.* spinach (G29: 30 Bq.kg^{-1}), beetroot (G45: 21 Bq.kg^{-1}) and maize (G58: 35 Bq.kg^{-1}). The high LOD could not be explained, and was probably due to an experimental or calculation error.

Concentrations in milk were low, which indicate low transfer rates and insignificant contribution of the feed-cow-milk-human pathway to exposure. The LODs for milk were low due to the large volume of sample used (1 litre) and pre-concentration by ashing.

Concentration in vegetables varied, but was mostly lower than 0.5 Bq.kg^{-1} for all nuclides, except for ^{210}Pb and ^{210}Po. The concentrations in root- and leafy vegetables were in the same range, although based on the literature study one would expect some differences in uptake (2.4.4). Activity concentrations in leafy crops are determined by both deposition and root uptake, whereas concentrations in root crops are mostly determined by root uptake and re-suspension of soil. The higher concentrations measured in spinach (G30-G31) compared to other leafy vegetables (cabbage: G37-39 and lettuce: G40-G41) suggests dominance of atmospheric deposition. Outer leaves of cabbage were removed, whereas spinach was analysed as received. Higher concentrations of radium isotopes compared to thorium isotopes were found in most of vegetables, due to higher mobility and bio-availability of Radium (2.4.6). High concentrations of ^{228}Ra and ^{226}Ra were measured in the lemon sample (G55).

High concentration of ^{210}Pb and ^{210}Po compared to the other nuclides were found in most of the cereal samples, which can be attributed to deposition. For some cereals activity concentrations will be low since the edible parts are protected by inedible plant parts (chaffs),

and therefore not affected by atmospheric deposition. Only edible part should be analysed for evaluation of dose from ingestion. The very high concentration found in the rye sample (G68) is of concern, but may be partly explained by inclusion of soil particles, which was not removed from the leaves. Rye, barley and lucern (G66-70) were analysed as received with all plant parts included and should be considered as animal feed and used for evaluation of the secondary fodder-cattle-human pathway only.

Phosphate Industry

Low concentrations were found in most of the food samples from this area, with high values reported only for some individual nuclides. Higher concentrations of ^{228}Ra and ^{228}Th were observed in some of the fruit and vegetables (P37, P39, P40: 1-2 Bq.kg^{-1}). Concentrations of ^{228}Th were an order higher than that of ^{232}Th. ^{228}Th is probably only present as decay product of ^{228}Ra, since Th has low solubility and uptake by plants (2.1.3).

The average for ^{210}Po in freshwater fish (P8-P15) was 1.16±1.50 Bq.kg^{-1}. The concentrations were lower than reported values in an earlier study (P1-P7: 1.90-23.3 Bq.kg^{-1}) in which it was concluded that most of the samples had elevated radioactivity levels (Faanhof & Louw, 2001). Those results were obtained before the radio analytical methods for analysis of food samples had been optimized. ^{210}Pb was measured by low-energy gamma with a high LOD. With the introduction of the radiochemical separation method for ^{210}Po, the LOD for this nuclide decreased with almost a factor 50 (see Table 4-22). The sensitivity for measurement of ^{228}Ra, ^{226}Ra and ^{228}Th has also improved with a factor 10 with introduction of a broad energy detector for analysis of ashed samples (P11-P15) compared to the higher LODs obtained when analysing dried samples with high energy gamma spectrometry (P8-P10) – see Table 4-22. As shown in Tables 5-5 and 5-6 the use of data obtained by measurement techniques with inadequate sensitivity can result in overestimation of dose and the wrong conclusion that samples are "contaminated to such an extent that it might be regarded as unsuitable to be used as a food source".

In SA it is still practise to discharge phosphogypsum to the sea as dilute slurry (IAEA, 2013). To monitor for contamination in this area fish samples taken directly at the outlet of the waste stream, as well as from a background area 20 km upstream from the facility, are analysed regularly. Concentrations of ^{210}Po in some of the fish samples close to the outlet

(P16-P20), were higher (average 4.26±2.10 Bq.kg^{-1}) compared with the average of 1.53±0.91 Bq.kg^{-1} found in the background area (P23-P31), which might indicate some contamination in the area. The measured concentrations were of the same order as reported concentrations for ^{210}Po in fish worldwide (Table A-18, Appendix A) and the UNSCEAR reference levels of 2 Bq.kg^{-1} (Table 2-3). This is similar to results reported by Dahlgaard (1996) that radioactivity in fish from two locations close to former phosphate industries were not different from background values. Enhanced levels of ^{210}Po in some areas in the Adriatic seas due to the presence of a phosphate fertilizer industry, was reported by Desideri *et al*. (2010). The high concentrations of ^{210}Po and ^{210}Pb measured in the crayfish and crab samples (P21-P22: ~ 10 Bq.kg^{-1}), were within limits as expected for marine species.

Baseline study

A variety of food samples were analysed as part of a baseline study for proposed future industrial activities. Of interest here was the high concentration of 12-59 Bq.kg^{-1} for ^{210}Po in the seafood (B1-B4), especially in the mussel samples, which was comparable to the concentrations found in Korea (Kim *et al.*, 2017; Lee *et al.*, 2009). ^{210}Po in the marine environment is mostly present as decay product of deposited ^{210}Pb, with only a small amount occurring from atmospheric deposition of polonium itself. Mussels have the ability to concentrate heavy metals, and are therefore commonly used as bio-indicators to monitor environmental pollution (2.1.5), so these high concentrations are not totally unexpected.

Activity concentrations in milk were low and comparable to literature values. High concentrations of ^{210}Po were found in all the meat samples (B8-B16: 0.73-2.1 Bq.kg^{-1}), except in the rib sample (B12:0.4 Bq.kg^{-1}), which had higher ^{228}Ra (1.31 Bq.kg^{-1}) and ^{228}Th (supported by ^{228}Ra) than the other meat samples. The ratio of Pb/Po > Ra > U, with lower ^{232}Th series activity concentrations is similar to what has been reported by UNSCEAR (2000). From the results it was clear that natural radioactivity is already present in most biota and confirms the importance of conducting a baseline study to determine the natural radioactivity level in an area before introducing any industries which may further enhance the levels of radioactivity.

Mineral sands industry

Not much data was available for this area. The activity concentrations in meat (M1-M3) and

grape samples (M4-M7) were low and comparable to world averages. The only sample with significant activity concentrations for all nuclides was the oats sample (M8). This was also the only sample of all the analysed food samples from the different areas with a measurable ^{232}Th concentration. Since some mineral sands are known to have very high thorium concentrations (as confirmed by analysis of solid samples from the industry - see 5.4.4), it is not totally unexpected to find high thorium concentrations in a sample originating from this area. However, only a single sample has been analysed and the high result should be confirmed by analysis of more samples.

Annual effective dose

The consumption rate of food by individuals, as well as the concentration of the radionuclides of concern, will determine intake of radioactivity via the ingestion pathway (2.3.5). Using equation 2.3 and the ICRP recommended dose conversion factors for ingestion (ICRP, 1996) the dose from annual intake was calculated. Default consumption values for foodstuffs recommended by the NNR were used (NNR, 2013). The overall estimated annual dose is reported in Table C-1 (Appendix C). The dose is shown per product and not summarized for total diet from all products. Only the dose to adults was considered.

The estimated dose for the majority of the foodstuffs was well within the "single facility" dose constraint of 0.25 mSv.a^{-1}, as well as the public dose limit of 1 mSv.a^{-1} prescribed by the NNR. The dose is mostly of the same order as the UNSCEAR (2008) assessed dose from natural radionuclides in food (0.29, with a range of 0.2-0.8 mSv.a^{-1}). ^{40}K was not reported and excluded from the dose calculation. As an essential element in the body, potassium is under homeostatic control, and concentrations and dose received from ^{40}K are therefore not affected by any variation in diets (2.3.5).

The dose may be underestimated if contribution of radionuclides reported as a "< *MDA value*", are ignored. Therefore for values reported as lower than detection limit, it is common practise to use a value of half the LOD in dose calculations. However, the dose may be overestimated if the radiometric technique used was not sensitive enough and results were reported with a high MDA (and unfortunately reported as a "true" value in the press). Care should therefore be taken when using this approach in environmental monitoring not to overestimate the dose and produce meaningless results. For accurate dose estimations it is

essential to develop/use adequately sensitive radioanalytical techniques (4.9.3). Good progress has been made in our laboratory over the last few years to implement techniques with better sensitivity. The improvement is clear from the results summarized in Table 5-5. For the majority of vegetable samples the calculated dose was relatively low where the sample was analysed using broad energy gamma spectrometry on ashed samples compared to measurements obtained by high energy gamma. The higher dose obtained for the samples from the gold mining areas shown in Table 5-5 is probably further overestimated because of the high LOD for ^{238}U reported for the specific samples (and assuming ^{230}Th to be in equilibrium.

Table 5-5: Improvement of dose for samples from the gold mine industry with a more sensitive technique (mSv.a^{-1})

	High gamma (dried)		Broad gamma (ashed)	
Spinach	G29	0.57	G30-32	0.17-0.25
Cabbage	G35	0.21	G36-37	0.018-0.034
Beetroot	G45	0.73	G46-47	0.16
Chicken	G14	0.72	G15	0.51

The high dose for meat sample G16 in Table C-1 (0.75 mSv.a^{-1}) could be attributed to the high LOD for ^{210}Pb, which was measured by low-energy gamma, similar to what is shown for fish samples in Table 5-6. Using the radiochemical value for ^{210}Po and assuming equilibrium, the dose decreased from 0.75 to 0.14 mSv.a^{-1}. In the liver sample (G26-G27) ^{210}Pb and ^{210}Po were the main contributors to dose, with ^{210}Po contributing 60-70%, which confirms known accumulation of ^{210}Po by internal organs. The high consumption rate (30 kg.a^{-1}) used in the dose calculation contributed to the high dose for liver (1.7-2.7 mSv.a^{-1}). This is the RG-002 value for consumption of beef and is probably not realistic for consumption of liver.

The relatively high dose observed for the lemon sample (G55:0.36 mSv.a^{-1}) was mainly caused by high concentrations of ^{228}Ra and ^{226}Ra. Similarly a high ^{228}Ra concentration, as well as the high consumption value for root vegetables (170 kg.a^{-1}) contributed to the high dose in one of the beetroot samples (G50:1.0 mSv.a^{-1}) – see Figure 5.27. Samples of concern (with dose > 1 mSv.a^{-1}) in the gold mining areas seem to be the maize G58, rye G68, lucern G70 and the cereal samples (G59-G65), which is mostly used as animal feed (fodder). Since these samples are not directly consumed by humans, the dose should be calculated via the animal pathway and not for human ingestion as was done here. Since possible contamination

of these samples cannot be ignored, it is important for further analysis to be conducted, since decisions should not be made based on analysis of single samples. It is likely that results may differ depending on season and monitoring over a longer period is therefore important.

^{210}Po was the main contributor to dose in the majority of the foodstuff, whereas the contribution from ^{238}U and ^{232}Th was less than 10 %. Figure 5-26 shows contribution of dose per nuclide for a lettuce sample (G41). This distribution was typical for many of the vegetable samples. ^{210}Po contributed about 20-40%; ^{228}Ra, ^{226}Ra and ^{210}Pb were the other main contributors. Another typical distribution is shown in the graph for beetroot G45 (Figure 5-28) in which ^{230}Th contributed significantly to dose. The high contribution by ^{230}Th was as result of the high dose conversion factor for this nuclide, which was not measured but assumed to be in equilibrium with ^{238}U, which was, in the case of the beetroot sample, measured with poor sensitivity. As shown in Figure 5-28 this "overestimated" contribution to dose was as high as 40%. Actual measurement of ^{230}Th by a radiochemical procedure and not assuming equilibrium will help to improve the accuracy of the dose estimation. Equilibrium assumption is probably incorrect due to differences in mobility and uptake of U and Th in plants.

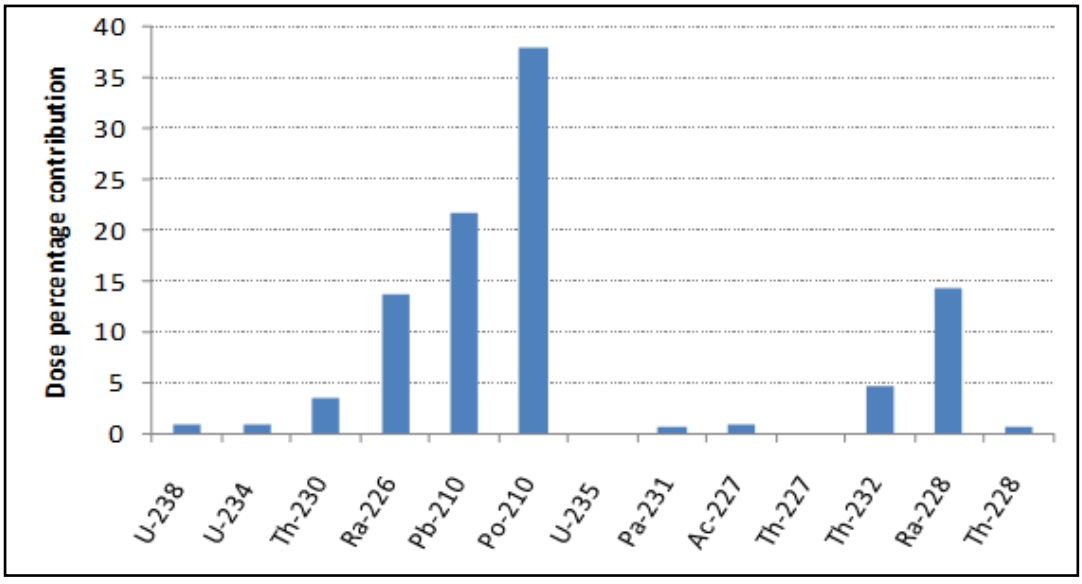


Figure 5-26: Typical dose contribution for most vegetable samples

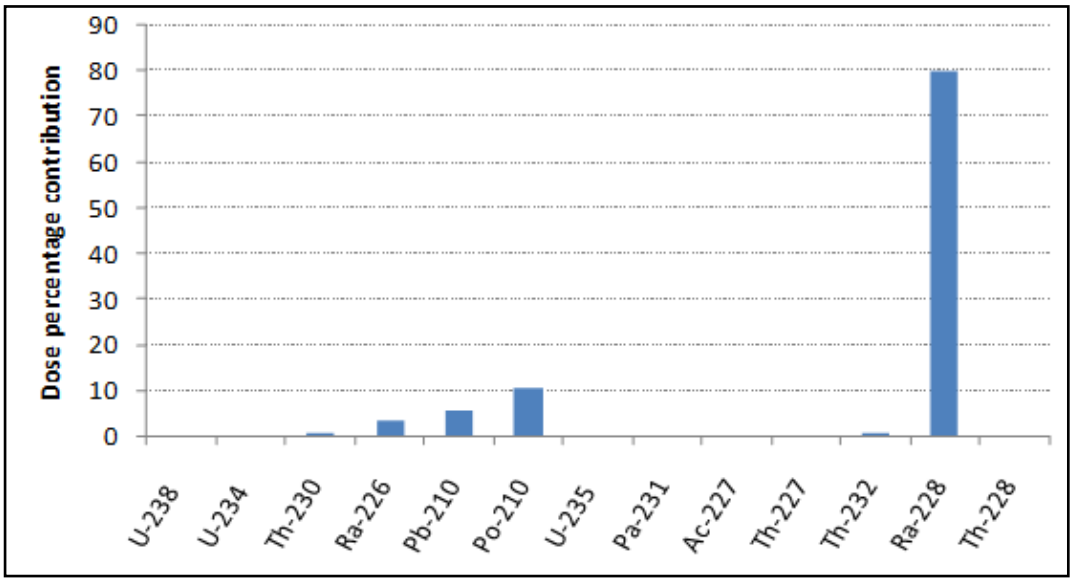


Figure 5-27: Showing large contribution of ^{228}Ra to dose for some vegetable samples

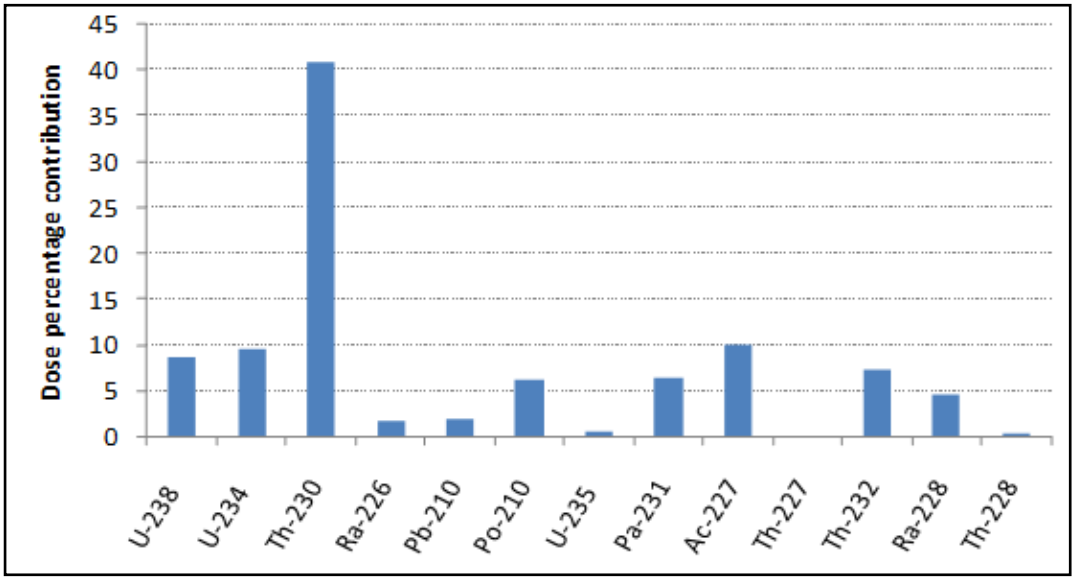


Figure 5-28: Dose overestimation due to high limit of detection for ^{238}U (=^{230}Th)

Samples with high uranium concentrations (G3, G6, G9 fish) have potential for both radiological hazard and chemical toxicity. However, as shown in Figures 5-26 to 5-28, from the radiological perspective, the total radiation dose from all the radionuclides is important and contribution of U is often negligible compared to other nuclides. Therefore, dose calculations based only on uranium and thorium content as done by some authors (Misdaq & Elamyn, 2006) will grossly underestimate the exposure.

Most of the food samples collected from other areas was of little concern with dose less than 0.1 mSv.a^{-1}. The exception was some of the fish and seafood samples, even from the baseline study area, of which consumption can result in a dose of more than 1 mSv.a^{-1}. In these samples the contribution from ^{210}Po to the dose was as high as 90%. Also of concern was the oats from the mineral sands industry (M8: 1.9 mSv.a^{-1}) with enhanced levels of all nuclides, including those from the thorium series. These samples were analysed with optimized techniques with the broad energy detector and radiochemical determination of ^{210}Po.

Table 5-6: Analyses of two fish samples in catchment area near mining activities
(Consumption 25 kg per year for adult population)

Nuclide	x001: Instrumental – low energy gamma		x001: Radiochemical		x002: Instrumental – low energy gamma		x002: Radiochemical	
	mBq.g^{-1}	µSv.a^{-1}	mBq.g^{-1}	µSv.a^{-1}	mBq.g^{-1}	µSv.a^{-1}	mBq.g^{-1}	µSv.a^{-1}
^{238}U	9.00	10.1			1.33	1.50		
^{234}Th*		0.77				0.11		
^{234}U*		11.0				1.63		
^{230}Th*	ND	47.3				6.98		
^{226}Ra	34.6	**242**			< 27	**< 190**		
^{214}Bi*		0.12				< 0.09		
^{214}Pb*		0.10				< 0.07		
^{210}Pb	<24	**< 410**	1.2	20.2	< 70	**< 1200**	0.7	11.9
^{210}Bi*		< 0.8				< 2.3		
^{210}Po*		**< 720**	13.9	418		**< 2100**	7.55	226
^{235}U	0.415	0.49			0.061	0.07		
^{231}Th*		0.00				0.00		
^{231}Pa*	ND	7.37				1.09		
^{227}Ac*	ND	11.4				1.69		
^{227}Th*		0.09				0.01		
^{223}Ra		1.04				0.15		
^{232}Th	3.17	18.2			< 0.31	< 1.8		
^{228}Ra*	38.7	**668**			< 8.1	**< 140**		
^{228}Ac*		0.42				< 0.09		
^{228}Th	15.2	27.4			< 6.3	< 11		
^{224}Ra		24.7				< 10		
^{212}Pb*		2.28				< 0.095		
Max mSv.a^{-1}		**< 2.20**		< 1.51		**< 3.67**		< 0.61

Radionuclides in bold were measured in this study
**Assumed mother-daughter equilibrium*
ND – Not Determined

In the area affected by the phosphate industry the doses due to consumption of fish was acceptable and less than 0.25 $mSv.a^{-1}$. Slightly enhanced dose occurred from fish at the outlet with a maximum dose of 0.34 $mSv.a^{-1}$ and ^{210}Po as main contributor (>50%). The overestimation of dose due to a high LOD of less sensitive older techniques was clear from this data (P1-P7: 1.0-1.8 $mSv.a^{-1}$), showing significant improvement with the implementation of more sensitive techniques.

The importance of using analytical techniques with good sensitivity is further illustrated from the data in Table 5-6. The analytical results for two fish samples are shown, together with the dose calculated for the adult age group. The dose was overestimated when analysis of ^{210}Pb in food samples was done using a low energy gamma detector with poor sensitivity (see LOD in Table 4-21) and assuming ^{210}Po to be in equilibrium. The dose estimation improved considerably when using the results obtained with the radiochemical procedure for ^{210}Po. ^{228}Ra, ^{226}Ra and ^{228}Th were also measured with poor sensitivity in this specific sample (using high energy gamma spectrometry on dried samples).

Uncertainty and Conservatism analysis

The estimated annual effective dose values presented in Table C-1 (Appendix C) were based on a predefined set of exposure conditions and associated parameter values. The inherent nature of a safety assessment is such that uncertainties exist. Unfortunately, the conservatism build into dose calculations are seldom understood by the public resulting in unnecessary concern and press attention.

To obtain the annual dose a conservative approach has been followed by assuming that all intake of an individual food source(s) is from the contaminated product and that the food is consumed immediately after harvest with no processing. In UNSCEAR (2016) it is recommended to assume that only 25% of food is produced locally *i.e.* in the area being evaluated. Since the radioactive content of final edible products can be reduced by food processing; ignoring these losses can result in an overestimated dose. Concentrations in vegetables in different years and seasons may vary. For meaningful estimation of the dose sampling should be done throughout the year; results for a single sample should not be used.

For those radionuclides not analysed for, equilibrium were assumed (^{210}Pb = ^{210}Po; ^{238}U = ^{234}U = ^{230}Th). This assumption is probably accurate for samples from an area where uranium

is dominantly present. In foodstuffs with low $^{210}Po/^{210}Pb$ ratios, assumed equilibrium between ^{210}Pb and ^{210}Po may result in an underestimated dose. Equilibrium can only be assumed if the food was stored for longer than a year. Assumption of equilibrium of ^{230}Th with its parent U nuclide is also not necessarily true, since Th generally has lower mobility than U. The assumption of equilibrium may result in overestimation of the dose as illustrated in Figure 5-28.

Results are reported as activity per wet weight after the analysis has been done on a dried or ashed sample. There were some differences between the "true" experimental values and the recommended NNR values for conversion of dry weight to fresh weight (see Table A-10, Appendix A). Using literature values will contribute to the uncertainty in the calculated dose, therefore the experimental values were used. The NNR should use the accumulated experimental data, which shows vary good comparison with literature values, to update their recommended values.

The consumption values used in dose calculations have a very large impact on the final calculated dose. Dose estimates based on real consumption rates may vary from those using theoretical consumption rates. The dose will be overestimated when using overly conservative values as illustrated for the liver sample. Recommended values by regulators should be a compromise between country-specific consumption rates and a worldwide recommended value. The values recommended by the NNR are very conservative when compared to world averages and much larger than the per capita consumption published by DAFF (2016). For example total vegetable consumption according to this survey was ~ 50 kg whereas NNR (LG1032) specifies 170 kg for root- and 130 kg for "other" vegetables. The consumption rate to be used for vegetables is open for interpretation and depends on how a vegetable is classified, *e.g.* which vegetable is classified as "other"? Fruit is seasonal and the consumption rate of 75 kg should be changed accordingly - if only available for three months (*e.g.* grapes) it should be divided by four.

For fish the NNR recommended consumption value is 25 kg irrespective of type of fish. It is uncertain as to whether this value adequately represents the intake of subsistence groups utilising this resource in the Gauteng Province, especially when compared with literature values (Table A-8, Appendix A). For example, a consumption rate of 8.8 kg per year is used in Canada (Chen *et al*., 2016). For freshwater fish UNSCEAR (2016) recommends a

consumption rate of 5.7 $kg.a^{-1}$ worldwide and 2.7 kg for Africa. Using the RG-002 recommended value of 25 kg the dose from consumption of ingestion of fish will almost always be overestimated.

The reason for the disproportionately large dose attributed to the ingestion of cereal is due to the ingestion rate of cereal prescribed in RG-002. Since maize and its by-products represent a staple in the diet of a large proportion of the South African population, cereal ingestion (including all types of grain consumed by humans) was assigned an ingestion rate of 250 kg per person per year. This amounts to almost 700g of grain per person per day and is almost twice the value of 130 kg assigned by UNSCEAR for Africa (UNSCEAR, 2016). Although this value may be appropriate to use in some areas of the country where the population have access to only maize and maize products, it is not necessarily the case in all regions in South Africa. It is unlikely that a person near a specific NORM industry will be able to obtain maize, grown in the area where it may have become contaminated, in a large enough quantity to meet the rate of cereal consumption prescribed by RG-002. Using the prescribed value as is, therefore represents a very conservative assumption. For evaluation of a specific industry, the dose estimation via ingestion will be more accurate if site-specific data can be collected and used *e.g.* via a household survey of inhabitants in the areas based on individual consumption over as specific period.

5.2.4 Conclusions

The results presented in this study were for foodstuffs collected in the vicinity of NORM industries. Through assessment of the natural radioactivity food that may present some risk to the public via consumption were identified. The estimated dose was compared to limits set by the regulator. This kind of data is not currently available in South Africa.

The estimated dose for adults for the majority of analysed foodstuffs was less than the "single facility" dose constraint of 0.25 $mSv.a^{-1}$. This dose is only a small fraction of the natural background radiation dose of 2.4 $mSv.a^{-1}$ (UNSCEAR, 2000). Further investigation is mandatory for those samples which exceeded the dose limit of 1 $mSv.a^{-1}$, as this is of obvious concern. For the majority of samples where the dose limits were exceeded it could be explained by either poor sensitivity of the analytical technique resulting in high LODs, assumption of equilibrium for some nuclides with high DCF which were not measured (*e.g.* ^{230}Th and ^{210}Po) or unrealistic high consumption rates. Some of the cereal samples (rye, oats),

could result in public exposure of more than a few mSv per year and presented a potential risk even when considering the fodder-animal-human pathway.

The results did not seem to indicate any major impact of the industrial activities on food grown in any of the areas. More work need to be done to determine the exact impact of specific NORM industries, since the possibility of contamination in some areas could not be excluded. Accurate baseline data on the natural radioactivity in food in unaffected areas in SA will be very helpful to determine any potential impact, especially since the results presented for the baseline study showed high background concentrations of some nuclides in samples including fish and seafood.

Although the results give some idea of radioactivity concentrations in local products, the data cannot be used to assess daily intake of natural radionuclides in people working and living in the area and determine their dose from total diet. The typical consumer does not use the sample as analysed. Since activity concentrations in the final product will probably be reduced through food processing, dose will be overestimated when using results for unprocessed foodstuffs.

From data collected over many years the importance of using appropriate analytical methods with the required sensitivity for evaluation of annual dose was clear. The overestimated dose observed for some of the samples could be explained by poor detection limits of the technique used. The limit of detection of the direct instrumental techniques was greatly improved by using a broad energy gamma spectrometer for measurement of ashed samples. Radiochemical separation after acid digestion is required for analysis of ^{210}Po (and ^{230}Th) to provide results with the necessary sensitivity not to overestimate the dose. The analytical method implemented for determination of ^{210}Po in foodstuffs after microwave digestion proved to be applicable for this purpose. Ingestion of food was shown to be an important pathway for intake of this nuclide, which had relatively high concentration in many of the analysed samples.

Since conclusions based on analysis of single samples should be made only with caution, this study should be considered as a first order assessment only. Due to the high variance of data further studies are recommended to properly evaluate any suspected contamination of foodstuff in a specific area and to determine the potential radiological impact. Considering the uncertainties as discussed care must be taken not to use results for a limited number of

grab samples to make any conclusion on “radiation exposure exceeding limits”, as frequently done by activists and in the press.

5.3 Protection of the environment

5.3.1 Introduction

Historically the focus of radiation protection has always been on the impact on humans, assuming that non-human species are also protected. Environmental protection from ionizing radiation has become more important during the last decade, especially in Europe. In line with international development, SA also needs to demonstrate that the environment is adequately protected. Although environmental protection has been introduced at a conference of SARPA in 2009, current regulations from the NNR does not specify the requirements or give guidance on how to assess radiological impact on biota.

To date the field of radio-ecology (effect of radioactivity on non-human biota) remains relatively unexplored in South Africa. This section describes case studies in which the ERICA integrated approach (2.4.7) was followed to assess the radiation dose to biota in areas exhibiting elevated levels of NORM. Included are studies of the impact of radioactivity in water on fish and crocodiles, as well as the impact of contaminated soil and pasture on cattle. Results for the transfer of radioactivity in environmental media are also presented. These include transfer from soil/sediment to plants, as well as the soil-grass-cow-milk-human and water-fish-human pathways.

Information on the radioactivity content of any animal that lives and feeds in close proximity to NORM industries will be very valuable to add to the databases used in dose assessment models (2.4.7). Unfortunately availability of samples for analysis depends on death of the animal and samples are therefore not often available. Only a few samples from wildlife and domestic animals have been analysed over the last few years, of which some results are presented here.

5.3.2 Application of environmental assessment methodology

In 5.3.3 to 5.3.6 the use of the ERICA tool is demonstrated at selected sites containing elevated levels of NORM as a result of mining or industrial activities, or due to specific incidents. The presented data focus on the radio-ecological situation at the sites, using the

highest average radionuclide concentrations available.

Since the aim of routine monitoring programmes required by CoRs of industries is to assess dose to humans, limited biota samples have been available for analysis over the period of this study, 2011-2016. Samples included fish and vegetation, and on rare occasions, animals. A generic approach was followed in this study. Radiation doses were calculated for reference organisms (RO) or for sampled biota (where available). The purpose was to do an estimation of any radiological impact on the environment by quantifying the radionuclides contributing to dose and identifying organisms likely to receive the highest dose.

The ERICA assessment tool (version 1.2.2; updated 2016) was used to calculate dose to ROs. The assessment was done at Tier 2 for all ROs. Measured activity concentrations in environmental media (soil, sediment, water) were used as input for the model. Equilibrium was assumed between $^{238}U \rightarrow ^{226}Ra$, $^{226}Ra \rightarrow ^{210}Pb \rightarrow ^{210}Po$ and $^{232}Th \rightarrow ^{228}Ra \rightarrow ^{228}Th$, where data was unavailable. ERICA default parameters for K_d (Table A-7), CRs (Table A-12), DCF (Table A-11) and weighing factors (10 for alpha and 3 for beta) was used (Tables in Appendix A). A default dose rate screening value of either 10 or 40 $\mu Gy.h^{-1}$ was selected for the assessment. These were derived from IAEA (1992) dose limits (2.2.9).

Where available, the measured biota concentrations were compared with ERICA tool modelled concentrations using default CRs. Radionuclide concentrations were added as $Bq.kg^{-1}$ wet weight for biota and $Bq.kg^{-1}$ dry weight for soils. Experimental dry-fresh ratios were used for conversion from dry to fresh weight (Table A-10, Appendix A).

5.3.3 Natural radionuclides in the terrestrial environment - transfer to cows

To consider dose from consumption of animal products such as milk and beef, one must have knowledge of the radionuclide concentrations in the tissues of animals. Quantifying transfer of natural radionuclides through the food chain from soil via fodder to milk is especially important due to the high consumption rate for milk. Uptake of radionuclides is also important when considering the impact to the animal itself. Although some studies concerning natural radioactivity concentrations and transfer to livestock have been published worldwide (2.4.6), data is still fairly limited. In SA information is even scarcer - only one article on uptake of U in sheep tissue in was found with the literature survey (Winde *et al*.,

2017).

The objective of this study was use measured concentrations of ^{210}Po and U in biota from the WCA to obtain information on the behaviour of ^{210}Po and U in the environment, including pathways to humans. This work was done because limited information is available for concentrations of natural radionuclides in edible farm animal tissues and transfer in the pasture-cow pathway. ^{210}Po was chosen as nuclide of interest based on the higher contribution to dose due from ingestion, as shown in 5.2. U was analysed because it is known to occur in high concentrations in the area.

Field site and sampling

The Wonderfonteinspruit (WFS) catchment area (Figure 5-29) was identified as study area since it is known to have elevated levels of uranium in certain locations as observed in a number of studies (2.12.4). Water, sediment, soil, grass, milk and cattle tissue samples were collected on a farm in the area known to be influenced by gold-mining activities. Water was sampled at two sites along the WFS. Cattle drink directly from the WFS. Sediment samples were collected from a dam on the farm. The farm produces "natural beef" and, as such, all feed (hay and pasture grasses) are grown on the premises. Cattle graze on natural pasture adjacent to the WFS and on planted pasture that are irrigated from the WFS. The grasses found along the dam are also actively grazed by the cattle throughout the year, and the cattle feed sample was collected here.

One soil sample was collected next to the dam. A second soil sample was collected at a site consisting of wetlands. Milk was collected from two cows also fed only by hay and pasture grown on the farm. Liver, muscle tissue (meat) and bone samples were collected from cattle slaughtered at a local abattoir. Background samples were collected from a farm located along the Mooi River not impacted by mining activities. Samples were refrigerated and send for analysis. Due to high analysis costs, a limited number of samples of each type were analysed.

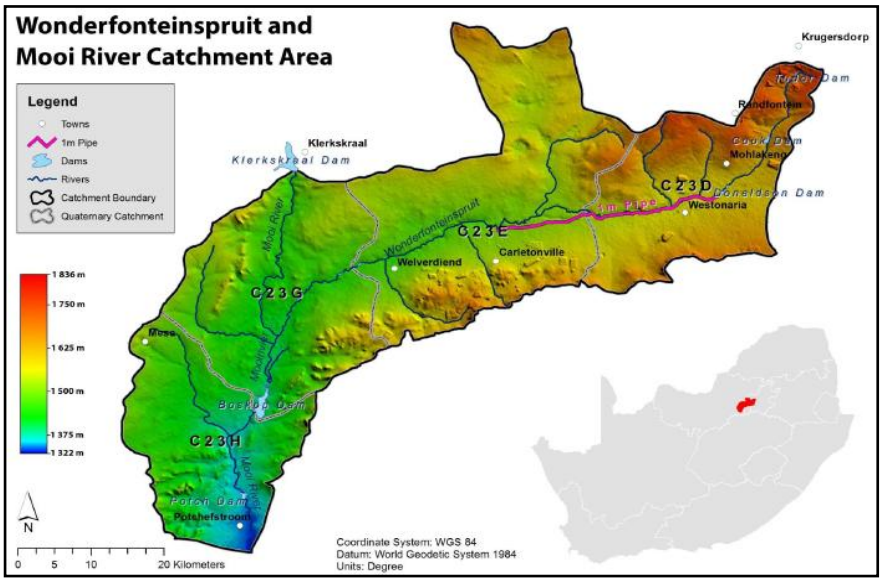


Figure 5-29: Map of the WonderfonteinSpruit (Hamman, 2012).

Sample preparation

Water samples were filtered and acidified (4.3.1). Soil and sediment samples were dried sieved and homogenized (4.3.3). The grass, beef, bone and milk samples were prepared as described for biological samples (4.3.2). The grass sample was not washed due to the fact that cattle will ingest pasture with adhering soil. For analysis of ^{210}Po, samples were not ashed; the dried samples were acid digested in a microwave as for food samples (5.2.2).

Radioactivity analysis

Water samples were analysed for ^{210}Po and ^{238}U by radiochemical separation and alpha spectrometry. Grass, milk, tissue and organs were analysed for ^{210}Po after sample digestion, using alpha spectrometry. For soil and sediment ^{210}Pb was measured with low energy gamma spectrometry and ^{210}Po assumed to be in equilibrium. NAA was used for analysis of ^{238}U in soil, sediment, grass and animal tissue (see 4.12). All concentrations were reported on a fresh weight basis.

Results and discussion

Activity concentrations

Activity concentrations of ^{210}Po and ^{238}U in soil, sediment, water, grass, cattle tissue and milk

are shown in Table 5-28. For ^{238}U the activity concentration was converted to mass concentration units using the specific activity values in Table A-1 in Appendix A.

The activity concentration of ^{210}Po in grass, as the known food source for cattle in the area, fell in the range as noted in Table C-1 (Appendix C) for oats and rye, and was also similar to the measured concentration in a background sample. As mentioned in 2.4.4 ^{210}Po contributes significantly to the natural radioactivity in leafy plants and grass due to direct deposition of ^{222}Rn daughters from atmospheric precipitation. Grass dried in the sun for hay is further exposed to atmospheric deposition, which may explain the high concentration of this nuclide. The concentration of ^{210}Po in water used to irrigate the crops was very low compared to other media. This indicates that the majority of ^{210}Po uptake in cattle feed is not from irrigation, but from deposition. Radon concentrations in the air can be quite high due to the presence of uranium rich deposits in the area. If ingested by humans the dose due to ^{210}Po in water will be negligible.

Concentrations of ^{210}Po in sediment and soil were relatively high with a large variation between samples. It is for this reason that it is better to use individual soil concentrations in the calculation of (tissue/soil) concentration ratios rather than averages. The concentration in sediment was lower than the mean activities reported for 38 sediment samples in the NNR study (NNR, 2007) and those reported in a previous study conducted at RA (Ramathlape *et al.*, 2010).

^{210}Po concentrations in the muscle of the cattle were high for both samples and much higher than values reported in Table C-1 (Appendix C) for meat from farms in the same area. Slightly lower concentrations were found in the bone sample. Elevated levels of ^{210}Po were found in the liver sample, which is expected from known accumulation of ^{210}Po in internal organs (Bunzl *et al.*, 1979). Therefore, transfer of ^{210}Po to cattle seemed to be higher than predicted from the activity concentration in soil. The ^{210}Po concentration in the milk sample was lower than reported in Table C-1 (Appendix C), but higher than the milk samples from a background area and the worldwide reference value of 0.015 $Bq.kg^{-1}$ (UNSCEAR, 2000). Compared to data from other countries, accumulation of Po in muscle and liver was elevated (see Table A-18, Appendix A).

Water from the WFS is no longer used as a source for domestic water and the quality should actually be compared to water used for agricultural and livestock purpose. Even so, the ^{238}U

concentration in the water samples that were collected from the experimental site (WFS) were found to be lower than the target value of 890 $mBq.L^{-1}$ (~70 $\mu g.L^{-1}$) assuming natural ratio) for radioactivity in water intended for domestic use (DWS, 1996a). There is no uranium target value set for livestock watering in SA (DWS, 1996c). Cattle drinking directly from the WFS may disturb the underlying sediment thereby increasing concentrations within the water prior to ingestion.

In his research, Hamman (2012) analysed the exact same samples for heavy metal content using ICP-MS. For comparison, the average results for uranium are shown in Table 5-28. Only selected samples were used for radioactivity analysis. The U concentrations in soil measured with NAA were slightly lower than the values reported by Hamman, but higher than background (1.6 $mg.kg^{-1}$) and the worldwide average concentration of U in soils of 3 $mg.kg^{-1}$ (UNSCEAR, 2000). In sediment similar high values, much higher than the reported background of 0.12 $mg.kg^{-1}$ was measured. The concentration for U in grass was much lower than reported by Hamman and similar to the value for the control grass of 0.04 $mg.kg^{-1}$. The U concentrations measured in the liver and meat samples were three orders of magnitude lower than the values reported by Hamman. Compared to the background and reference values referred to in Hamman, the U concentration did not exceed the normal range and no accumulation of U in the tissue samples was observed. The results confirm what have been suggested by Winde (2013) that "results reported by Hamman seem to be in contrast with results of other studies conducted in the very same area". Unfortunately these seemingly high (incorrect) values have already been freely quoted in presentations and in the press: "U intake from consumption of meat from the WFS area is 8000 times above the average U-intake worldwide" and "The uranium concentration in the liver was 126.75 times higher than in the control group" (Liefferink, 2015).

Annual human ingestion dose from milk and meat consumption

In 5.2.3 it has been reported that the contribution of ^{210}Po to the overall dose due to ingestion of foodstuffs, was about 20-40% and as high as 80% for organs, such as kidney and liver. Therefore considering only ^{210}Po will give a good indication of the expected dose to humans due to ingestion. The calculated annual dose due to ^{210}Po for adults consuming meat, milk and water from the farm where the samples were collected, are given in Table 5-28. The dose conversion factors for ingestion and consumption rates as prescribed by the NNR in RG-002

(NNR, 2013) were used in the dose calculations using equation 2-3 (see 2.3.5).

The estimated dose was less than 0.25 $mSv.a^{-1}$ for all samples, except for the liver. The dose from meat was relatively high compared to the milk and water samples. The use of a consumption rate of 30 kg (recommended for beef consumption) in the calculation of the dose from the liver sample, was a very conservative approach, since it is very unlikely that any person will eat 30 kg of liver originating from one specific animal on the specific farm. Since it is well-known that internal organs accumulate ^{210}Po (2.1.5), exposure can be reduced by dietary choices, such as avoiding the consumption of these products. However, the high accumulation of ^{210}Po in liver is of concern when considering the impact on the cow itself.

The calculated dose due to ingestion of milk collected in the vicinity of the WFS was 0.012 $mSv.a^{-1}$, which was slightly higher than the milk from the reference location (0.002 $mSv.a^{-1}$), but still negligible. Again, it is a very conservative approach to assume that all milk consumed comes from the specific farm, since the average person mostly consume milk bought from shops and do not buy directly from farms. The exception to this may be the farmer's family and workers.

Table 5-7: South African default parameters for Polonium (NNR, 2013)

Parameter	Value	Unit
Ingestion Dose coefficient for adult age group (DCF)	1.2E-06	$Sv.Bq^{-1}$
Annual Consumption		
Water	600 (730)	$L.a^{-1}$
Milk	120 (250)	$L.a^{-1}$
Beef	30 (100)	$kg.a^{-1}$
Transfer		
Transfer Soil – Feed (F_v)	1.2E-01 (1.0E-01)	
Transfer to beef (F_f)	5.0E-03	$d.kg^{-1}$
Transfer to milk (F_m)	2.1E-04 (3.0E-03)	$d.L^{-1}$
Beef or milk cow daily consumption		
Water	75	$L.d^{-1}$
Dry feed	16 (25)	$kg.d^{-1}$
Soil ingestion	1.25	$kg.d^{-1}$
Wet:Dry mass ratio pasture/grass	0.20 (0.10)	

Previous NNR parameters shown in parenthesis

The dose for humans from cattle feed, via the milk and meat pathways, was calculated to be 0.09 $mSv.a^{-1}$, using equation 2.5. The calculations, using the default NNR transfer parameters in Table 5-7, are shown in Table 5-8. The reported measured activity concentration was in $Bq.kg^{-1}$ wet weight, so for the purpose of the calculation the data was converted to dry weight activity. The NNR parameters were revised in 2013 to be more realistic and less conservative (NNR, 2013), specifically the comsumption rates. Using the previous parameters from LG-1032 (NNR, 1997) the dose was calculated as 2 $mSv.a^{-1}$.

Table 5-8: Calculation of dose to humans from ^{210}Po in cattle feed via the meat and milk pathways

Parameter	Calculation	NNR, 2013	NNR, 1997
Activity feed ($Bq.kg^{-1}$) wet	Measured concentration	5.36	5.36
Activity feed ($Bq.kg^{-1}$) dry	Activity feed ($Bq.kg^{-1}$) wet X wet:dry ratio	26.8	53.6
Intake by cow ($Bq.d^{-1}$)	Activity dry ($Bq.kg^{-1}$) X consumption ($kg.d^{-1}$)	429	1340
Activity meat ($Bq.kg^{-1}$)	Intake ($Bq.d^{-1}$) x F_f ($d.kg^{-1}$)	2.14	6.70
Activity milk ($Bq.kg^{-1}$)	Intake ($Bq.L^{-1}$) x F_m ($d\ L^{-1}$)	0.09	4.02
Human: Intake from meat ($Bq.a^{-1}$)	Activity meat ($Bq.kg^{-1}$) x consump ($kg.a^{-1}$)	64.3	67.0
Human: Intake from milk ($Bq.L^{-1}$)	Activity milk ($Bq.L^{-1}$) x consump ($L.a^{-1}$)	10.8	1010
Total intake ($Bq.a^{-1}$)	Intake meat + Intake milk	75.1	1680
Dose due to ^{210}Po ($Sv.a^{-1}$)	Total intake ($Bq.a^{-1}$) x DCF ($Sv.Bq^{-1}$)	0.00009	0.002

Transfer from feed to animal products

Transfer coefficients, F_m and F_f, describe the transfer from feed to animal products (2.4.3). Calculations are usually done on a dry mass basis. The activity in meat and milk can be predicted from the nuclide concentration in the feed using the TC value.

Using the NNR default transfer factors in Table 5-7 the expected activity concentrations in milk and meat were calculated from the measured ^{210}Po activity in the feed samples. The calculated concentrations shown in Table 5-8 (in green) compared fairly well with the actual measured values (in green in Table 5-28). However, the measured concentration in one of the meat samples, as well as the liver, was much higher than predicted from transfer. Site-specific TC values for ^{210}Po were calculated from the measured activities in the milk and meat and the activity intake from feed. The calculated TC values and some published values are given in Table 5-9. The calculated TC value for milk was comparable to published results

and those of meat and liver slightly higher than published values. TC values for ^{238}U in meat also compared relatively well with published values and those recommended by the NNR, especially with the revised 2013 value (Table 5-10).

Transfer from soil to feed (plant-soil concentration ratio)

The transfer Factor, TF, is used to describe uptake of radionuclides by plants from sediment or soil (2.4.3). Calculated soil-to-feed transfer factors are presented in Tables 5-9 and 5-10. The calculated transfer values for ^{210}Po varied from 0.15 to 0.30, which compared well with published values and those recommended by the NNR (NNR, 2013). The predicted activity concentrations in feed using the NNR default value was 10.6 -21.5 $Bq.kg^{-1}$ (dry weight), which showed good comparison with the measured activity concentration of 26.8 $Bq.kg^{-1}$ (Table 5-8). The transfer values for ^{238}U were 0.009-0.015, which was lower than the value recommended by the NNR.

Table 5-9: Concentration ratios (CR), Feed transfer coefficients (F_m, F_f) and Transfer factors (F_v) for ^{210}Po [xE-04]

	This study	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Beef (F_f); $d.kg^{-1}$	77-118	50	50	50	-	30	-	-
Liver (F_f); $d.kg^{-1}$	1215	-	-	-	-	800	-	-
Milk (F_m); $d.L^{-1}$	1.94	30	2.1	0.89-3	-	3	2.3	-
Soil–Feed (F_v)	1500-3045	1000	1200	220-10000	412	230	1610	-
Soil-Beef CR	185-576	-	-	-	-	-	-	890
Soil-Liver CR	2351-4784	-	-	-	-	-	-	-

(1) NNR, 2007 (2) NNR, 2013 (3) IAEA, 2010a (4) Strok & Smodis, 2012 (5) Ewers *et al*., 2003
(6) Howard *et al*., 2009 (7) Brown *et al*., 2016

Table 5-10: Concentration ratios (CR), Feed transfer coefficients (F_m, F_f) and Transfer factors (F_v) for ^{238}U [xE-04]

	This study	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Beef (F_f); $d.kg^{-1}$	4-62	300	3.9	3	2	2.5-6.3	-	-
Liver (F_f); $d.kg^{-1}$	9.8	-	-	-	-	-	-	-
Milk (F_m); $d.L^{-1}$	-	6.1	18	5-61	6	-	32	-
Soil–Feed (F_v)	88-154	2000	460	-	60	-	34	-
Soil-Beef CR	0.58-15.5	-	-	-	-	-	-	55
Soil-Liver CR	1.4-2.4	-	-	-	-	-	-	-

(1) NNR, 2007 (2) NNR, 2013 (3) IAEA, 2010a (4) Ewers *et al*., 2003 (5) Howard *et al*., 2009
(6) Strok & Smodis, 2012 (7) Brown *et al*., 2016

Transfer from soil to muscle

The Concentration Ratio (CR*)* describes accumulation in the plant or animal (2.4.3). CR values are commonly available in databases and are used in models to predict the impact on non-human biota. The soil-tissue (muscle) CR for ^{210}Po, calculated for all possible combinations of the measured concentrations, varied from 0.02 to 0.06 for beef muscle, as shown in Table 5-9. The CR for liver (0.2 to 0.5) was about a factor 10 higher than for muscle. The derived soil-muscle CR for ^{238}U (Table 5-10) was much lower than that of ^{210}Po. The CR values for Po and U in the present study were lower than the default values in the model; therefore when using ERICA the activity concentrations in the muscle were overestimated (Table 5-11).

The advantage of using soil-tissue CRs is that it is independent of the route of exposure (*i.e*. ingestion or inhalation). It is however reliable only if there is a definite linear dependency of the tissues concentrations on the soil concentration. Therefore transfer coefficients, as derived in the previous paragraph, are most often used to predict activity concentration in animal tissues.

Ingestion pathways and estimated dose for cattle

Contamination of cattle feed do not only have an impact on human health, which has been the focus of radiological protection for many years, but also on animal health. It is therefore important to determine the radioactivity concentrations in cattle feed in contaminated areas and relate the results to both the impact on humans, as was done in the previous paragraphs, as well as the animals itself.

The activity concentrations in the different media (highest measured value in Table 5-28) were used to calculate the total ingestion by the cattle per radionuclide per day.

Ingestion ($Bq.day^{-1}$) = activity ($Bq.kg^{-1}$) * consumption ($kg.day^{-1}$).

It was assumed that the cattle grazing the contaminated site ingest all water, soil and grass only from this site. The NNR default consumption rates in Table 5-7 were used. As seen from Figure 5-30, the major route of ingestion for both ^{210}Po and ^{238}U was calculated to be via soil.

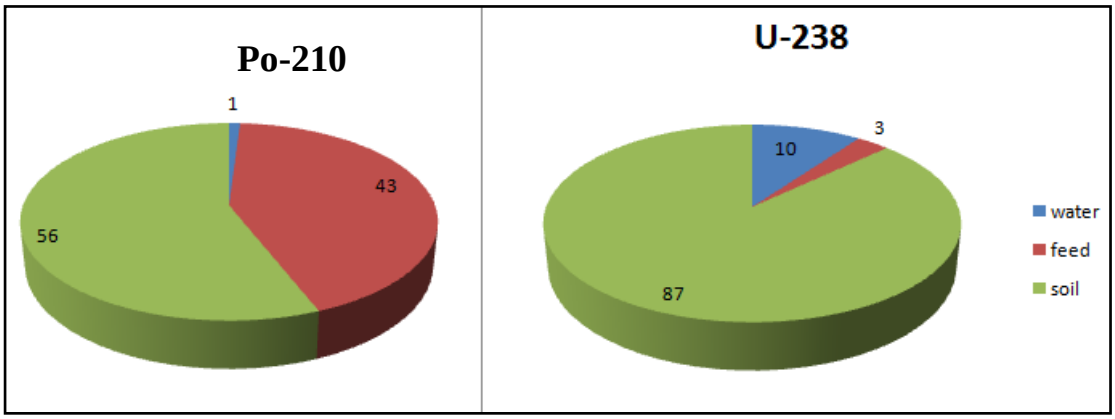


Figure 5-30: Cattle Ingestion percentages from soil, grass and water

Table 5-11: Dose rates to cattle living on contaminated soil from exposure to natural radionuclides (µGy.h^{-1})

		^{210}Po	^{238}U	^{226}Ra
INPUT				
Soil concentration	Bq.kg^{-1}	**179**	**717**	**717**
Assumptions and default parameters				
Screening	µGy.h^{-1}	40		
Background exposure	µGy.h^{-1}	0.069		
Weighing factor	-	10		
Occupancy	-	1		
Uncertainty	-	3		
DCF internal	µGy.h^{-1} per Bq.kg^{-1}	3.10E-03	2.40E-03	1.38E-02
CR	Bq.kg^{-1} per Bq.L^{-1}	8.8E-02	5.47E-03	4.43E-02
OUTPUT				
External dose rate	µGy.h^{-1}	1.54E-07	7.17E-06	1.29E-01
Internal dose rate	µGy.h^{-1}	4.93E-01	9.41E-02	4.42E+00
Total dose rate	µGy.h^{-1}	4.93E-01	9.42E-02	4.55E+00
Activity conc predicted	Bq.kg^{-1} fw	15.9	3.92	
Activity conc measured	Bq.kg^{-1} fw	3.32	0.632	
Total dose rate to organism outcome Tier 2 (µGy.h^{-1})				**5.14**
Risk				0.128

It is usually recommended to use a model to predict impact on an animal, since it is expensive and impractical to have an analysis done on each animal when they are slaughtered. The ERICA tool (2.4.7) was used to estimate the absorbed dose rate to the cow using the default transfer parameters of ERICA for mammals. The soil concentration in Table 5-28 was used and log-normal distribution assumed for all input data. Secular equilibrium was assumed for all nuclides in the ^{238}U-series. Input and output parameters are summarized

in Table 5-11. When screening at Tier 2 the probability was less than 5% for the selected screening dose rate of 40 μGy.h^{-1} to be exceeded. The resulting dose rate is given in Table 5-11. External exposure was insignificant compared to internal exposure, with ^{226}Ra being the most important contributor.

Conclusions

This study provided activity concentrations and transfer factors for cattle from a mining area with elevated NORM concentrations in soil. The revised NNR transfer parameters, which are less conservative, were shown to be more realistic. As far as known this is the first published set of CR values for cattle in South Africa. The data set is however limited in scope and highlights the need for additional studies. More samples should be collected, including some from other livestock, such as sheep, pig and chicken.

Despite the relatively high activity concentrations in the soil and sediment on this farm located in the Wonderfonteinspruit area, consumption of any of the animal products analysed in this study, resulted in a dose of less than 0.2 mSv.a^{-1} to humans. The only concern was the high dose from the liver sample, if consumed at a rate of 30 kg/a, which is unlikely. The predicted dose to the cow itself was below the screening level of 40 μGy.h^{-1} for terrestrial animals.

The calculated transfer factors for soil-plant transfer compared well with published values and those recommended by the NNR. Predicted activity concentrations in feed using the NNR default value compared well with the measured activity concentration in the feed sample. There was also good correlation between the transfer coefficients for ^{210}Po and ^{238}U in the feed-animal pathway derived from this study and the latest default parameters recommended for use by the NNR for milk and beef. Use of the default parameter of beef to predict transfer to liver resulted in an underestimated activity concentration.

Soil-to-muscle CR values were slightly lower than the ERICA tool reference values. Use of the reference value overestimated the concentrations in the muscle of cattle. Use of models for prediction of activity concentrations in cattle, based on measurement of soil concentrations, seems to be limited. The results highlight the need for appropriate system-specific transfer parameters to support models used for assessment of the radiological impact on livestock.

5.3.4 Application of ERICA tool: Mineral sands industry

Data from the mineral sands industry were used to illustrate the application of the ERICA tool to determine the impact on biota in the area.

Samples and radioactivity analysis

Samples from the impacted area received for analysis included soil (analysed annually) and vegetation (grass). A dead small antelope was found in the vicinity of the plant. Its death was not related to any specific incident and it probably died of natural causes. Nevertheless, because of public concern it was decided to analyse a sample for radioactivity. Samples were prepared as in 4.3, after which a full nuclide analysis was performed as summarized in 4.12.1 for solids and biological material.

Results and discussion

Table 5-12 shows activity concentrations of biota and soil from the area. Based on the soil concentrations an assessment was done at Tier 2 using the ERICA tool. Since ^{210}Pb was measured with a high MDA, equilibrium of both ^{210}Pb and ^{210}Po with ^{226}Ra was assumed. A graph of the risk quotient output from ERICA is shown in Figure 5-31. Only for the limiting organism lichen there was some probability of being exposed to dose rates higher than 10 μGy.h^{-1}.The risk for mammals was very small.

Table 5-12: Activity concentrations (Bq.kg^{-1} dry weight) in biota and environmental media from mineral sands industry; MDA in brackets.

Radionuclide	Soil (composite)	Grass	Mammal
^{238}U	40.5±0.8 (0.64)	0.206±0.016 (0.014)	0.0252±0.0042 (0.0097)
^{234}U	40.8±0.8 (0.65)	0.208±0.016 (0.014)	0.0255±0.0043 (0.0098)
^{226}Ra	31.6±3.7 (9.8)	0.730±0.169 (0.52)	0.201±0.035 (0.15)
^{210}Pb	< 98	0.766±0.173 (0.54)	< 0.61
^{210}Po	Not measured	0.497±0.189 (0.23)	0.35±0.19 (0.75)
^{232}Th	37.0±1.1 (4.8)	0.695±0.031 (0.14)	0.068±0.012 (0.079)
^{228}Ra	27.4±5.8 (14)	0.997±0.079 (0.23)	< 0.35
^{228}Th	38.5±10.2 (22)	0.305±0.016 (0.046)	< 0.11

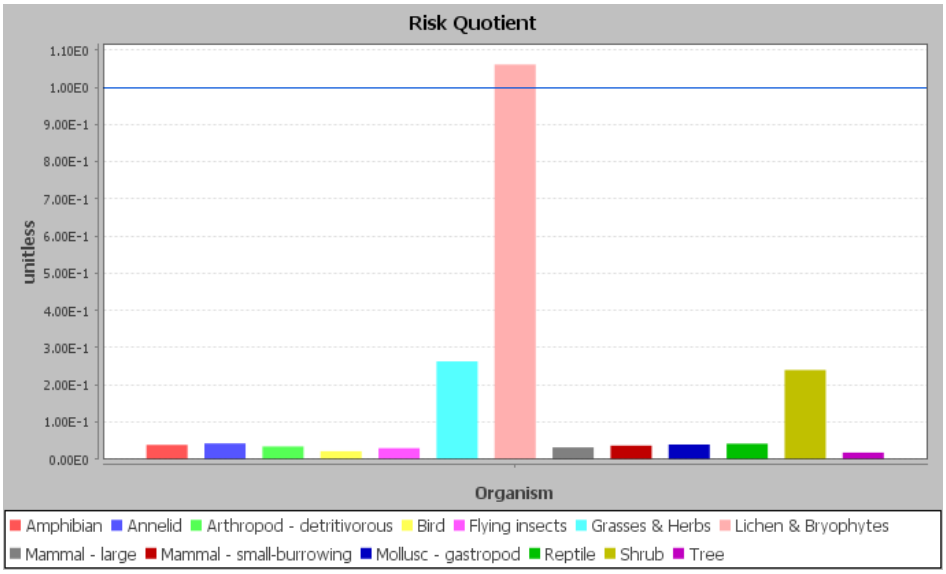


Figure 5-31: Risk Quotient for Tier 2 screening Terrestrial environment (Mineral sands site)

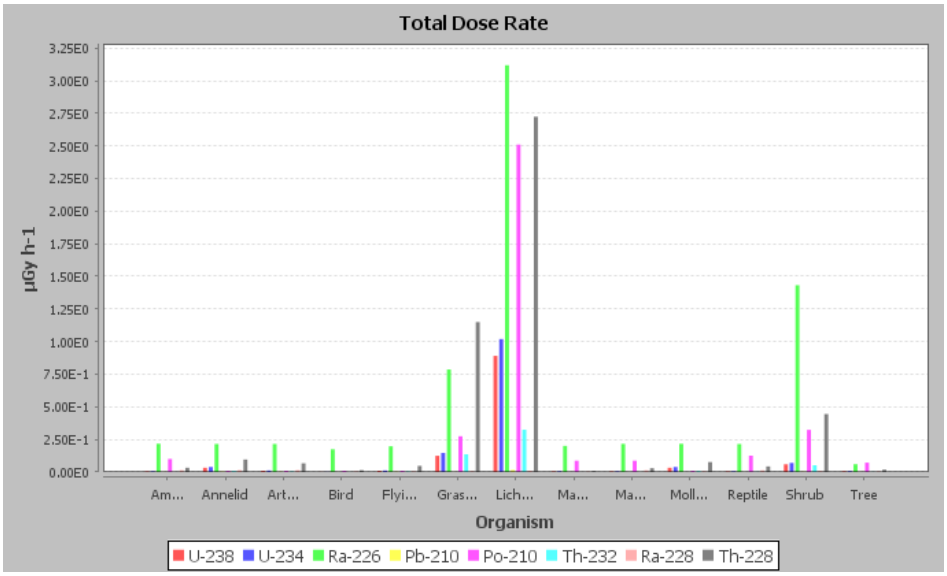


Figure 5-32: Dose rates (µGy.h^{-1}) to terrestrial reference organisms for mineral sands site.

Figure 5-32 shows the dose rate to ERICA ROs from the individual radionuclides, based on site-specific soil activity concentrations (Table 5-12). Lichens received the highest total dose rate at the terrestrial site (10.6 µGy.h^{-1}). The internal dose from ^{226}Ra and ^{228}Th dominated for all organisms, with some contribution from ^{210}Po. For grass the total dose was 2.62 µGy.h^{-1}, with ^{228}Th contributing 43.8% and ^{226}Ra 30%. For mammals the total dose was 0.31 µGy.h^{-1}, with ^{226}Ra contributing 64.7% and ^{210}Po 28.1%. External dose was insignificant (~0.4%).

compared to internal dose (~99.6%).

The ERICA derived concentration in grass (Table 5-13) based on the site-specific soil concentrations was higher than measured concentration of vegetation at the site (Table 5-12). This indicates poor correlation between site-specific and model soil-plant CRs. The measured soil-grass CR for all nuclides was more than an order of magnitude lower than the default soil-grass CR in the model. The measured soil-mammal CR for all nuclides, except for ^{232}Th and ^{228}Th was also less than the default values.

Table 5-13: Comparison of predicted RO concentration with measured values (CRx10^{-4}) – Mineral Sands site

Nuclide	Predicted ERICA concentration (Bq.kg^{-1})		CR Erica		Measured CR	
	Grass	Mammal	Grass	Mammal	Grass	Mammal
^{238}U	5.18	0.22	1279	54.7	50.9	6.22
^{226}Ra	5.69	1.4	1800	443	231	63.6
^{210}Pb	3.79	1.18	1200	374	242	98.1
^{210}Po	8.85	2.81	2800	443	157	111
^{232}Th	5.92	0.005	1600	1.36	188	18.4
^{228}Ra	4.93	1.21	1800	443	364	58.4
^{228}Th	6.16	0.005	1600	1.36	79.2	13.0

Conclusions

The data presented in this study gave an indication of the exposure to biota in a mineral sands area. It should be seen as of illustrative value only, since the limited available data do not support derivation of soil-organism CRs. The screening level dose rate of 10 μGy.h^{-1} used in the modelling could possibly be exceeded for lichen, although the predicted dose rate received by lichen was much lower than the proposed dose limit of 400 μGy.h^{-1} (10 mGy.d^{-1}) for terrestrial plants (2.2.9).

5.3.5 Aquatic environment - Transfer to fish

Background

To illustrate use of the ERICA model to predict the impact on aquatic organisms in a specific water body, results from an area impacted by phosphate mining were used. Water concentrations were used to predict transfer of radioactivity to fish, expected activity

concentrations in the fish and to estimate the dose. These values were compared with the actual measured values. Accumulation of radioactivity in fish will directly contribute to human exposure when consumed.

Sample Treatment and radioactivity analysis

Fish samples were gutted in accordance with the normal practice when preparing fish as food. Only the edible parts were used for analyses. When considering the impact on biota, the activity in the whole animal is of interest and not only that in the edible part. Dose (to biota) may be underestimated if only the edible parts are analysed.

Samples were prepared as in 4.3.2, after which a full nuclide analysis was performed as summarized in 4.12.1 for solids and biological material. For ^{210}Po analysis, the dried sample was digested in a microwave using HNO_3 and H_2O_2 and analysed using the procedure of spontaneous deposition, U and Th was analysed by NAA and ^{210}Pb and ^{226}Ra by broad energy gamma spectrometry. Full nuclide analysis of the water samples were done after acidification and filtration (4.12.2).

Results and discussion

Activity concentrations of water and fish from the area are shown in Table 5-14. The results shown are averages for bi-annual analysis of water and fish in four surface bodies from 2011-2015. No results for sediment samples were available. The results of the nuclide specific analysis of the water- and fish sample were used to predict dose to humans and to biota that may occur in the aquatic ecosystem. The highest ingestion dose for the adult age group from drinking water from the dam was calculated as 0.035 mSv.a^{-1} and 0.078 mSv.a^{-1} from eating fish. Similar to what has been reported in 5.2.3, ^{210}Po contributed 40% of the dose from fish and only about 4% to the dose from water.

The water concentrations of surface body 3 were used to conduct an assessment at Tier 2 using the ERICA tool. A graph of the risk quotient is shown in Figure 5-33. The model predicted a lower risk for organisms living in the water (mammal, bird, amphibian, and pelagic fish) whereas the risk was higher for organisms living within the sediment or at the water-sediment interface. The probability of exceeding the screening dose rate of 10 µGy.h^{-1} was above the selected probability (=3) for all organisms except for pelagic fish.

Table 5-14: Activity concentrations in water and fish from Phosphate industry

Nuclide	Water from surface body (mBq.L^{-1})				Fish from surface body (Bq.kg^{-1})			
	1	2	3	4	1	2	3	4
^{238}U	46±30	47±17	64±11	30±7	0.15±0.059	0.13±0.025	0.13±0.048	0.096±0.025
^{234}U	86±32	84±26	109±53	47±8	-	-	-	-
^{230}Th	39±36	63±93	41±2050	20±9	-	-	-	-
^{226}Ra	3.5±3.4	4.6±3.9	7.4±6.1	3.4±2.8	0.41±0.34	0.84±0.39	0.75±0.21	0.37±0.33
^{210}Pb	8.4±9.6	5.0±6.0	6.2±5.5	5.8±4.4	<1.33	<0.92	<2.65	<0.84
^{210}Po	4.4±4.9	1.9±2.8	5.2±6.8	4.7±5.0	0.69±0.43	0.52±0.15	0.79±0.47	0.46±0.29
^{232}Th	7.2±8.3	8.1±7.0	5.8±6.1	6.3±4.3	0.47±0.60	0.60±0.88	0.65±0.81	0.42±0.61
^{228}Th	5.5±2.9	5.9±4.9	9.4±4.4	8.1±4.2	0.29±0.15	0.16±0.035	0.53±0.49	0.18±0.017
Dose (<1a)	0.212	0.190	0.210	0.194	-	-	-	-
Dose (>17a)	0.033	0.032	0.035	0.033	0.048	0.041	0.078	0.031
Dose (%Po)	4.5	4.0	2.7	3.5	40	39	35	40

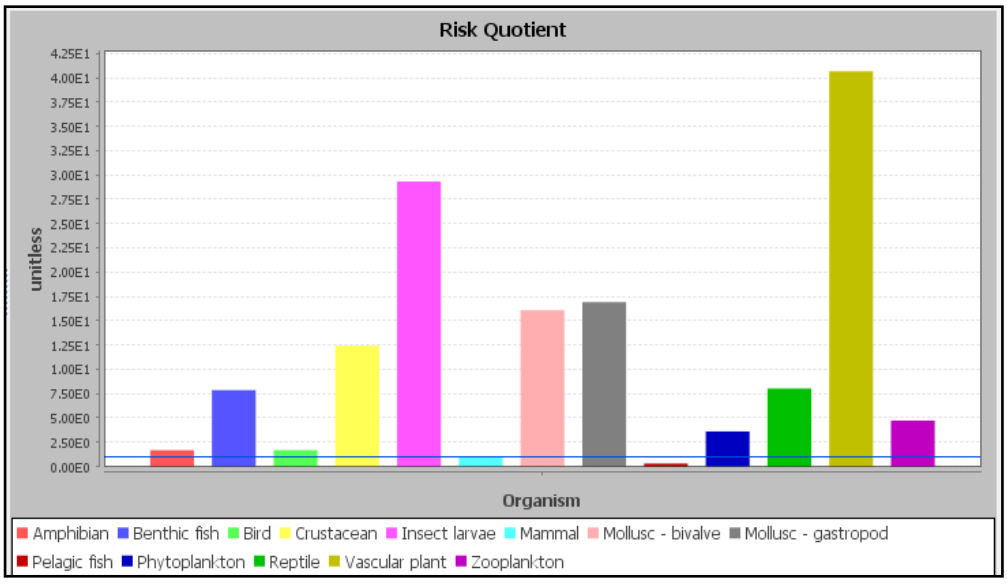


Figure 5-33: Risk Quotient for Tier 2 screening Aquatic environment (Phosphate industry)

Figure 5-34 shows the dose rate to ERICA ROs from the various radionuclides based on the measured activity concentrations in water (Table 5-14). The predicted dose to all organisms, except pelagic fish was higher than10 µGy.h^{-1}, with vascular plants receiving the highest dose (407 µGy.h^{-1}). The internal dose from ^{228}Th dominated for all organisms with some contribution from ^{230}Th. For pelagic fish the total dose was 2.97 µGy.h^{-1}, with ^{228}Th

contributing 41.4% and ^{230}Th 25.6%. Compared to internal dose the contribution of external dose was insignificant, due to the very low DCF for external radiation (see Table A-11, Appendix A).

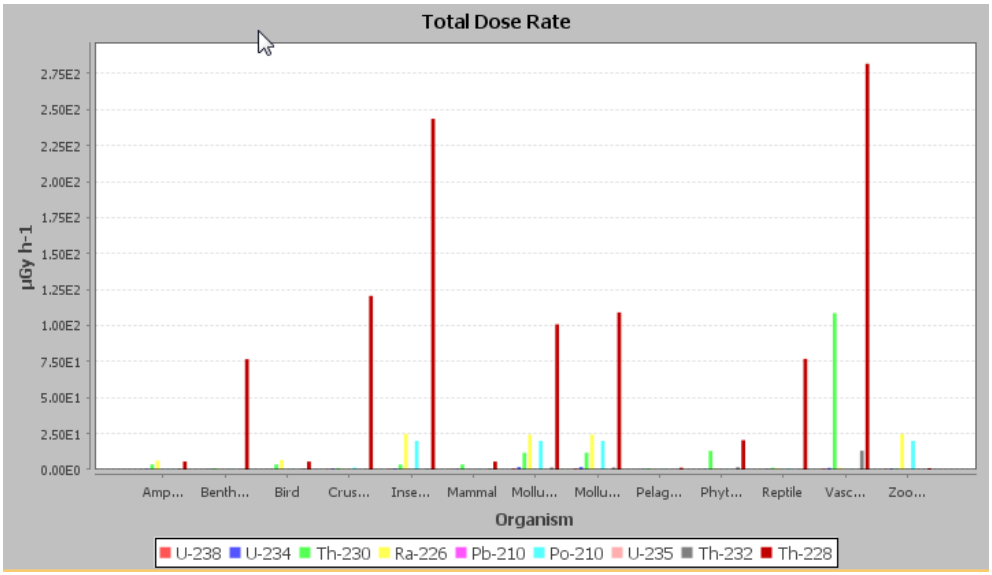


Figure 5-34: Dose rates (µGy.h^{-1}) to aquatic reference organisms for phosphate industry site.

The tier 2 screening was done at a very low level of 10 µGy.h^{-1}. As an optional choice in the model it is also possible to do the screening at 400 µGy.h^{-1} for aquatic animals. At this level of chronic exposure, it is not expected for any measurable effects to occur (2.2.9). Using the 400 µGy.h^{-1} screening level, only the most sensitive organism, vascular plant, showed some probability of being exposed to dose rates of which the impact may not be negligible. To establish the likelihood of any harmful environment impact a more detailed assessment (at Tier 3) using site specific information is required (2.4.7).

The dose predicted by the model was based on measured water concentrations. In the absence of measured concentrations for sediment, the K_d default values in the model were used to predict the sediment concentrations. As can be seen from Table 5-15, the predicted concentrations were quite high, especially for the Th isotopes, thereby contributing to the higher estimated risk. The high predicted sediment concentration for all the Th nuclides is a result of the high K_d value for Th of 1.97E7 (Table A-7, Appendix A). It is clear that use of the default K_d value in the model resulted in a high estimated risk. For a more realistic assessment, the actual sediment concentrations should preferably be measured or site specific

K_d values should be used.

Table 5-15: Comparison of predicted RO concentration with measured values (Phosphate industry)

Nuclide	Activity concentrations ($Bq.kg^{-1}$)			CR Fish($Bq.kg^{-1}$ per $Bq.L^{-1}$)		
	Predicted ERICA		Measured	Erica	NNR	Measured
	Sediment	*Fish*	*Fish*	*Fish*		
^{238}U	18.4	4.64	0.13	72.4	0.96;2.4 (50)	2.0
^{230}Th	8.02E5	29.2		713		-
^{226}Ra	104	1.34	0.75	181	4;210 (200)	101
^{210}Pb	111	2.23	<2.65	359	25;370(2000)	<428
^{210}Po	92.8	10.6	0.79	2030	(500)	152
^{232}Th	1.13E5	4.13	0.65	713	6;190 (1000)	112
^{228}Th	1.84E5	6.70	0.53	713		56

NNR: First value refers to muscle, second to whole body, LG1032 in brackets

The ERICA derived concentrations in pelagic fish (Table 5-15), based on the measured water concentrations were higher than the measured concentration of fish in the surface water body for all nuclides. This indicates poor agreement between site-specific and default CRs. The measured CR for all measureable nuclides was lower than the corresponding default CR in the ERICA tool. CRs may have been underestimated because only edible parts of the fish were analysed, whereas ERICA CR values refers to the whole body of the organism. The measured CRs showed fairly good correspondence with literature values for most of the nuclides (Table A-14, Appendix A), and much better correspondence with the revised NNR values in RG-002 than with the previous LG1032 values, which were very conservative, representing the upper end in the range of values in Table A-14.

Due to its mobility, high concentrations of U are often found in surface water. However, studies showed little evidence of accumulation of U in freshwater fish (2.1.2). Th is insoluble in water and readily sorbs to suspended matter. Th does not accumulate in fish muscle, but may be present in bone tissue (2.1.3). Higher CR value for Po in literature may refer to whole body concentrations and is therefore based on elevated concentrations commonly found in organs such as liver of fish (Brown *et al*., 2004).

Conclusions

The case study has shown that analysis of water only will probably not provide sufficient

information to determine contaminant levels in aquatic biota. Even though bio-accumulation factors can in theory be used to predict activity concentrations in fish tissue from the concentrations in water (and calculate dose to humans using equation 2.6), discrepancies between predicted values from models using literature K_d and CR values, and actual measured values were found. Due to uncertainties in the use of models and the large variation in concentration factors, actual measured activity concentrations of biota (fish), as well as sediment samples, is preferred for dose calculations.

The data presented in this study gave some indication of exposure to aquatic biota in an area influenced by phosphate mining. Based on the limited results, it seems as if only the most sensitive organism, vascular plant has some probability of being exposed to dose rates higher than the dose limit of 400 $\mu Gy.h^{-1}$ suggested for aquatic plants and animals (2.2.9).

5.3.6 Application of ERICA tool: Estimation of exposure to biota due to spilling incident

Background

A fertilizer plant based near Phalaborwa produces phosphogypsum as a by-product. The phosphogypsum is stored in large stacks and water with a low pH seep through the stacks into impounding dams from where it is pumped to other storage dams. At the end of December 2013, due to heavy rain, one of the impounding dams overflowed into the Selati River, which flows into the Olifants River in the Kruger National Park (KNP).

This incident received considerable press coverage (SANews, 2014, Citizen, 2014). The spill occurred near the Phalaborwa entrance to the KNP. The Olifants River is an important river for the economies of South Africa and Mozambique and a very important component of the ecosystem of the KNP (Sanparks, 2014). The fertilizer plant was confident that the incident caused no harm to the environment due to dilution by the Selati River's strong flow (SA Press Association, 2014). Since the media attention has created perceptions and fears of high radiation levels in the water, an investigation was launched to evaluate the impact on the aquatic ecosystem and to determine whether the water was safe to be used. The evaluation included analysis of samples for radioactivity. The aim of this case study was to investigate the potential risk of the radioactive discharge on the aquatic environment around the fertilizer plant.



Figure 5-35: Contamination of Selati River (Citizen, 2014)

Samples and radioactivity analysis

In a study conducted by the North-West University, which formed part of a wider investigation to assess the health of crocodiles in the KNP, muscle samples were collected from the tails of twelve crocodiles (CS1-CS12 – see Figure 5-36) from rivers in the KNP area. One of these samples, CS16; closest to the contamination site, was sent for radioactivity analysis. Other samples from the impacted area received for analysis included process water from the impounding dam and water samples taken in the Olifants River 50 km downstream from the plant.

The crocodile sample was dried and digested with HNO_3 and H_2O_2 prior to analysis of ^{210}Po by alpha spectrometry. An ashed sample fraction was analysed by NAA (U/Th) and broad energy gamma spectrometry (^{210}Pb, ^{226}Ra). The water samples from the river were screened for gross alpha/beta activity only, but a full nuclide analysis was performed on the process water.

Results and discussion

The measured activities in the crocodile sample were very low and at the detection limit of the analytical technique for most of the nuclides (Table 5-16). The gross activity concentrations results of the river samples were low, complying with WHO screening limits for drinking water, whereas elevated levels of radioactivity were observed in the dam water sample. A full nuclide analysis of the dam sample was performed, of which the results are shown in Table 5-17. Based on the WHO guidance levels (WHO, 2011) for individual nuclides (Table 2-4), the quality of this water was good with concentrations below the

guidance levels for drinking water quality.

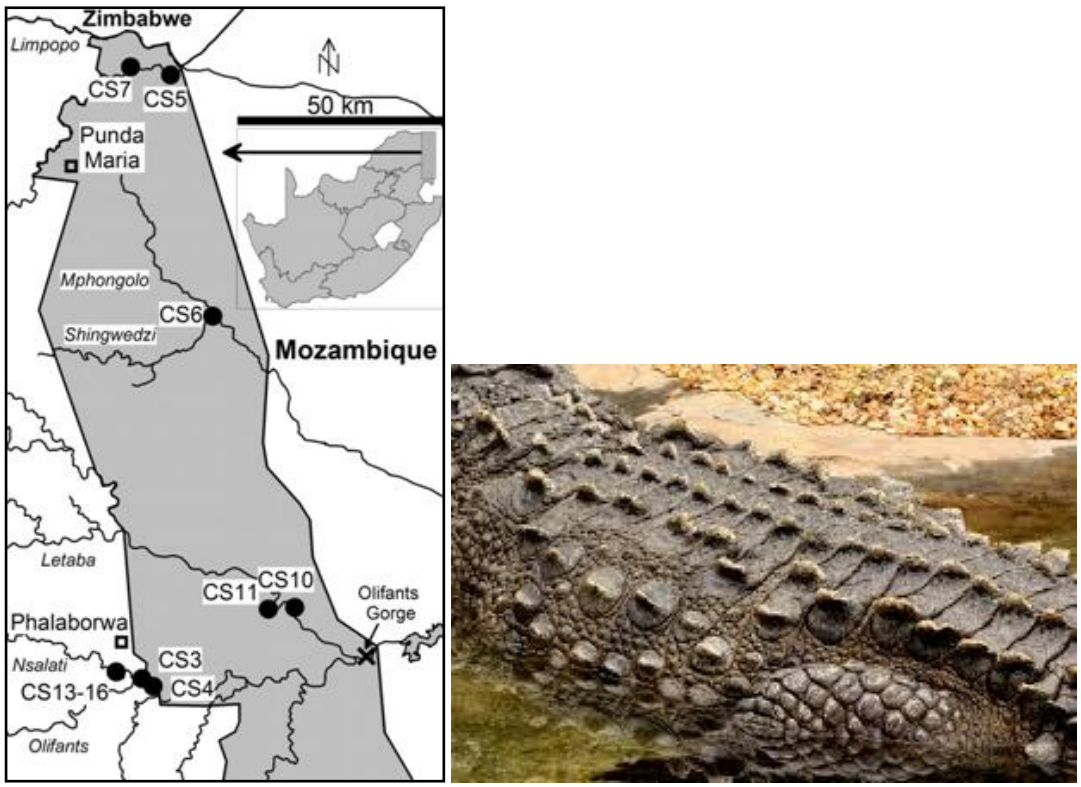


Figure 5-36: Sampling points Crocodile

Table 5-16: Measured activity concentrations in water (Bq.L^{-1}) and crocodile sample (Bq.kg^{-1} fw) close to a fertilizer production plant

CROCODILE	Bq.kg^{-1}		WATER	Bq.L^{-1}	
Nuclide	**Activity**	**MDA**		**GA**	**GB**
^{238}U	1.11 ± 0.22	0.57	River 1	0.093±0.01	0.18±0.08
^{234}U	1.10 ± 0.22	0.56	River 2	0.126±0.02	0.13±0.08
^{226}Ra	<	0.65	Dam	1.67±0.3	4.44±0.82
^{210}Pb	1.9 ± 0.067	2.3			
^{210}Po	3.90 ± 0.80	0.40			
^{232}Th	<	0.65			

Table 5-17: Nuclide specific analysis of impounding dam sample at fertilizer plant

Nuclide	Activity (mBq.L^{-1})	MDA
^{238}U	1510 ± 50	4.2
^{234}U	1470 ± 50	4.2
^{230}Th	77.5 ± 14.0	30
^{226}Ra	2.08 ± 0.85	0.94
^{210}Po	98.6 ± 9.7	2.1
^{235}U	69.6 ± 2.2	0.19
^{227}Th	18.0 ± 3.9	2.1
^{223}Ra	2.14 ± 1.09	1.3
^{232}Th	11.6 ± 3.0	2.1
^{228}Th	16.2 ± 3.7	5.6
^{224}Ra	4.36 ± 1.78	2.0
Dose to adult = 0.29 mSv.a^{-1}		

The results of the nuclide specific analysis of the dam sample were used to predict dose to humans and to biota that may occur in the aquatic ecosystem. Similar as in 5.1.2 the annual ingestion dose for the adult age group was calculated using not only the analysed nuclides, but all nuclides in the series, assuming equilibrium for those which had not specifically been measured. For humans the ingestion dose for the adult age group from drinking water from the dam was calculated as 0.29 mSv.a^{-1}, exceeding the NNR dose constraint of 0.25 mSv.a^{-1}. The regulatory framework in SA requires for a dose of between 0.25 and 1 mSv.a^{-1} to be disclosed to the regulator who will decide on regulatory requirements on a case-to case basis (2.2.4).

Since no information on specific species in the ecosystem was available, ERICA ROs was used in the assessment on biota. Using the ERICA tool it was found that the screening dose rate was exceeded for reptile, insect larvae, mollusc, vascular plant and zooplankton, as shown in Figure 5-37. As explained in 2.4.7 RQ>1 indicates increased risk in which case the tool recommends continuing the assessment at Tier 3, for which site specific data is required.

Organism	Risk Quotient [unitless]
Amphibian	9.07E-1
Benthic fish	3.88E-1
Bird	7.82E-1
Crustacean	6.58E-1
Insect larvae	2.13E0
Mammal	8.63E-1
Mollusc - bivalve	1.61E0
Mollusc - gastropod	1.65E0
Pelagic fish	4.05E-2
Phytoplankton	2.01E-1
Reptile	4.13E0
Vascular plant	2.06E0
Zooplankton	1.01E0

Figure 5-37: ERICA output – Risk for aquatic ecosystem at fertilizer plant

Table 5-18: Dose rates (µGy.h^{-1} due to exposure to natural radionuclides for crocodiles (RO = reptile)

		^{210}Po	^{238}U
INPUT			
Organism concentration	Bq.kg^{-1} fw	**3.9**	**1.11**
Screening	µGy.h^{-1}	40	
Uncertainty	-	3	
DCF internal	µGy.h^{-1} per Bq.kg^{-1}	3.06E-03	2.41E-03
CR	Bq.kg^{-1} per Bq.L^{-1}	3.63E+03	1.16E+02
Kd	L.kg^{-1}	1.78E+04	2.87E+02
OUTPUT			
Total dose rate	µGy.h^{-1}	1.19E-01	2.68E-02
Activity water	Bq.L^{-1}	1.07E-03	9.55E-03
Activity sediment	Bq.kg^{-1}	1.92E-01	2.74E+00
Total dose rate to organism outcome Tier 2 (µGy.h^{-1})			**0.146**
Risk			0.0036

Using the measured activity concentrations of ^{210}Po and ^{238}U in the crocodile, the ERICA tool was used to predict the dose received by the crocodile. Activities in the water and sediment were predicted from the activities in the organism (crocodile). Input and output parameters

are summarized in Table 5-18. The default transfer parameters of ERICA were used in the calculations (5.3.2). The resulting dose rate was about 0.004 $mGy.d^{-1}$, which is much lower than the IAEA recommended chronic dose rate limit of 10 $mGy.d^{-1}$ for aquatic animals (see 2.2.9).

Conclusions

The data presented gave an estimate of exposure to biota using the analytical data obtained at the time of a specific incident. It was found that the risk was minimal and that the water from the river was of drinking water quality. Water from the specific impounding dam under investigation may present a low risk to humans and biota. However, access to this water is restricted and no release to the environment is expected under normal operating conditions.

There has been some suggestion in the press that chronic seepage from the plant due to ailing infrastructure has contaminated ground- and surface water, and that the problem was worse than an isolated incident. No scientific prove of this was found; all monitoring results of the ground- and surface water sources in the area before and after time of the incident showed normal background levels of radioactivity (see 5.1.5).

5.3.7 Conclusions and Recommendations

The case studies illustrated some aspects of the application of modelling tools for dose assessment to biota. The impact on non-human biota and application of models should however be addressed in much more detail and is the scope of a full PhD thesis. The accuracy of bio-kinetic tools such as ERICA, which are used to estimate the radionuclide concentration in an organism from soil concentration, depends on the accuracy of the parameters available in the database. Confirmation of theoretical parameters in the database is limited by access to suitable samples, especially in the case of wildlife where samples only becomes accessible after the accidental death of animals. Actual measured values as presented in this section can make an important contribution to these databases.

It was clear that current utilization of the ERICA tool in South African industries is limited, especially since default organisms do not necessarily reflect the South African biotic types and environmental conditions. More detailed assessments will require biota-to-soil CR values for South African animals and plants. The process requires selected biota sampling from the local environment and radioactivity measurement. The support of the radio analytical

laboratory is essential in this regard. Until specific data becomes available for SA a more suitable approach will be to actually measure the activity concentrations in biota, rather than using default values in models to predict the activity concentrations.

At the international level, the ICRP has established a framework for radiological assessment and protection of biota. National guidance in this regard is still lacking in South Africa. Hopefully, the present study will initiate some scientific effort in this regard and support activities of the planned radio-ecology study group under direction of the NNR.

A critical element for experimental studies like those presented here is the quality of the analytical method used for analysis. Analytical techniques with high sensitivity and accuracy are essential for successful study of the environmental behavior of radionuclides. Unfortunately the high cost of radionuclide analysis did not allow for sufficient samples to be collected and analyzed to provide adequate statistical confidence in comparisons between the experimental data and literature values; any results based on limited data and single grab samples must always be interpreted with caution.

Expect for limited data presented by Bain *et al*. (1994) specific TFs for South African conditions have never been determined. Therefore RG-002 (NNR, 2013) uses IAEA derived values, which are not necessarily applicable to South African conditions. To determine more realistic soil to plant transfer factors it is recommended that future studies are conducted to study transfer under controlled experimental conditions in collaboration with concerned farmers in affected areas. Preferable vegetables that are most often consumed in South Africa should be used in the study. Transfer studies to domestic animals are also important to confirm NNR recommended values especially in the light of the large discrepancies in literature values for some nuclides.

5.4 Natural radioactivity in solids

5.4.1 Introduction

Gamma radiation emitted from natural radionuclides is one of the main sources of external radiation exposure to humans (Figure 1-1). Terrestrial radiation levels depend on soil and mineral composition and vary significantly around the world. Many studies have been conducted to determine natural terrestrial radiation in other countries (2.7.1). However, published results for South Africa are scarce (2.7.4). The focus of this case study was on the

natural radioactivity in solid samples. Results for soil, sediment, tailings and other geological solid samples received from various NORM industries for analysis as part of their environmental monitoring programmes, are presented.

It is widely recognized in the literature that a difference in mobility of radionuclides may cause disequilibrium. Elements present in non-lattice sites of soil and sediment can be considered potentially mobile, whereas those in the lattice (residual) sites are immobile. In the South Africa context radionuclides accumulated in sediments in the WCA (2.12.4) can be remobilized into water by chemical and physical processes. If leached significantly from sediments to ground- and surface water, transfer through the food chain may occur causing internal exposure to humans. To evaluate the availability of the naturally occurring radionuclides from solids leaching procedures can be applied. Mobility of natural nuclides under specific conditions was investigated in limited laboratory studies. The results are presented in 5.4.3.

5.4.2 Radioactivity analysis of soil, sediment, tailings and waste rock samples

To comply with regulatory requirements soil and sediment samples from NORM industries in South Africa are analysed for radioactivity on a regular basis. Tailings samples from both active TSFs, as well as tailing footprints, from the gold mine areas are also analysed. In this case study the ample results available were used to get an indication of the levels of natural radioactivity in soil in different areas in SA. Due to client confidentiality the location of the specific areas can not be disclosed.

Experimental

Soil, sediment and tailings samples were collected as prescribed by the sampling plan of the Certificate of Registration (CoR) held by the specific NORM industry regulated by the NNR. Samples were prepared as in 4.3.3. Nuclide specific analysis was performed using NAA and gamma spectrometry as per the prescribed procedures for solid samples (4.12.1). Solid samples were also routinely measured for gross alpha/beta following the procedure as in 4.4.2. The equilibriums as in 4.12.3 were assumed to calculate gross alpha/beta activity from individual nuclide concentrations.

Results and discussion

Tables 5-29 and 5-30 present summarized results for activity concentrations of the natural radionuclides in sediment, soil, tailings and waste rock samples collected from different sites in the period 2012-2017. Raw data are available in Tables D-3, D-4 and D-5. The average activities varied depending on the area of origin, and also over the period of monitoring.

Important to mention is that the reported results for ^{238}U and ^{232}Th are actual measured values (by NAA), whereas in many publications the reported values are based on measurement of the decay products assuming secular equilibrium, due to the limitations of gamma spectrometry for direct measurement of ^{238}U and ^{232}Th (2.13.4). Some of these authors failed to mention that the actual nuclide measured was ^{226}Ra and not ^{238}U, or ^{228}Ra and not ^{232}Th.

Due to the preferred leaching of ^{234}U, the $^{234}U/^{238}U$ activity ratio in water is often > 1, as was shown for many of the water samples analysed (5.1.4 and 5.1.5). Therefore measurement of all three uranium isotopes are adviced for water samples. However, in sediments and soil, a $^{234}U/^{238}U$ ratio of unity is expected, even more so when influenced by mining activities. For the results presented here the concentration of ^{234}U was derived from the measured ^{238}U results assuming a natural isotopic ratio. Two different techniques are routinely used to measure the uranium concentration: NAA, measuring ^{238}U, and DNC, measuring ^{235}U (4.6). Comparison of the results obtained by the two complementary techniques, for some of the analysed solid samples, are shown in Table 5-19. The results obtained by the two techniques showed excellent comparion confirming that a natural uranium ratio does exist in the sample.

A natural ratio was also proved in 248 sediment samples from the WFS analysed in a previous study in this laboratory (Faanhof *et al.*, 2010). Poor correlation is indicative of enriched or depleted ratios, as was typically found for MAPEP proficiency samples (4.11.2). For samples where a natural ratio cannot be confirmed nuclide specific analysis of ^{234}U by a destructive (radiochemical) method will be required (4.8.2). As discussed in 2.13.11, total dissolution of the sample is essential for analysis of U in soil, since U is often present in the crystal lattice of the sample. For sediments, leaching will probable be sufficient, since sediment is in essence rotted plant material, and it is not expected for U to be present in the crystal structure. Radiochemical determination of uranium isotopes in solids was not

routinely done.

For many of the solid samples analysed poor correlation was found between measured "gross" alpha/beta and the expected 'total" alpha and beta activities of the sample calculated from summation of gamma spectrometry results for individual nuclides (2.13.3). As shown in Table 5-19, the correlation calculated for 113 soil samples varied from 0.18 to 4.34 for alpha activity and 0.15 to 3.80 for beta activity .The poor correlation for individual samples is not readily explained. It may be due to the differences in beta energies between the calibration samples and the actual field samples containing mainly uranium:

Calibration standards: $^{90}Sr/^{90}Y$ with beta energies of 0.546 and 2.282 MeV

Solids: $^{234}Th/^{234m}Pa$ with beta energies of 0.273 and 2.271 MeV

Table 5-19: Solid samples – Measured ratios and MDAs

	DNC/INAA ratio	**Gross alpha Measured/Calculated**	**Gross beta Measured/Calculated**
SOIL			
Average	1.04 ± 0.09	1.50 ± 0.92	0.97 ± 0.68
Range	0.91 – 1.33	0.18 – 4.34	0.15 – 3.80
N	44	48	49
SEDIMENT			
Average	1.01 ± 0.07	1.26 ± 0.68	1.37 ± 0.74
Range	0.92 – 1.36	0.34 – 3.62	0.50 – 2.95
N	43	42	42
TAILINGS			
Average	0.97 ± 0.08	0.99 ± 0.74	1.39 ± 0.43
Range	0.90 – 1.32	0.37 – 3.56	0.63 – 2.23
N	52	23	23
MDA ($Bq.kg^{-1}$)	Average		Range
^{238}U	0.55 ± 0.23		0.32 - 1.27
^{226}Ra	30.1 ± 19.6		5.77 - 78.4
^{210}Pb	**123 ± 52**		**48 - 303**
^{232}Th	3.27 ± 2.78		0.80 - 17.9
^{228}Ra	49.1 ± 34.3		7.45 - 128
^{228}Th	84.4 ± 57.9		9.76 - 217
^{40}K	209 ± 148		19.8 - 655
Gross alpha	1172 ± 861		258 - 4440
Gross beta	115 ± 79		32 – 318

Accordingly, the lower energies (especially the 0.273 MeV) will be more absorbed in the solid samples giving rise to lower values for the measured beta activities. To obtain better comparable results one should preferably use calibration standards spiked with certified natural uranium reference standard chemicals. Sample inhomogenieties can also not be excluded although the samples were thoroughly ground to a fine powder to avoid inhomogeniety at the different sub-sample quantities taken for gamma-spectrometry and gross alpha/beta counting.

The average measured MDAs in $Bq.kg^{-1}$ reported for 144 solids samples are summarized in Table 5-19. The recommended sensitivity of the NNR is 10 for ^{238}U, 4 for ^{232}Th and 100 $Bq.kg^{-1}$ for ^{226}Ra, ^{228}Ra, ^{228}Th, ^{210}Pb and ^{40}K (NNR, 2013). The MDAs as indicated were sufficient for the purpose of measurement of radioactivity in solids, which was evaluated against a allowable limit of 500 $Bq.kg^{-1}$ (2.2.4).

^{210}Pb in solid samples was measured with a low energy gamma detector, which has poor sensitivity. For most of the solid samples the MDA (typically ~ 100 $Bq.kg^{-1}$), was assumed for ^{210}Pb. The seemingly high observed ^{210}Pb/ ^{226}Ra ratio was therefore most likely due to poor sensitivity of the measurement technique. The higher results reported for some samples should be used with caution, although higher ^{210}Pb concentration might be due to the presence of unsupported ^{210}Pb in surface soils, mainly derived from atmospheric deposition, as discussed in 2.1.5. For confirmation of this disequilibrium and enhanced concentrations of ^{210}Pb it should be measured by the more sensitive broad energy gamma spectrometer used for analysis of food samples, or alternatively via radiochemical determination of ^{210}Po after dissolution of the sample.

Soil

The activity concentrations of all nuclides in soil from different areas (Table 5-29, Figure 5-38) were much lower than the legislative exemption level for natural radioactive materials of 500 $Bq.kg^{-1}$ (2.2.4) and compared favourably with the respective median concentrations in the world for undisturbed soils (Table A-19, Appendix A). These data can be seen as “control area” data.

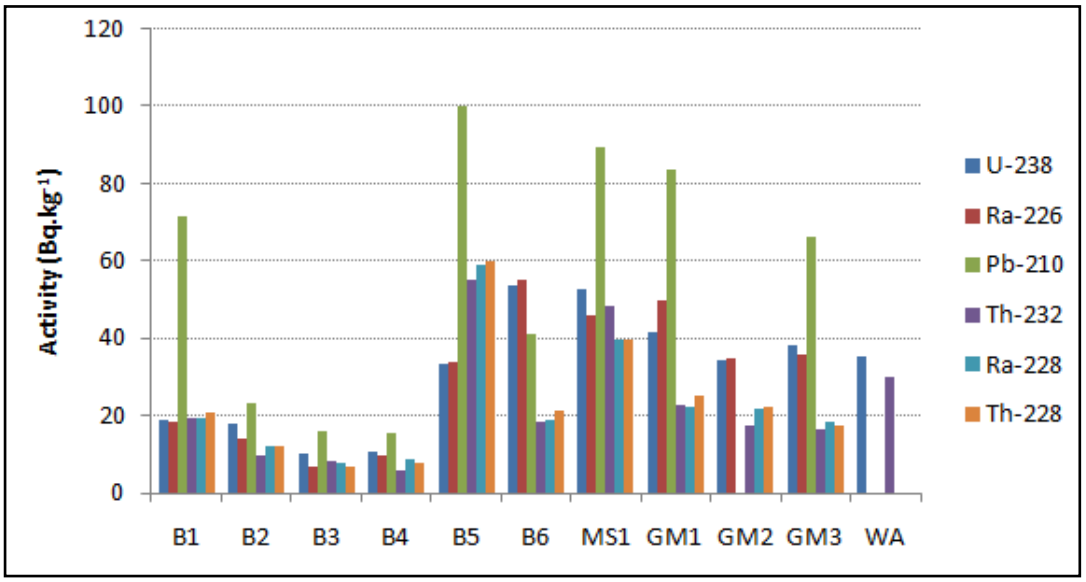


Figure 5-38: Average activity concentrations in soil samples from areas affected by NORM industries
(B-Baseline; MS-Mineral Sands; GM-Gold Mine; WA-World Average)

The average ^{238}U activity was 29±16 Bq.kg^{-1}, ^{226}Ra activity concentrations averaged 28 ± 19 Bq.kg^{-1} and the ^{210}Pb average activity was 66±33 Bq.kg^{-1}. There was a good correlation between ^{238}U and ^{226}Ra (average ratio 1.10±0.37) confirming equilibrium of the uranium/radium chain as generally expected for soil (2.1.1) and supports the assumption of equilibrium between ^{234}U and ^{238}U (which was proved by comparison of DNC and NAA results). The average value of ^{238}U/^{226}Ra in UNSCEAR (2000) is about 1.03 and is based on assuming equilibrium between ^{238}U and ^{226}Ra. The average ^{210}Pb/^{238}U (and ^{210}Pb/^{226}Ra) ratios were greater than one showing consistently higher ^{210}Pb concentration in soil compared to that of the parent nuclide, which may be due to reasons as explained above.

The ^{232}Th-chain has relatively short-lived progeny compared to the age of the soils. ^{228}Ra was determined by the activity of its short-lived daughter ^{228}Ac, while ^{228}Th was determined from its daughters ^{212}Pb and ^{208}Tl. The average ^{228}Ra activity was 23±20 Bq.kg^{-1}. The average ^{228}Th activity was 24±20 Bq.kg^{-1}, and that of ^{232}Th was 23±21 Bq.kg^{-1}. The results confirmed equilibrium of all nuclides in the thorium chain. An average concentration of 150±151, with a maximum of 734 Bq.kg^{-1} was observed for ^{40}K, which is within the range of values reported worldwide (Table A-19, Appendix A) and much lower than the SA exclusion limit for ^{40}K of 10000 Bq.kg^{-1} (2.2.4).

As mentioned in 2.1.2 U and Th occur at almost the same activities in the earth's crust. Since U is more soluble than Th, it is sometimes found in deficit with respect to Th in solid samples from the environment. The $^{238}U/^{232}Th$ activity ratio was > 1 for most of the soil samples with an average of 1.26±0.65, which is similar to the UNSCEAR ratio of 1.12 (UNSCEAR, 2008). Ratios can be used to predict contamination. Since all concentrations were very low, contamination of uranium in the specific areas was not suspected.

Sediment

Activity concentrations varied between sites and even for a specific sampling point, as indicated by the large standard deviation (Table 5-29). Samples for environmental monitoring are usually submitted annually, or for some sampling points bi-annually. Depending on operational activities at the sites, the concentration may vary over time. Since no information on the process followed for sampling was available, it might also be possible that samples were not taken at the same position every time, and that "hot spots" occured at the specific source.

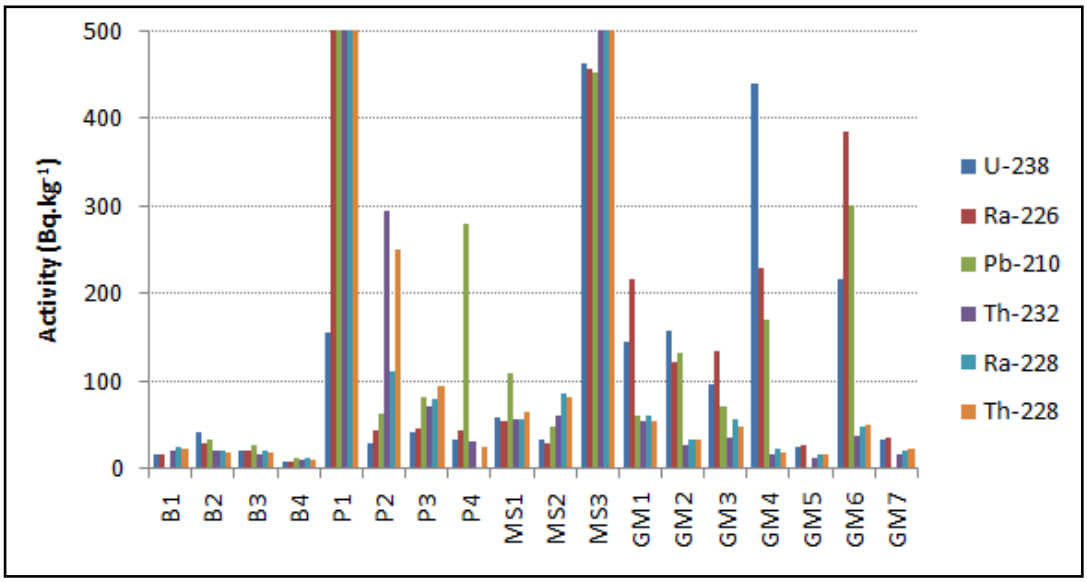


Figure 5-39: Average activity concentrations in sediment samples from areas affected by NORM industries

The measured activity concentrations in the *background areas* (B1-B4) were similar and lower than world averages. The ratio of $^{238}U/^{226}Ra$ varied between 0.63-1.44, mostly indicating equilibrium, whereas the ratio of $^{226}Ra/^{210}Pb$ was mostly lower than one (0.70±0.22), which can be explained as above. Activity concentrations in most of the

samples in proximity to NORM industries were higher than in the background areas (Figure 5-39). This illustrates the importance of conducting a baseline study prior to the start of any mining activities, which can then be used to evaluate any increase in radioactivity concentration contributable to mining. Unfortunately for most of the industries currently operational in South Africa, no baseline study data are available.

For the *gold mining industry* the U series nuclides varied from normal natural background levels to slightly enhanced concentrations of ~700 $Bq.kg^{-1}$. Less than 5% of readings indicated activity concentrations higher than the legislative exemption level for natural radioactive materials of 500 $Bq.kg^{-1}$. Concentrations of ^{40}K, ^{232}Th and ^{226}Ra compared fairly well with results previously reported for sediment from the gold mining areas (Faanhof *et al*., 2010). ^{238}U was on average (156±150 $Bq.kg^{-1}$) lower than previously reported values of (934±14 $Bq.kg^{-1}$), but higher than the uranium concentrations in baseline studies and the word average of 30 $Bq.kg^{-1}$, indicating some contamination of the sediment. Since U is known to be relatively mobile, high concentrations of U in sediment suggest that adsorption exceeds re-mobilisation over long periods resulting in accumulation of U in sediment.

The nuclides of the uranium series seem to be mostly in equilibrium with the average $^{238}U/^{226}Ra$ ratio 1.10±0.57. A low $^{238}U/^{226}Ra$ ratio in upper layers of soil or sediment can be explained by the difference in mobility: ^{226}Ra is immobile and remains constant whereas ^{238}U may be leached from the surface and transferred to deeper soil where it accumulates. This difference in mobility was observed in the leaching study discussed in 5.4.3. Another explanation is that uranium and radium released from mining- and mineral processing activities through pumping of underground water, which contains these two nuclides at different concentrations, accumulate at different rates in sediments, which at certain points may be aggrevated by direct contamination from mine tailings either through direct run-off or wind-blown dust deposition. The $^{226}Ra/^{210}Pb$ activity ratio was close to unity (1.28±0.48) for the sediment samples. It was likely that ^{226}Ra has been deposited, from which ^{210}Pb in-growth occurred, taking into consideration the relative short half-life of ^{210}Pb (~22 years) compared to the age of the sediments (build-up over ~150 years).

Concentrations of ^{232}Th series nuclides were much lower than that of the ^{238}U series nuclides, and compared well with world background averages (Table A-19, Appendix A). The $^{238}U/^{232}Th$ ratio was > 1 for many of the samples with an average of 6.9 ± 9.2, which deviates

from natural distribution (ratio=1.12) suggesting significant contribution of U series members in the area.

Samples from the impounding dams of the *mineral sands industry* (MS3) and the *phosphate industry* (P1) had very high concentrations for the ^{232}Th series nuclides with concentrations of both ^{232}Th and ^{228}Th higher than 5000 Bq.kg^{-1}. The ^{232}Th series nuclides were enriched compared to ^{238}U series nuclides with a ^{238}U/^{232}Th ratio of less than 0.1. High radioactivity concentrations are expected in these storage and retention dams, which contain the contaminated residues and process water from the plant. Samples from P1 had high concentrations of ^{210}Pb and ^{226}Ra (> 500 Bq.kg^{-1}), and were enriched with respect to ^{238}U (^{238}U/^{226}Ra = 0.2, ^{226}Ra/^{210}Pb = 1). This may be expected in samples from the phosphate industry (2.9.1). Higher than world average concentrations of ^{40}K and the thorium series nuclides were found in samples from the mineral sands industries (MS1).

Tailings

Results from eight different TSFs/footprints from a selected goldmine area in Gauteng as summarized in Table 5-29 are shown in Figure 5-40. The higher concentrations found in these storage facilities compared to the soil and sediment samples, confirmed contribution of mining activities to elevated levels of ^{238}U. Individual nuclide concentrations for most of the samples were lower than the 500 Bq.kg^{-1} exemption limit (16% exceeded the limit). ^{238}U ranged from 82.5-668, with an average of 338 Bq.kg^{-1} for all tailings samples, which was about an order of magnitude higher compared to unaffected soil (Table A-19, Appendix A). The average ^{238}U concentration was lower than recent results published by Kamunda *et al.* (2016), but higher than those reported by Njinga & Tshivise (2017) for measurement at a tailings footprint at Tudor Shaft.

The results from selected TSFs from only one mine group are shown. Concentrations may differ for TSFs from other areas. The average ^{238}U concentration for 15 samples from a reprocessed TSF in a different area used for a leaching study (5.4.3) was 217$\pm$30 Bq.kg^{-1}. In some tailings, values might be higher, depending on whether it has been reprocessed. The resuls reported by Kamunda *et al.* (2016) showed that the ^{238}U concentration in TSFs that still has to be processed can be as high as 1556$\pm$27 Bq.kg^{-1} due to the presence of high concentrations of uranium in the gold mine residue. In Coetzee *et al*. (2006) the average U-

concentrations in tailings from 46 mines in the Witwatersrand basin was reported to range from 124 to 4266 Bq.kg^{-1} (own conversion), with an average for all tailings of 1243 Bq.kg^{-1}. The highest value measured in 160 samples from other mining groups (not reported in this study) was 2457 Bq.kg^{-1} ^{238}U, which was of the same order of magnitude to published results for tailings from the Gauteng area.

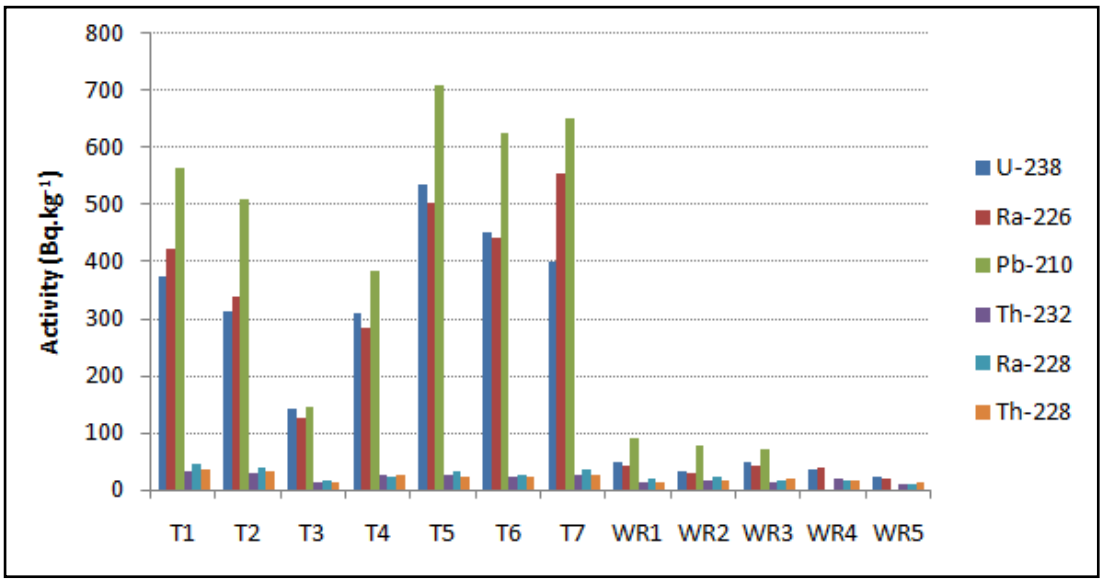


Figure 5-40: Average activity concentrations in tailings and waste rock samples from a gold mine

Activities of the nuclides from the uranium series were higher than those of the thorium series, whereas potassium was relatively low. It is generally expected that ^{238}U and ^{226}Ra being in the same series, are in equilibrium. This seemed to be the case for most of the tailings samples represented here with an average ratio of ^{238}U/^{226}Ra of 1.04 ± 0.28. As for soil the concentration of ^{210}Pb seemed to be higher than that of ^{226}Ra in most samples, with an average ratio of ^{226}Ra/^{210}Pb of 0.77 ± 0.14.

The ^{238}U/^{232}Th ratio was >> 1 for most of the samples with an average of 14.8 ± 6.9. This deviation from a natural distribution confirmed that there was significant contribution of uranium series members in the study area, which is expected for tailings material known to contain uranium as by-product. Nuclides in the thorium series seemed to be in equilibrium with average concentrations of 23.3 ± 8.5, 23.9 ± 14.5 and 23.7 ± 9.3 Bq.kg^{-1} for ^{232}Th, ^{228}Ra and ^{228}Th respectively. For these samples the result for ^{232}Th would have been accurate even if not specifically measured, but based on gamma measurement of the decay products of

^{228}Th and assuming secular equilibriumim, as is done by many laboratories. ^{232}Th concentrations were lower than the already mentioned published results for tailings material in the Gauteng area (Table A-19, Appendix A).

Waste rock from gold mines

The activity concentrations of all nuclides in the waste rock were low and comparable to world averages for undisturbed soils. The average ^{238}U activity was 37 ± 17 Bq.kg^{-1}, ^{226}Ra activity concentrations averaged 35 ± 20 Bq.kg^{-1} and the ^{210}Pb average activity was 74 ± 47 Bq.kg^{-1}. There was a good correlation between ^{238}U and ^{226}Ra (average ratio 1.20 ± 0.50) confirming equilibrium of the uranium/radium chain. As in all other solids reported the concentration of ^{210}Pb seemed to be higher than that of ^{226}Ra in most samples with an average ratio of ^{226}Ra/^{210}Pb of 0.79 ± 0.39.

The ^{238}U/^{232}Th activity ratio was > 1 for most of the soil samples with an average of 2.53 ± 1.07, which is higher than the UNSCEAR ratio of 1.12 (UNSCEAR, 2008). This higher ratio can be explained by the natural presence of uranium in ore in this area.

In the ^{232}Th-chain the average ^{228}Ra activity was 18 ± 7 Bq.kg^{-1}. The average ^{228}Th activity was 15 ± 5 Bq.kg^{-1}, and that of ^{232}Th was 15 ± 5 Bq.kg^{-1}. The results confirmed equilibrium of all nuclides in the thorium chain.

An average concentration of 354 ± 127 with a maximum of 813 Bq.kg^{-1} was observed for ^{40}K, which is within the range of values reported worldwide (Table A-19, Appendix A).

Dose evaluation and potential radiological risk

Various parameters were used to quantify the radiation from the solid samples. The calculated parameters are shown in Tables D-3 to D-5 and summarized in Tables 5-29 and 5-30. The radium equivalent activity (Ra_{eq}) and external hazard index (H_{ex}) (equations 2.10 and 2.11) was used to compare activity of the different solids. The external gamma dose rate, (D), was calculated using equation 2.8 in 2.3.6. Where direct gamma measurement results are not available, the calculated gamma dose rate gives a good indication of the expected external exposure. According to UNSCEAR (2000) the ratio of calculated soil dose rate versus direct gamma measurement results is typically 0.6-1.5.

The annual effective dose (AED) for adults was derived from the soil dose rate using an outdoor occupancy factor of 0.2 and conversion factor of 0.74 $Sv.Gy^{-1}$ (equation 2.9). The AED accounts for both internal and external radiation exposure (for adults). The expected external dose from soil was calculated using both the simplified equation 2.9 (estimate dose using the concentrations of ^{238}U, ^{232}Th and ^{40}K only) and equation 2.7 (sum of dose from all individual nuclides; dose from ^{40}K not included). Both equations gave similar results for the estimated dose, which confirmed that the simplified equation 2.9 can be used to estimate dose.

Soil:	eq. 2.7	0.032±0.028	eq. 2.8	0.039±0.027	ratio: 0.95±0.19
Sediment:	eq. 2.7	0.21±0.76	eq. 2.8	0.18±0.26	ratio: 1.01±0.18

Soil

All parameters for prediction of radiological impact indicated that the submitted samples did not have any potential radiological risk. Ra_{eq} was < 370 $Bq.kg^{-1}$ and H_{ex} <1 for all samples. The gamma dose rate was less than the average of 59 $nGy.h^{-1}$ from earth's crust (UNSCEAR, 2000). AED was < 0.25 $mSv.a^{-1}$, and was with single exceptions, similar to the world background average of 0.07 $mSv.a^{-1}$.

Sediment

The gamma dose rate for sediment from the background areas was similar or less than 59 $nGy.h^{-1}$. For the majority of sediment samples from all areas Ra_{eq} was less than 370 $Bq.kg^{-1}$ and H_{ex} less than one. The predicted AED for most samples were low. A dose higher than the NNR dose constraint limit of 0.25 $mSv.a^{-1}$ was predicted for only three individual samples from GM1, GM4 and GM6 due to higher ^{226}Ra and ^{210}Pb activities measured in these samples. The predicted dose was less than the internationally excepted limit of 1 $mSv.a^{-1}$. The higher ^{40}K concentrations measured in some samples contributed very little to the dose.

As expected samples with higher activity concentrations from the impounding dams (P1, P2, MS3), exceeded the limits of Ra_{eq} < 370 $Bq.kg^{-1}$ and H_{ex} <1 and the AED in these areas was > 1 $mSv.a^{-1}$ About 90% of the external dose was from ^{232}Th, with 9 % from ^{226}Ra and less than 1% from ^{40}K. Water flow in impounding dams is usually low and there is an opportunity for organic matter to accumulate. Under these conditions radionuclides, such as ^{232}Th, may be immobilized. Impounding dams (settling ponds) are designed to contain radioactive effluent

waste and to minimize seepage to the environment. They are usually fenced off and therefore do not present any risk to the public.

Tailings

Compared to the soil- and sediment samples the average Ra_{eq} was > 370 and H_{ex} > 1, with dose rate of 182 $nGy.h^{-1}$. Despite higher concentrations the average calculated AED of 0.22 ±0.11 mSv was lower than the NNR dose constraint of 0.25 $mSv.a^{-1}$. For some individual samples the calculated dose was higher than 0.25 mSv, mostly due to high ^{226}Ra concentrations, but none exceeded the internationally accepted dose limit of 1 $mSv.a^{-1}$. Njinga & Tshivise (2017) reported an average AED of 0.25 $mSv.a^{-1}$ and Kamunda *et al.* (2016) a dose of 0.5 $mSv.a^{-1}$ The reported dose in these studies were slightly higher mainly due to higher ^{232}Th concentrations.

Waste rock from gold mines

All parameters for prediction of radiological dose indicated that the submitted samples did not have any potential radiological risk. Ra_{eq} was < 370 $Bq.kg^{-1}$ and H_{ex} <1 for all samples. The AED was < 0.25 $mSv.a^{-1}$, with a range of 0.03 to 0.08 $mSv.a^{-1}$ similar to the world average of 0.07 $mSv.a^{-1}$. The calculated gamma dose rate, D, was less than the world average of 59 $nGy.h^{-1}$ (UNSCEAR, 2000).

Conclusions

For the majority of samples, the activity concentrations were not exceptionally high, especially when considering the internationally recommended exclusion value of 1000 $Bq.kg^{-1}$ for radionuclides of natural origin (IAEA, 2014b). The radiological risk seemed not to be significant when compared with the world average for annual effective dose from terrestrial gamma radiation of 0.45 mSv (UNSCEAR, 2000).

This study did not aim to provide a complete dose assessment and not all pathways were considered. As mentioned in 2.12.2, informal settlements are often established on or adjacent to TSFs, which may result in exposure of residents to ingestion of radionuclides, direct external gamma radiation and inhalation of radon gas. The dose evaluation was done considering external dose only. Radon concentrations in the atmosphere depend on the ^{226}Ra concentration in the soil, the exhalation rate and atmospheric dispersion. Radon

concentrations are most often modeled using a set exhalation rate, but can also be calculated from ^{226}Ra concentrations. Evaluation of the inhalation pathway was not considered in this case study. For any future land use scenario all pathways should be considered for dose evaluation.

As a worst case scenario it can be assumed all nuclides present in solids will become equally mobile and end-up in the water used by the local community for drinking purposes. The relative dose received by the public from every individual nuclide can then be calculated using a similar approach as for water. The assumption of equal release of the nuclides to the waterbody relative to their observed concentrations in the sediments, soil or tailings footprint, is questionable as all nuclides will have different distribution coefficients and may be re-adsorbed to sediments downstream. Therefore it is important to have information available on excact K_d values (5.4.3).

The purpose of the presented study was mainly to illustrate the application of radiometric techniques for accurate measurement of radioactivity in solid samples to support decision making by authorities in NORM industries. The disequilibrium found for some samples illustrated that results will be in error if ^{226}Ra is used to report ^{238}U, and assuming equilibrium, as is done by many authors and that nuclide specific analysis should preferably be performed.

5.4.3 Mobility of natural radionuclides in the environment

Studies on the mobility of radionuclides in the environment, specifically in the vicinity of NORM industries, are useful to predict the chemical conditions which will influence leaching of the nuclides. These types of studies are scarce in South Africa. By knowing the leaching behaviour the potential rate of release from solids can be evaluated and accordingly the expected water concentrations and resulting intake through direct consumption, as well as via secondary pathways such as uptake by animals and plants. In a laboratory this information can be obtained from sorption or desorption (leaching) tests (2.7.3). The fraction of the total content that is available (mobile) under the given leaching conditions is required for the prediciton of the leaching rates (calculation of distribution coefficients, K_d).

Although typical values of soil distribution coefficients for radionuclides can be found in published references, a better estimate of the risk will be obtained by the use of site-specific

K_d values in pathway analysis models. To obtain accurate estimates of site-specific K_d values, accurate (radionuclide-specific) radioanalytical methods should be used.

Leaching of solids

Leaching tests are widely used to assess the release of contaminants into the environment. Tests need to be conducted at conditions where the variables such as pH and ionic strength, are as close to the system being studied as possible. However in reality the test methods applied are often chosen with very extreme test conditions (finely ground samples, low pH values), which do not always accurrately predict actual leaching.

In this case study distribution coefficients (K_d values) for the natural radionuclides was determined by a selective leaching experiment conducted with contaminated solids from a mining area. The results of the laboratory study can be used to predict environmental behaviour of the nuclides absorbed in soil and sediment in contaminated areas around mines.

Experimental

Sixteen solid samples were received from a site in a mining area known to be contaminated by natural radioactivity, of which one was a sample collected from a background area. The samples were dried and milled as described for solid samples (4.3.3). Nuclide specific radioactivity analysis of the solid samples was done as described in 4.12.1 - NAA (U and Th), high energy gamma analysis (^{226}Ra, ^{228}Ra, ^{228}Th and ^{40}K) and low energy gamma analysis (^{210}Pb) was used.

500 g of each sample was leached using a nitric acid solution with a pH of 2. Due to the high analytical costs only one leaching agent was investigated in the laboratory. A 1:1 soil to solution ratio was used. The samples were shaken for 24 hours using an automatic shaker, after which they were filtered and the leachate transferred into a container for radioactivity analysis. Radiochemical separation and alpha spectrometry as described in 4.12.2 was used for determination of the isotopes of U, Th, Ra and ^{210}Po in the solution. Since ^{210}Pb was measured in the solid, and ^{210}Po in the liquid, it was assumed for the purpose of this study that equilibrium exists between the two nuclides.

The experimental procedure was based on the summary of metal leaching procedures (Mills, 1996), which includes ASTM and EPA recommended procedures. The procedures are

designed to mobilize potential contaminants present in the solid, so that the resulting extract can be used to assess leachate that could potentially be produced in the field.

Results and discussion

The radioactivity concentrations of the solids were of the same order as reported for tailings from another gold mine area (Table 5-29) with average concentrations of 27.3±14.9, 420±248, 552±288 and 217±130 Bq.kg^{-1} for ^{232}Th, ^{226}Ra, ^{210}Pb and ^{238}U respectively. The radioactivity concentrations of the solid and liquid phases were used to predict the mobility of each nuclide by calculating the distribution coefficient (2.7.2). The calculated K_d values are shown in Table 5-20.

Table 5-20: Distribution coefficient (K_d) values in L.kg^{-1}

Sample	U	Ra	Pb/Po	Th
X001	1.7	489	85.3	6.5
X002	2.1	345	128	6.3
X003	1.1	136	170	3.3
X004	1.7	210	206	3.9
X005	2.2	390	176	7.2
X006	3.2	708	539	11.3
X007	2.4	120	376	6.4
X008	1.8	657	120	1.3
X009	2.7	323	71.9	8.7
X010	2.0	241	442	8.6
X011	2.2	341	98.6	8.5
X012	1.5	594	331	4.3
X013	2.0	304	858	5.9
X014	1.4	496	584	2.3
X015	0.3	6.8	44.5	22.2
average	2.0	382.6	299.1	6.0
min	1.1	121.3	71.9	1.3
max	3.2	707.5	857.7	11.3

The calculated K_d values indicate low mobility of Ra and Pb/Po in acidic conditions (pH ~2), with K_d values ranging from 300 to about 800 L.kg^{-1}. This shows some comparison with the IAEA values in Table A-7 in Appendix A (IAEA, 2010a). The K_d values for U and Th were very close to zero, which implies that these nuclides migrate essentially at the same rate as

the water flow. This is as expected for U, again showing good comparison with literature values. Th, however, is not expected to be mobile, with K_d values of > 3000 $L.kg^{-1}$ mentioned in literature. No clear explanation was found for the seemingly low sorption of thorium under the acidic conditions, except for the analytical constraints with measurement of the very low concentrations of Th close to the LOD in both the solid and leachates. Th concentrations were about 10-20 times lower than for the nuclides from the U series. The low measured $^{238}U/^{226}Ra$ ratio (0.61 ± 0.38) of the solid samples can be explained by their different mobility. ^{238}U may have been leached from the soil surface to deeper levels, whereas ^{226}Ra stayed put since it is immobile.

From the results it seems as if only uranium may contribute to future contamination in the area, since Th was present at very low concentrations (< 20 $Bq.kg^{-1}$). These results also have important implications for remediation strategies. With U present in the mobile, not strongly retained fraction, it is amenable for phyto-remediation or heap leaching.

Exchange between solid and liquid phases in tailings

Experimental studies as conducted in the previous paragraph have some limitations. The best approach to determine mobility would be to use samples from the environment where physical and chemical equilibrium has already been established, and where adsorption of dissolved contaminants onto the solid phase equilibrated with the release from the solid back into the water.

Experimental

A number of solid-water-mixture "slurry" samples from TSFs were received for analysis. Both the solid and liquid phase were analysed and the results interpreted with respect to the mobility of the respective nuclides in the solid and liquid phases in the TSF. The samples were analysed for ^{238}U and ^{226}Ra using DNC/NAA and gamma spectrometry for the solid phase, and alpha spectrometry for the liquid phase, as summarized in 4.12.

Results and discussion

The typical scenario expected at TSFs is desorption where activity is leached from the tailings with acid rainwater. The results shown in Table 5-21 indicated more leaching of U than Ra with K_d values of about an order of magnitude lower. This was as expected from

literature, with many studies confirming immobility of Ra (IAEA, 2014a). K_d values were of the same order as IAEA values and NNR values (which are based on IAEA values), and support the results obtained in the laboratory study.

Table 5-21: K_d values from radioactivity results for slurry samples from TSFs

Sample	^{238}U			^{226}Ra		
	Liquid ($Bq.L^{-1}$)	Solid ($Bq.kg^{-1}$)	K_d ($L.kg^{-1}$)	Liquid ($Bq.L^{-1}$)	Solid ($Bq.kg^{-1}$)	K_d ($L.kg^{-1}$)
x001	2.68± 0.04	609± 16	227	0.152± 0.007	1510± 30	9934
x002	2.44± 0.04	766± 20	314	0.155± 0.010	1430± 30	9225
x003	2.97± 0.05	633 ± 6	213	0.268± 0.022	1580± 30	5896
x004	15.5± 0.2	1170 ± 10	76.5	0.761± 0.036	3190± 60	4192
x005	14.9± 0.1	1270 ± 10	85.2	0.544± 0.029	2730± 50	5018
x005	5.17± 0.1	1510 ± 40	292	0.262± 0.010	3030± 60	11520
x006	8.53± 0.14	1400 ± 10	164	0.289± 0.012	2240± 40	7750

Conclusions and recommendations

The K_d value is an important parameter used in models to predict environmental behaviour of natural nuclides, with literature values showing a wide range, with low K_d indicating high mobility in the water-solid system and *vice versa.* The variance in K_d values found in this study was no different from most literature studies, in which reported values for different types of soil vary widely, as indicated in Table A-7 in Appendix A. The variability is also due to the difference in experimental methods used for determination (EPA, 2004).

For desorption studies the contaminant concentration in the solid should reflect only the reversible sorbed fraction, and not the fraction incorporated in the mineral structure, which are not available for leaching. The K_d values might be overestimated, if the concentration include sorbed elements, as was done in the first study. Desorption tests will be a more accurate if leaching is done with "real" ground- or surface water from the area, and not simulated solutions.

The work discussed here should only be considered as preliminary. For more scientific (and useful) results better planning of the analytical protocol should be done. Nevertheless, the good comparison of the measured K_d values with theoretical values was promising. The study confirmed higher mobility of U compared to Ra, Pb and Th and confirmed that uranium in solids is bio-available and can be leached under acidic conditions. Considering this, the long-

term chemical stability of radionuclides in TSFs may be of concern. Most TSFs have residual pyrite in them, which is subject to atmospheric oxidation to sulphuric acid, creating an ideal condition for dissolution of uranium.

5.4.4 Solids from the Mineral sands industry

South Africa is one of the major producers of zircon and mineral sands minerals worldwide. Due to the high radioactivity, which is common in these minerals, the mineral sands industry operates under the restrictions of a CoR as required by the NNR to manage and mitigate radiological risk. To comply with regulatory requirements, samples from the mineral sands process streams are sent for radioactivity analysis on a regular basis. In this case study the ample results available at the laboratory were used to get an indication of the levels of natural radioactivity in these minerals. Due to client confidentiality no details of the specific industries concerned are given.

Experimental

Samples were collected as prescribed by the sampling plan of the CoR held by the specific NORM industry. Samples included solids from the mineral separation plant (heavy mineral concentrate, rejects), slimes dams and waste rock stockpiles. As part of the environmental monitoring programme, soil and sediment samples were also submitted for radioactivity analysis – results were presented in 5.4.2.

Samples were prepared as in 4.3.3. Nuclide specific analysis was performed using NAA and gamma spectrometry as per the prescribed procedure for solid samples (4.12.1).

Results

Table 5-33 summarizes the activity concentrations of radionuclides in rutile, ilmenite, monazite, zircon and other by-products (raw data in Table C-8 in Appendix C). The activity concentrations in most of these samples were relatively high and comparable to worldwide values, with many of the samples having concentrations > 500 $Bq.kg^{-1}$. The high concentrations in samples from zirconia production were of the same order as those reported in literature (Table A-16, Appendix A). The highest concentrations were found in monazite with concentration in the Th series ranging from 20000 $Bq.kg^{-1}$ to more than 150 000 $Bq.kg^{-1}$. The concentrations in ilmenite, and the by-products gypsum and slag were mostly less than

500 $Bq.kg^{-1}$. Concentrations in the heavy mineral concentrate, intermediate products and tailings were as expected, although one would have expected concentrations of Th series nuclides to be higher in comparison with that of U. As is common in mineral sands deposits, the concentrations of Th series nuclides were higher than those of the U series in monazite, as well as ilmenite. Similarly U-series nuclides dominated in Zircon and Zirconia.

For most of the samples equilibrium between nuclides of both the U- and Th series observed, in which case the activity of the mineral can be assessed by measuring the concentrations of the parent nuclides only. A noticeable exception was the fumed silica samples, which showed enrichment of ^{226}Ra and ^{210}Pb compared to ^{238}U, as well as higher ^{228}Th compared to ^{232}Th. Since zirconia is manufactured from zircon by melting at a very high temperature, it is expected for most of the ^{210}Pb activity to end up in the silica fume during the manufacturing process (2.8.2). This also explains the very low ^{210}Pb concentration in zirconia, compared to that of the zircon mineral. The monazite, zircon and zirconium samples all seem to have higher concentrations of $^{228}Ra/^{228}Th$ compared to ^{232}Th.

Potential radiological risk

Since stockpiles are controlled and access to the public limited, the expected dose to members of the public is expected to be minimal. As discussed in 2.8.3 the potential risk to consider in the mineral sands industry is mostly that to the worker, more specifically external exposure to gamma radiation. The gamma dose coefficients in Table A-6 in Appendix A were used to calculate the incremental gamma dose rate associated with the handling, storage or upgrading of feedstock from the activity concentrations given in Table 5-33 using equation 2.8 (see 2.8.3). Since nuclide specific data was available the dose coefficient for the three individual chains were used in the calculations, and not the overall gamma dose coefficient, which is only applicable if the nuclide with the highest concentration is in fact the one as per the “indicative” radionuclide composition.

The results for the effective dose from gamma radiation are presented in Table 5-33. The dose was mostly less 3 $mSv.a^{-1}$, which is an acceptable dose for workers for which the dose limit is 20 $mSv.a^{-1}$ (2.2.2). The dose from ilmenite, gypsum and other by-products were less than 0.25 $mSv.a^{-1}$, whereas the high concentrations in the monazite may cause external gamma exposure of more than 20 $mSv.a^{-1}$. The effective dose was calculated assuming

conservatively that a worker spend 400 hours per year exposed to the specific source. Exposure to high sources of NORM in the workplace is usually limited by special measures such as shielding, restricted access and shorter occupancy time (2.8.3). The other possible sources of exposure, dose due to inhalation of dust, were not considered in this case study.

Conclusions

The presence of elevated levels of radioactivity in samples from the mineral sands industry, as shown here, is expected, therefore regulatory measures are in place to protect workers and the public. Suitably constriction and control by the NNR manage and mitigate potential risk to acceptable levels ALARA. To minimize external exposure, access to areas with accumulated radioactivity and potential high gamma dose rates is usually restricted.

5.4.5 Conclusions and recommendations

Natural radioactivity in soil and other solids, may present a radiological risk to humans via several pathways. In this section results were presented to quantify the distribution of natural radionuclides associated with solids from different NORM industries in SA. Solids with elevated radioactivity concentrations were identified.

It was shown that measurement of only gross alpha/beta activities will not be sufficient to evaluate radioactivity in solids and that nuclide specific determinations should be used to determine the overall impact. Average measured gross alpha/beta concentrations and the calculated total activities from gamma spectrometry compared reasonably well, although the observed extreme difference in calculated and measured activities observed for individual samples could not readily be explained.

In most ores, the relevant decay series can be assumed to be in equilibrium, as was shown for most of the samples of the mineral sands industry. In such cases, any radionuclide within the chain can be the target of the analysis. The analytical methods summarized in 4.12 were suitable for analysis of the solid samples of which the results were presented in this chapter.

Although an attempt was made to investigate the mobility of the radionuclides, the geochemical associations of the radionuclides were not determined. To assess the potential availability of particular radionuclides to plants, sequential extraction procedures as described in 2.7.3 should be applied. Understanding of radionuclide uptake and accumulation is

especially important when considering phyto-remediation since it may be less successful for nuclides with low mobility.

K_d values are important for modelling in risk assessment activities and site remediation, but show large variance. Similar to what is known from literature U isotopes were the most mobile, whereas isotopes of radium, lead and polonium were less mobile. Accurate radio analytical techniques are essential for these types of investigations. Due to the high costs of the analysis and the uncertainties involved, it is probably better to use default K_d values provided in models and literature databases, than attempting to determine site-specific K_d values.

5.5 Natural radioactivity in building materials in South Africa

5.5.1 Introduction

Natural radiation to which the public is exposed includes external exposure from building material, since all building material contains a certain amount of radioactivity. As established from the literature study, no data on levels of natural radioactivity of building material in South Africa are available in published literature. Standards and guidelines with regard to acceptable levels of natural radioactivity in BM are also not specifically defined by the regulatory authority in SA.

It is well-known that the natural radioactivity in cement is often enriched during manufacturing due to addition of raw material such as slag and fly-ash (Baranyai, 1986; Xinwei, 2005). It is one of the most important and expensive materials used by the building industry; most buildings in SA are constructed from cement blocks and cement concrete. A selection of samples from the cement industry in South Africa were analysed for natural radioactivity. The results were evaluated against the SA legislative exemption level of 500 $Bq.kg^{-1}$ for natural radioactive materials, as well as the European activity concentration index. The radon exhalation rate and emanation fraction was not determined, since dose due to inhalation is not within the scope of this thesis.

Use of radiochemical methods create the opportunity to analyse for and evaluate the exposure due to high radiotoxic nuclides like ^{210}Po, otherwise overlooked by the instrumental techniques (2.1.7). To confirm the effectiveness of the sample preparation procedure

described in 4.8.4 results obtained with closed vessel microwave dissolution and subsequent radiochemical analyses were compared with results from instrumental techniques (NAA and gamma-spectrometry). Samples from the cement manufacturing process were digested using microwave dissolution and analysed for ^{210}Po, ^{232}Th, and ^{228}Th using suitable radiochemical methods.

The study did not aim to give a representative picture of radioactivity in building material in South Africa. Since the building industry is not specifically regulated in South Africa, building material *per se* are not routinely analysed. The data used in the case study were of various samples of material often used in the building industry, analysed over a period of a few years. The activity concentrations of ^{40}K, ^{232}Th and ^{226}Ra for cement, concrete, gypsum and phosphogypsum are presented. Results for fly-ash and slag, which are also utilized in the building industry, are presented in 5.6.

5.5.2 Experimental

Sampling and sample preparation

Various building material samples were received for analysis of their radioactivity content. Included were several samples from the cement manufacturing industry such as cement, gypsum, fly-ash, silica fume and slag. Gypsum and phosphogypsum samples were mostly received from the fertilizer and phosphate industry.

Samples were dried overnight at 105 ^{0}C and then milled and homogenised. The drying temperature was kept relatively low in order to prevent losses of volatile elements such as polonium and lead. Samples were sealed in radon-tight containers for four weeks before being measured. Fractions of approximately 0.3 grams of sample material were brought into solution by microwave digestion after addition of a suitable tracer using a two-step program, as discussed in 4.8.4. After digestion, the samples were evaporated on a hot plate and dissolved in the suitable acid medium for radiochemical analysis.

Radioactivity Analysis

The various radio-analytical techniques as discussed in Chapter 4 were used for analysis of the cement samples. Nuclide specific radioactivity analysis of the solid samples was done as described in 4.12.1 using NAA (U and Th), high energy gamma analysis (^{226}Ra, ^{228}Ra, ^{228}Th)

and ^{40}K) and low energy gamma analysis (^{210}Pb). ^{210}Po and the isotopes of Th were determined using the described radiochemical procedures in 4.12.2 and alpha spectrometry.

5.5.3 Results and discussion

Radiochemical versus instrumental techniques

Twenty six samples from the cement manufacturing industry were analysed with both instrumental techniques, as well as radiochemically after dissolution of the samples. As can be seen from Table 5-32 there was good comparison between radiochemical and instrumental results for ^{232}Th and ^{228}Th for individual samples. The results for ^{210}Pb could not be compared with the radiochemical results for ^{210}Po, since the reported activity concentrations for ^{210}Pb (analysed with low energy gamma) for the majority of the samples were less than the MDA value. Where ^{210}Pb was measureable, *e.g.* fly-ash the results showed fairly good comparison. The results clearly illustrated that where the activity concentration of ^{210}Pb (= ^{210}Po) is required, measurement by LE gamma will not be sensitive enough, and radiochemical determination will be necessary.

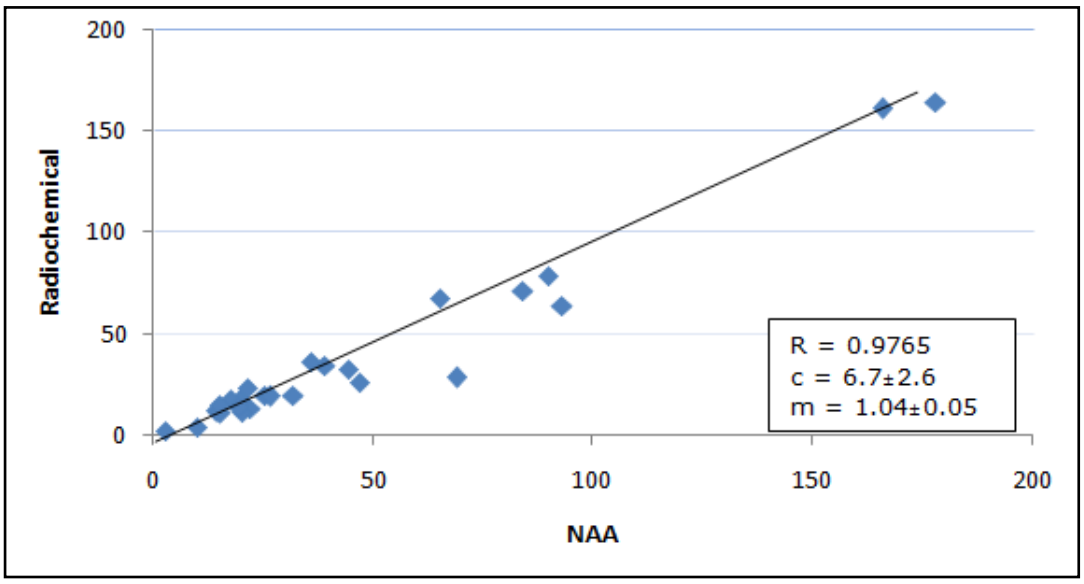


Figure 5-41: Correlation plot for ^{232}Th in cement samples (Activity concentration in Bq.kg^{-1})

Regression lines are useful to compare two methods over a range of concentrations (Miller & Miller, 1984). Correlation plots for the results obtained by instrumental techniques and radiochemical methods for ^{232}Th and ^{228}Th are shown in Figures 5-41 and 5-42. The

correlation coefficient of the two regression lines were 0.976 and 0.960 for ^{232}Th and ^{228}Th respectively, indicating good correlation between sets of results obtained by the two techniques. The deviation from unity was due to the relatively high uncertainty in the analyses by both methods. The slope in both cases did not differ significantly from 1, but there was a non-zero intercept. This combination indicates that the intrinsic accuracy of both methods is good, but the radiochemical method has a positive bias in both cases. The higher radiochemical results confirmed that total dissolution has been achieved. If not, it would have manifested in an observed systematic negative bias.

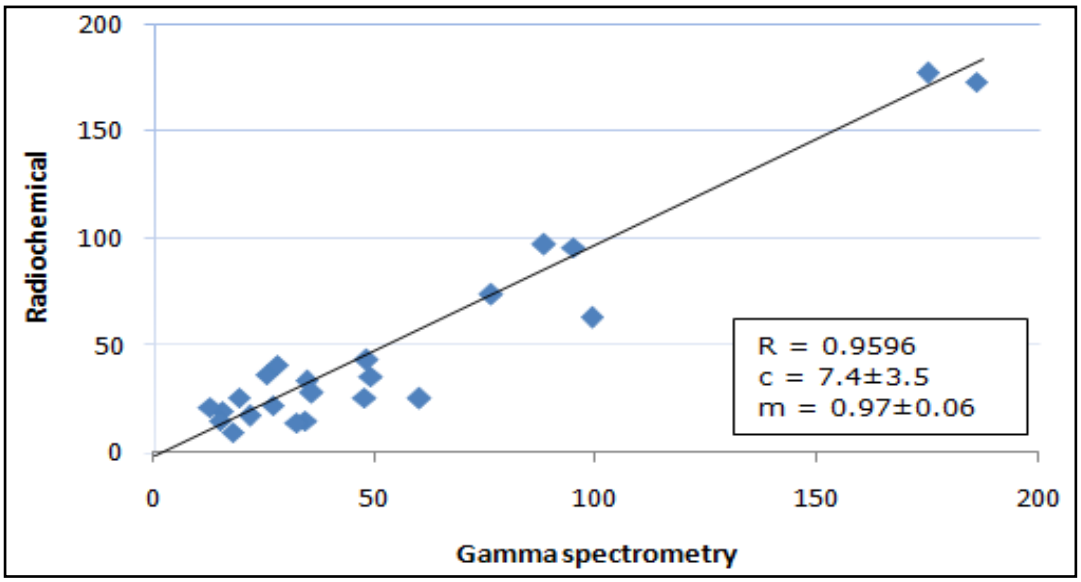


Figure 5-42: Correlation plot for ^{228}Th in cement samples (Activity concentration in Bq.kg^{-1})

Activity concentrations

Activity concentrations for the radionuclides of interest for samples of the building industry are presented in Table C-2 (Appendix C). Radiochemical results are also included for some of the samples. The reported ^{210}Po activity includes supported and unsupported ^{210}Po. For the cement industry analysis of ^{210}Po is important, since equilibrium with ^{210}Pb cannot be assumed under the manufacturing conditions. The combustion process may cause evaporation of ^{210}Pb and ^{210}Po, causing an enhancement of these nuclides in the fumes of the stack. Contact with the feed material will cause most of the condensed ^{210}Pb and ^{210}Po to be transferred and recycled at some disequilibrium concentration. Results for ^{210}Pb were not reliable because of the poor sensitivity of the low-energy gamma spectrometry technique. To

determine ^{210}Pb with more accuracy, it is recommended to repeat the ^{210}Po analysis after an in-growth period of at least three months (4.8.1). ^{234}U has not been analysed for, but since its chemical behaviour would be similar to that of ^{238}U, it was assumed that ^{238}U and ^{234}U was in equilibrium under the specific manufacturing conditions.

For evaluation of building materials usually only the activity concentrations of ^{40}K, ^{226}Ra, and ^{232}Th are required (2.10.3). In this case study full nuclide results were reported for most of the samples. The ratio of ^{238}U/^{226}Ra was close to unity for most of the samples, confirming that it is sufficient to measure only ^{226}Ra and assume equilibrium between ^{238}U and ^{226}Ra. The unity ratio also confirmed the accuracy of the two independent techniques used to measured ^{238}U (INAA) and ^{226}Ra (HE gamma). The ratio was >> 1 for the sand, silica fume, and gypsum and phosphogypsum samples, indicating enrichment of ^{226}Ra in these samples, in which case analysis of both ^{238}U and ^{226}Ra will be required.

Table 5-32 shows the average concentrations of ^{40}K, ^{232}Th and ^{226}Ra of the different materials. The highest concentrations of 710, 200 and 599 Bq.kg^{-1} for ^{226}Ra, ^{232}Th and ^{40}K respectively were measured in the ceramic sample. This can be expected because zircon sand, commonly used in the ceramic industry usually contains fairly high radioactivity levels (2.8.2). The slag and fly ash samples generally had higher activity content than the rest of the samples. Fly ash samples had nuclide specific activities varying just above and below 200 Bq.kg^{-1}.

Gypsum, phosphogypsum and the silica fume sample was enriched in radium (both ^{226}Ra and ^{228}Ra); the silica fume sample was also enriched in ^{210}Po. The gypsum samples had higher nuclide activities than the respective cement samples. Natural gypsum is sedimentary rock extracted from underground quarries and is generally expected to have lower radionuclide content than phosphogypsum that originates from fertilizer production and is expected to be enriched in radium (2.9.1). In this study the concentrations for both were very similar; the explanation probably being that samples submitted as “gypsum” was not of natural origin but also produced synthetically.

Evaluation against South African National regulations

At the time of this study there was no specific South African standard or guidelines for radioactivity in building material. However, in terms of regulation 388 of the South African

National Nuclear Regulator Act (SA government, 2006a) any material with a radioactivity content of less than 500 $Bq.kg^{-1}$ per individual nuclide (for naturally occurring radioactive nuclides of U and Th and their progeny) are exempted from legislation (2.2.4). For ^{40}K the level is 10000 $Bq.kg^{-1}$. When the level of 500 $Bq.kg^{-1}$ is exceeded for any of the nuclides, a more detailed analysis is required to determine dose. In the presented data (Table 5-32) the measured nuclide-specific activity levels of all the samples, except ceramic, were all well below the level of 500 $Bq.kg^{-1}$. Based on these results it seems as if the cement manufacturing industry in SA can probably be excluded from regulatory control. Analysis of more samples may be required.

The radioactivity in each final cement product can be calculated using the known mixing ratios of CEM 1 with associated additives (Concrete institute, 2013): $A = \sum F_i C_i$, with F_i the fraction of constituent *i* in the cement mixture and C_i the nuclide concentration of constituent *i*, with summation of all the constituents of the cement mixture. Using this equation, each product can be compared with the exclusion criteria. However since the majority of the results in Table C-2 (Appendix C) was well below the 500 $Bq.kg^{-1}$ limit, a more conservative process was followed. CEM 1 Portland cement usually contains only 5% of minor additional constituents, but even a cement mixture containing a high percentage of constituents (*e.g.* fly-ash 35%), was unlikely to have a radionuclide concentration exceeding 500 $Bq.kg^{-1}$.

The higher activity levels found in individual materials such as fly ash or gypsum should not have a significant effect on the final radioactivity in the cement since only small amounts are used for cement production (Figure 2-14).

Evaluation against European Radioactivity Index

A number of indexes are used for assessing the radiation risks of radioactivity in building materials, of which the .radium equivalent activity (Ra_{eq}), (also known as the Leningrad formula, is the most widely used. It is convenient for comparing radioactivity of materials (2.3.7). The radium equivalent for individual samples of this study, as well as the means for the different materials, is given in Table C-2 (Appendix C) and Table 5-32. The Ra_{eq} values for cement, concrete, gypsum, phosphogypsum and slag samples were all below the maximum limit of 370 $Bq.kg^{-1}$, and should therefore not present a radiological risk when used as building material. The only materials that might be of concern according to this index were

ceramic and fly ash, which both have restricted use in the building industry (Table 2-9). It should be clear that even though a material (*e.g*. fly ash) may be exempted from control based on South African legislation it could exceed the maximum radium equivalent. A process of negotiating with the NNR may be necessary, on the need to participate in the international process to harmonise exemption levels for BM to accommodate international trade.

Ra_{eq} is routinely calculated from the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th (equation 2.10). Our laboratory reports ^{232}Th measured by NAA and ^{228}Ra measured by HE gamma, whereas in most of the published studies ^{232}Th was determined by measuring ^{228}Ac (911 keV) by gamma spectrometry and assuming equilibrium of all nuclides in the Th series. ^{228}Ra is often enriched in South African gypsum (see Table 5-32). To prevent underestimation of the index one should therefore replace the ^{232}Th value in equation 2.10 with that of ^{228}Ra. In the EU-BBS directive (EU, 2013b) it is explicitly stated that ^{232}Th should be replaced by ^{228}Ra for samples where $^{228}Ra > {}^{232}Th$. Doing this, the resulting average Ra_{eq} increased from 214 ± 123 to 347 ± 210 for gypsum, and from 151 ± 39 to 383 ± 164 for phosphogypsum.

If cement or other building material is to be exported to countries of the European Community the activity concentration index or gamma index (I_γ) should be used as criterion to decide if regulatory control should be considered (2.2.8). The index is used as screening tool to identify material of concern, for which a dose assessment is performed to decide whether use of the material should be restricted. The index is applied to the final building material product; therefore combining of a material with high radioactivity (*e.g.* fly ash) with other raw material might result in a final product which meets the recommended condition.

The calculated gamma index, $I_{\gamma,}$ of the analysed samples, as well as the mean of all samples, is shown in Table C-2 (Appendix C) and Table 5-32. The gamma index for brick, cement, concrete, sand and silica fume were less than 0.5, which implies exposure of less than 0.3 $mSv.a^{-1}$ (Table 2-8). For gypsum, phosphogypsum and plasterboard $0.5 < I_\gamma < 1$, which implies that the dose to occupiers of buildings where these materials were used in bulk, would most likely be less than 1 $mSv.a^{-1}$. Though slag and fly-ash materials exceeded the recommended exemption level ($I_\gamma > 1$), these raw materials are used in restricted amounts (< 30%) and the final cement product is therefore expected to be exempted. Use of ceramic tiles will probably also be exempted based on the dose criterion of $I_\gamma < 6$, which applies for

superficial materials with restricted use such as tiles (Table 2-8). Again it should be noted that materials acceptable according to South African legislation for NORM can exceed the maximum gamma-index and discussions may be required with the NNR to accommodate international trade.

Comparison to world averages

The measured activity concentrations in building material from South Africa were compared with those in other countries, which show large variation depending on the origin of the raw material (Table A-20, Appendix A). Concentrations in SA material showed good comparison with the average value indicated for BM. For fly ash the SA values were high and similar to Australian samples. Phosphogypsum values were lower and gypsum values much higher than in samples of other countries. The Ra_{eq} value obtained for cement, slag, bricks and concrete were comparable to those obtained in other countries, with some countries having higher and others lower values than South African samples.

The data from this study were also compared to the respective world averages of soil (Table A-19, Appendix A). The activity concentrations of the final cement product did not exceed the world wide average for soil, although individual material (fly ash and slag) had significantly higher activities. Gypsum and phosphogypsum also had significantly higher concentrations than those of soil.

5.5.4 Conclusions

Based on the results for selected samples of building materials and constituents used in the manufacture of cement, it was concluded that the industry can probably be exempted from nuclear regulatory control in South Africa. In general, results obtained were comparable to similar studies in other countries. Even though some raw material (slag, fly ash) exceeded the recommended exemption levels for exposure, the final cement product is expected to be exempted, since only small amounts of these raw materials are used in the final product. However, exemption based on SA legislation for NORM does not automatically mean that the materials are acceptable according to international standards and accordingly could result in trade restrictions. Nevertheless, due to the financial implications to local manufacturers, the proposal at the SARPA conference (Pule, 2015) to recommend to government to regulate the building industry should be carefully considered before implementation.

Radiation indices were used to evaluate the radiation hazard of different BM in SA. The calculated radium equivalent concentration and gamma index for the majority of samples were within recommended limits, indicating that the materials are safe for use in construction. It should be mentioned that these results are not representative for all cement manufacturing industries in South Africa but only for the localities from where the samples have been collected. Since the radioactivity of different material and also in the same material from different origin can vary it is recommended that the radioactivity in material from any new source is monitored before being used as building material.

Suitability of use of different BMs was evaluated based on the regulations as discussed. Exact calculations of the external dose caused by BM were not done. To do this different scenarios have to considered *e.g.* the dimensions of the room and the structures in a building causing the irradiation *e.g*. floor, ceiling, walls; as well as the exposure time. Other limits to the study included the following: (1) Exposure to workers was not considered, (2) Measurement of indoor radon concentrations and radon exposure in dwellings were not considered.

The results obtained for samples prepared by using microwave digestion and radiochemical analysis showed close agreement with the values obtained using instrumental nuclear techniques. This creates the possibility to analyse for and evaluate the exposure due to high radiotoxic nuclides like ^{210}Po, ^{231}Pa and ^{227}Ac otherwise overlooked by the instrumental techniques. Dissolution and nuclide specific analysis are specifically of interest during manufacturing to determine the radiological impact due to inhalation of respirable dust on people working with the raw materials. When used in buildings, the high energy gamma radiation of ^{40}K and other gamma emitters such as ^{208}Tl and ^{228}Ac as well as radon, are of more interest.

5.6 Natural radioactivity in coal and coal fly ash

5.6.1 Introduction

As in many countries worldwide, electric power generation in South Africa households depends on coal. Coal is of radiological concern due to the presence of naturally occurring radionuclides that may be released to the environment through atmospheric discharge from coal-fired power plants. The quantity released depends on the radioactivity of the coal, the ash content and the efficiency of the electrostatic precipitators in removing fly ash from the

flue gas stream. Several studies have been published reporting on release and behaviour of radionuclides in CPPs (2.11). However, limited data for natural radioactivity of samples from the coal industry in South Africa were found in the literature survey.

In this study, the results of the radioactivity of coal, slag and ash samples are presented. The objective of the study was to give some indication of the situation in SA regarding possible radioactive pollution from CPPs. The study did not attempt to assess the radiological impact of CPP discharges, and did not evaluate releases from any specific CPP in any specific area in South Africa. The following was therefore not addressed: (1) Dose calculations for atmospheric releases of natural radionuclides from CPPs and (2) Environmental contamination in the area around the CPP (soil, vegetation and biota).

To investigate the possibility of the use of radiochemical methods for analysis of high radiotoxic nuclides like ^{210}Po in these types of samples, some samples were digested. The results obtained with closed vessel microwave dissolution and subsequent radiochemical analyses were compared with the results obtained by non-destructive instrumental techniques (NAA and gamma-spectrometry).

5.6.2 Experimental

Sampling and sample preparation

Samples were received from various role players including coal mines, power plants and fly ash suppliers and are not representative of the annual consumption of coal and annual production of ashes. Samples included coal, fly ash and bottom ash (slag).

Since the samples were not analysed for a specific research study no sampling program representative of all points in the power plant was followed. No conclusion can therefore be made with regard to enhancement of the radioactivity in various parts of the emission control system of the power station. Coal sampling was performed at feeders; slag was sampled during transportation below the boiler; whereas fly ash samples were obtained from the electrostatic precipitators of boilers of coal stations and from ash dumps and not from the filters from release stacks (Figure 2-16). It was assumed that the fly-ash collected is representative of the chemical composition of the dust that passes into the atmosphere.

Samples were dried overnight at 105 ^{0}C and then milled and homogenised. Samples were

sealed in radon-tight containers for four weeks before being measured by gamma spectrometry. Fractions of approximately 0.25 grams of sample material were brought into solution by microwave digestion after addition of a suitable tracer using the program indicated in Table 4-8.

Radiochemical versus instrumental techniques

Since equilibrium of all nuclides in the U and Th series can not necessarily be assumed, it may be necessary to determine the individual nuclides radiochemically for some samples. Total dissolution is essential because elements can form associations with both organic and inorganic matter in the coal.

One sample each of slag and fly ash was analysed radiochemically after microwave digestion. For samples with activity concentration of ~ 40 $Bq.kg^{-1}$ (*e.g.* coal) at least one gram of sample has to be dissolved, which can present a problem with microwave digestion where sample size is limited to ~0.25 g. The results shown in Table 5-22 were promising with some correlation between the non-destructive (NAA) and radiochemical results for ^{238}U and ^{232}Th. The lower results obtained with the radiochemical procedure suggest that the samples were not quantitatively digested, and that the undissolved fraction still contain considerable amounts of natural radionuclides.

Table 5-22: Comparison of results obtained for analysis of samples from the coal industry with NAA and radiochemical methods ($Bq.kg^{-1}$)

Sample	NAA		Radiochemical				
	^{238}U	^{232}Th	^{238}U	^{234}U	^{210}Po	^{232}Th	^{228}Th
Fly ash	170±6	160±3	126±9	134±8	124±10	130±5	161±4
Slag	2270±20	80±5	1870±20	2000±20	2230±20	100±6	93±5

Radioactivity Analysis

The radio-analytical techniques as discussed in Chapter 4 were used for analysis of the coal samples. Nuclide specific radioactivity analysis of the solid samples was done as described in 4.12.1 using NAA (U and Th), high energy gamma analysis (^{226}Ra, ^{228}Ra, ^{228Th}) and ^{40}K) and low energy gamma analysis (^{210}Pb). The digested samples were filtered through as 0.45 µm filter after which ^{210}Po and the isotopes of Th were determined in the solution using the described radiochemical methods in 4.12.2 and alpha spectrometry.

5.6.3 Results and discussion

Radioactivity results

The mean activity concentrations for coal, slag and fly ash samples are graphically presented in Figure 5-43 (raw data in Table C-6 in Appendix C). The activity concentrations varied from 35 to 246 Bq.kg^{-1} for ^{238}U, 35 to 237 Bq.kg^{-1} for ^{226}Ra, 63 to 320 Bq.kg^{-1} for ^{210}Pb, 11 to 212 Bq.kg^{-1} for ^{232}Th and 50 to 499 Bq.kg^{-1} for ^{40}K.

As expected activity concentrations were the lowest in the coal samples, and the highest in ash samples. Radionuclides accumulated in the ashes after combustion, with fly ash having higher enrichment than slag, especially for Th-series nuclides. Most of the carbonaceous matter in coal oxidises out during combustion and the radionuclides are concentrated in the remaining mass (2.11.2).

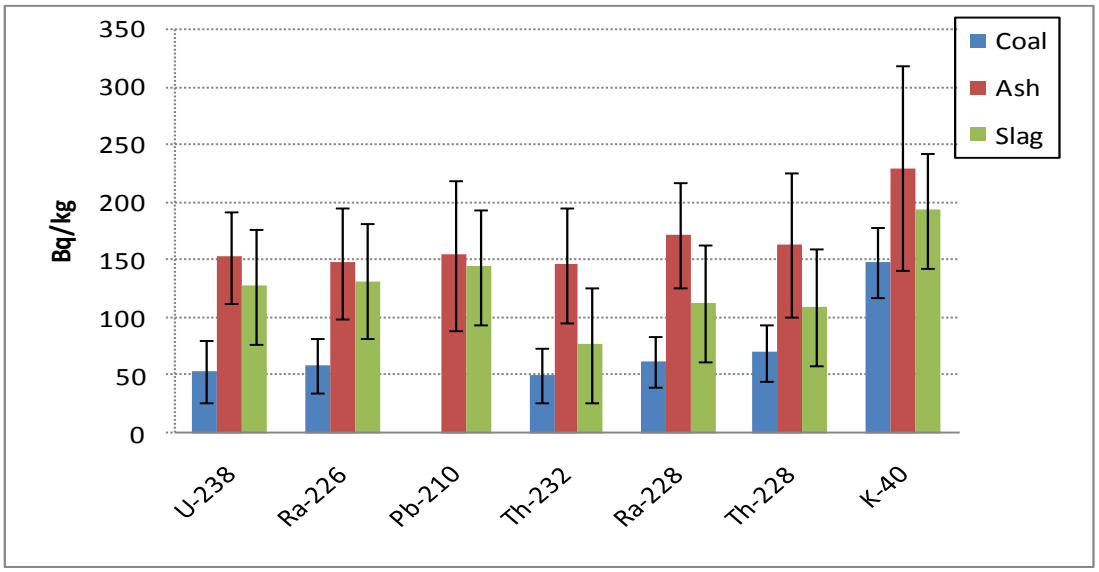


Figure 5-43: Activity concentrations in coal, ash and slag

There appears to be secular equilibrium between the radionuclides of the ^{238}U series in most of the coal, slag and fly ash samples (Table 5-23), which is as expected for coal (Table A-21, Appendix A). However, one will expect some disequilibrium in slag and fly-ash as many of the daughter radionuclides have different chemical and physical characteristics and the more volatile elements will follow the air stream and eventually re-condense on the fly-ash particles (2.11.2). This disequilibrium is dependent on the conditions in the plant (Corbett, 1983). Karangelos *et al.* (2004) reported large variations of radionuclide enrichment in

different fractions of ash whereas, similar to our findings, Tso & Leung (1996) found no significant disequilibria in the coal, slag or fly-ash.

According to Coles, Regani & Ondov (1978) there is some evidence that lead and polonium isotopes may be concentrated more than uranium, thorium and radium isotopes in the fly ash. Enrichment was not observed in this study - for most of the samples the ^{210}Pb concentration was of the same order as the other nuclides. Any loss of the volatile nuclides ^{210}Pb and ^{210}Po in the production of slag, which involves temperatures of up to 1700 ^{o}C, was difficult to evaluate due to lack of results for ^{210}Po. Any specific conclusions about ^{210}Pb were complicated by the fact that the reported values were mostly at or less than the MDA value. A more sensitive technique (radiochemical analysis) of all samples is required for any definite conclusions to be made.

Table 5-23: Radioactivity in samples from the coal industry

Parameter	Coal	Fly-ash	Slag
Ra_{eq}	142±60	370±114	256±34
I_γ	0.5±0.2	1.3 ±0.4	0.9±0.1
D	64±25	164±51	115±16
AED	0.08±0.03	0.20±0.06	0.10±0.02
$^{238}U/^{226}Ra$	0.90±0.20	1.01±0.19	0.94±0.23
$^{238}U/^{210}Pb$	-	1.01±0.24	-
$^{232}Th/^{228}Ra$	0.80±0.13	0.92±0.18	0.78±0.33
$^{228}Ra/^{228}Th$	0.89±0.16	0.97±0.14	1.03±0.12

The laboratory routinely reports results for ^{210}Pb, ^{226}Ra and ^{238}U for all solid samples. The results indicate that for most samples it will be sufficient to determine only ^{226}Ra in the U-series and assume radioactive equilibrium. The ratio of ^{238}U/^{226}Ra, which was close to one for most samples (Table 5-23), indicated good accuracy of the two techniques used for analysis of ^{226}Ra (gamma spectrometry) and ^{238}U (NAA).

For the ^{232}Th series the results indicated secular equilibrium between the radionuclides in most of the coal, slag and fly ash samples. Secular equilibrium between ^{228}Ra and ^{228}Th implies that the activity of both nuclides is supported by an equivalent amount of ^{232}Th activity and that the full thorium series is contained in the matrix. For some of the samples, especially for fly ash, ^{228}Ra and ^{228}Th seemed to be slightly enriched with regard to ^{232}Th.

This slight difference may however also be due to variances in results obtained by different analytical techniques: both ^{228}Ra and ^{228}Th were measured with gamma spectrometry, whereas ^{232}Th was measured by NAA. Discrepancies may be due to sample in-homogeneities incurred by the use of small aliquots (0.2 g) for NAA.

The measured activity concentrations for coal were comparable to the typical worldwide averages given in UNSCEAR (2008) *i.e.* ^{40}K: 50 Bq.kg^{-1}, ^{232}Th: 20 Bq.kg^{-1} and ^{226}Ra: 20 Bq.kg^{-1}; and were of the same order as in soils (Table A-21, Appendix A). For fly ash a world average of 265, 70, 240 and 200 Bq.kg^{-1} is reported for ^{40}K, ^{232}Th, ^{226}Ra and ^{238}U respectively (UNSCEAR, 2008), since on combustion, some of the radionuclides are enriched in fly ash. The ^{40}K (229$\pm$88 Bq.kg^{-1}), ^{226}Ra (147$\pm$48 Bq.kg^{-1}) and ^{238}U (152$\pm$40 Bq.kg^{-1}) activity concentrations of the fly ash samples analysed were lower than this world average, but the ^{232}Th concentration (146$\pm$49 Bq.kg^{-1} was higher. Several other countries reported similar high concentrations of ^{232}Th in fly ash (Table A-21, Appendix A). The measured concentrations showed good comparison with values reported for ash from South African coal used as fuel in a thermal power plant in Spain (Font *et al.*,(1993) and those reported by Madzivire *et al.* (2014).

Radiological Evaluation

The activity concentrations of all nuclides in all samples were less than the 500 Bq.kg^{-1} exemption level set by the NNR (SA government, 2006a). As done for solids (5.4.2) and building material (5.5.3), the radium equivalent (Ra_{eq}), gamma index (I_γ), external gamma absorbed dose rate (D) and annual effective dose (AED) were used to estimate the radiological impact of the radionuclides present in the coal products. The results are shown in Table 5-23.

All the parameters for prediction of dose indicated that the analysed samples from the coal industry do not have any potential risk for external exposure. None of the coal or slag samples exceeded the maximum admissible value of 370 Bq.kg^{-1} for Ra_{eq} and $I_\gamma < 1$. The AED was less than 0.25 mSv.a^{-1}. It can therefore be safe to assume that coal and slag can be exempted from all restrictions concerning their radioactivity and that people using these coals do not have a high risk of being exposed to radioactivity.

Some of the fly ash samples exceeded the limits of the radiological hazard indices and may

pose some risk, especially when accumulated in ash heaps. The predicted AED for all samples was less than the internationally accepted limit of 1 $mSv.a^{-1}$, but the NNR dose constraint of 0.25 $mSv.a^{-1}$ was exceeded for some samples. For fly ash the $I_\gamma > 1$, which means that the use of fly ash in building material may result in a dose of more than 1 $mSv.a^{-1}$ if used in bulk amounts (see Table 2-8). However, since blended cement in SA usually contains only 15-35% of fly ash (2.10.2), the use of fly ash as additive in cement should not be of radiological concern and the final cement product is expected to be exempted from regulation.

5.6.4 Conclusions and Recommendations

Internationally there has been increased concern with regard to the increase in natural radiation background originated by coal-fired power plants (UNSCEAR, 2016). Since the measurement of the radioactive elements released by the gaseous emission of CPPs is not compulsory in South Africa, there is limited information and the radiological impact from exposure to these elements is difficult to determine. The results obtained in this study provided essential basic data for environmental radiological risk analysis for CPPs. Based on the results presented the radioactivity in coal and fly ash samples should not be a source of alarm, since the activity concentrations of all samples were lower than the 500 $Bq.kg^{-1}$ exemption limit set by the NNR. Natural radioactivity in coal samples were found not to be significantly enriched in radioactive elements compared to common soils and rocks and of the same order of magnitude compared to other parts of the world.

A coal fired power plant produces large amounts of radioactive waste in the form of flue gasses and ash. In South Africa the fly ash generation has become a major concern for the government, with more than 25 million tons of ash produced annually (2.11.5). All the fly ash samples analysed in this study were found enriched with natural radionuclides, which was similar to the trend observed in worldwide studies on coal and ashes. However, based on the results, the by-products of coal-fired power plants in South Africa can be utilized as an additive in the cement industry, without any special restrictions according to the regulations dealing with BM and available European directives, as discussed in 2.2.8.

It is recommended that, if not already done, a radiological assessment of a coal-fired power plant in South Africa should be performed. It is impractical to carry out a full site-specific assessment for each site of electricity generation in the country that discharges radionuclides

to the environment. Similar to worldwide strategy, information on the discharges from one facility can be used to estimate the dose per unit electrical energy produced. In the case of relatively modern plants, such as Medupi, with fly ash removal > 99.5 %, the impact is probably negligible. As a starting point information has to be obtained on the radionuclide content of the various sources of coal and ash related products from the plant, as has been done in this study. If radiochemical analysis is required for nuclide specific analysis of any of the solid samples, the digestion method has to be refined in order to obtain quantitative digestion of the sample.

For a radiological assessment of the coal industry all sources and exposure pathways as in 2.3.4 have to be considered *i.e.* releases to atmosphere from the stack, disposal of ash in landfills and releases to atmosphere from ash piles, *etc.* Leaching of radioactive elements during ash utilization and disposal may also be of concern, although studies indicated that concentrations of radioactive elements leached from fly ash and ash disposal sites are below levels of human health concern (Madzivire *et al.*, 2014). The scope of this study was limited: the gamma dose emitted from ash piles was not measured and the dose due to inhalation of respirable airborne dust was also not calculated. To conduct an assessment of the atmospheric pathways, information on stack release parameters is required to model atmospheric transport and resulting wet and dry deposition. It is also necessary to measure radionuclide concentrations of the ash released through the chimney. To evaluate the environmental impact of the CPP in the area, concentrations of natural radionuclides in environmental media should be determined.

5.7 Phosphate Industry

5.7.1 Introduction

Phosphate rock is mined on a large scale as a source material for fertilizers and other phosphorous containing products, such as phosphoric acid and gypsum. The potential problem of high concentrations of NORM in the phosphate industry has been recognized for many years. The industry is responsible for the production of millions of tons of phosphogypsum waste, which is usually stockpiled and might impact the surrounding environment. Although there are many studies on phosphogypsum and the phosphate industry worldwide, limited information is available for SA products.

To comply with regulatory requirements, samples from the fertilizer industry are sent to the radio analytical laboratory for radioactivity analysis on a regular basis. The presented case study aims to use available data to assess the natural radioactivity concentrations and the radioactive equilibria in raw and waste sub-products from phosphate mining and fertilizer production in South Africa.

5.7.2 Experimental

Samples

Samples were collected as prescribed by the sampling plan of the CoR held by the specific industry. Analysis was performed on samples of phosphate rock (4), phosphogypsum (55), phosphate tailings (7), fertilizer (6) and scale from the fertilizer plant (3). As part of the environmental monitoring programme water, soil, sediment, fish and food samples were also submitted for radioactivity analysis – the results for environmental media were presented in other relevant sections (5.1 to 5.4).

Radioactivity Analysis

Samples were prepared as described for solid samples in 4.3.3. Nuclide specific analysis was performed using NAA and gamma spectrometry as per the prescribed procedure for solid samples (4.12.1). Gross alpha/beta screening is routinely performed on all solid samples. If both the gross alpha and beta activities are less than 500 $Bq.kg^{-1}$ no potential risk is expected since this is below the exemption level in SA.

5.7.3 Results

Activity concentrations in solids

The measured activity concentration results are shown in Table C-7 (Appendix C) and summarized in Table 5-34. Figure 5-44 shows the distribution of the activity concentrations of ^{238}U, ^{226}Ra and ^{232}Th in phosphate rock, fertilizer, phosphogypsum, tailings and sediment in the industry. The concentrations were similar to values reported in other studies in SA (see Table A-22 in Appendix A).

In *phosphate rock* the concentration of ^{238}U ranged from 122 to 137 with an average of 130±7 $Bq.kg^{-1}$. This concentration was at the lower limit of the worldwide reported range of 50-

2004 Bq.kg^{-1} (UNSCEAR, 2016). The concentration of ^{226}Ra ranged from 97 to 131 with an average of 119±157 Bq.kg^{-1}, which was high compared to much lower concentrations in background soil from the area, but related well to studies conducted by other authors (Table A-22, Appendix A). The activity of the ^{210}Pb in the phosphate rock was in the same range as that of ^{238}U and ^{226}Ra confirming equilibrium of the series. Concentrations of the Th series nuclides (^{232}Th, ^{228}Ra) were similar to what has been reported by other authors for phosphate rock from South Africa (Masok *et al*., 2016; Van der Westhuizen, 2007). ^{232}Th concentrations ranged from 483 to 527 Bq.kg^{-1}, which were higher than U, as expected for igneous rocks (2.9.1).

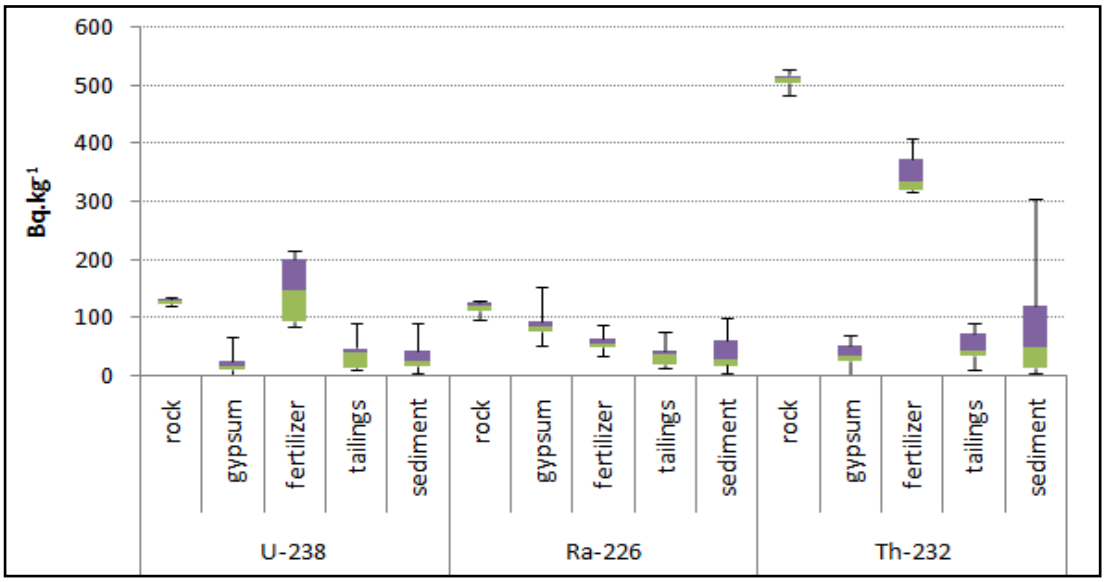


Figure 5-44: Minimum, median, 75% percentile and maximum concentrations for solids from the phosphate industry (Bq.kg^{-1})

In *phosphogypsum* the activity concentrations of ^{238}U were less than 100 Bq.kg^{-1} as reported worldwide (IAEA, 2013). The ^{226}Ra concentration compared to the range of 100-700 Bq.kg^{-1} expected for phosphogypsum from igneous origin, which is lower than values found in sedimentary ores (IAEA, 2013). As reported by Msila *et al.* (2016) Ra and Pb were enriched with respect to U, which is expected due to similar chemistry to Ca (2.9.1). The ^{226}Ra/^{238}U ratio varied from 1.18 to 24.7. ^{210}Po was not specifically analysed for, but according to literature ^{210}Po may be enhanced in phosphogypsum (Al-Masri & Al-Bich, 2002). The results for ^{210}Pb, however, seemed to indicate equilibrium of the ^{226}Ra-^{210}Pb chain. ^{232}Th concentrations were lower than reported values by Van der Westhuizen (2007). ^{228}Ra concentrations in phosphogypsum were higher than ^{226}Ra, due to high ^{232}Th concentrations

found in the igneous ore found in South Africa. The activity of ^{228}Ra was enriched compared to ^{232}Th, due to similar chemistry of Ra and Ca. The ^{228}Ra/^{232}Th varied from 0.45 to 19.8. Therefore, as discussed in 5.5.3 the concentration of ^{228}Ra, and not ^{232}Th, should be used in the building activity index to estimate the suitability of use of phosphogypsum as building material. The dose will be underestimated when the ^{232}Th activity concentration is used. ^{228}Th as decay product of ^{228}Ra, was in equilibrium.

South African *phosphate fertilizer* had low concentrations of the nuclides ^{226}Ra, ^{228}Ra and ^{210}Pb with slightly higher concentrations up to 202 Bq.kg^{-1} for ^{238}U in MAP fertilizer. The MAP fertilizer showed enrichment of ^{238}U compared to the original ore, which is as expected from literature, which mentions enrichment of 150% for U in fertilizer (2.9.1). The concentrations of the U-series nuclides were much lower than the worldwide range of 300-3000 Bq.kg^{-1} (IAEA, 2013). Concentration of the Th-series nuclides were similar to reported values from Brazil (Saueia & Mazzilli, 2006) and Serbia (Todorovic *et al*., 2015). The relatively low concentrations of ^{238}U and ^{226}Ra compared to other countries, makes it more suitable to be used for fertilizer production, and therefore increases the demand for export of rock phosphate and fertilizer from SA.

The nuclides of the U-series and of the Th-series were clearly in equilibrium in the rock samples as is expected from literature (29.1). The activity of the mineral can therefore be assessed by measuring the concentrations of the parent nuclides only. After the chemical process this equilibrium is disturbed and the radionuclides migrate according to their chemical properties. Measurement of only the parent nuclides will then no longer be adequate to provide information about all nuclides. As known from literature natural nuclides from apatite ore are partitioned during processing in such a way that ^{238}U accumulate in the phosphate fertilizer, while ^{228}Ra, ^{226}Ra and ^{210}Pb accumulate in the phosphogypsum. Similar equilibria as described in literature were observed in the analysed samples and almost all the ^{228}Ra and ^{226}Ra present in the phosphate rock was observed in the phosphogypsum (2.9.1). The results indicated that more than 60% of the ^{232}Th present in the original rock were present in the fertilizer, whereas a lower percentage remained in the phosphogypsum.

Concentrations of all nuclides in the *tailings* were relatively low and lower than what were reported by Van der Westhuizen (2007). Nuclides from both chains seemed to be in equilibrium. Scales from process equipment in the plant had very high concentrations of

^{210}Pb, which might be of concern when evaluating occupational exposure (2.9.3). Higher concentrations of ^{232}Th compared to the original ore were also observed in the scales.

Only the activity concentration of ^{232}Th in some of the phosphate rock samples were slightly higher than the 500 Bq.kg^{-1} limit proposed by the NNR, but was well below the average concentrations reported worldwide (Table A-22, Appendix A). Concentrations in all other solids were less than 500 Bq.kg^{-1}. Therefore, in terms of NNR regulations the industry needs to be considered for regulation as a practice. The concentrations in all solids from the phosphate industry were less than the 1000 Bq.kg^{-1} exclusion value proposed internationally for regulation of NORM (2.2.3). The lower limit imposed by the national regulator may restrict international trade and should be reconsidered in an attempt to harmonize with internationally accepted practices.

Potential radiological risk

The radiological risk was quantified in terms of the external radiation hazard index (H_{ex}), from which the gamma dose rate and annual effective dose (AED) were calculated using equations 2.8 and 2.9 in 2.3.6. The calculated hazard indices are plotted in Figure 5-45.

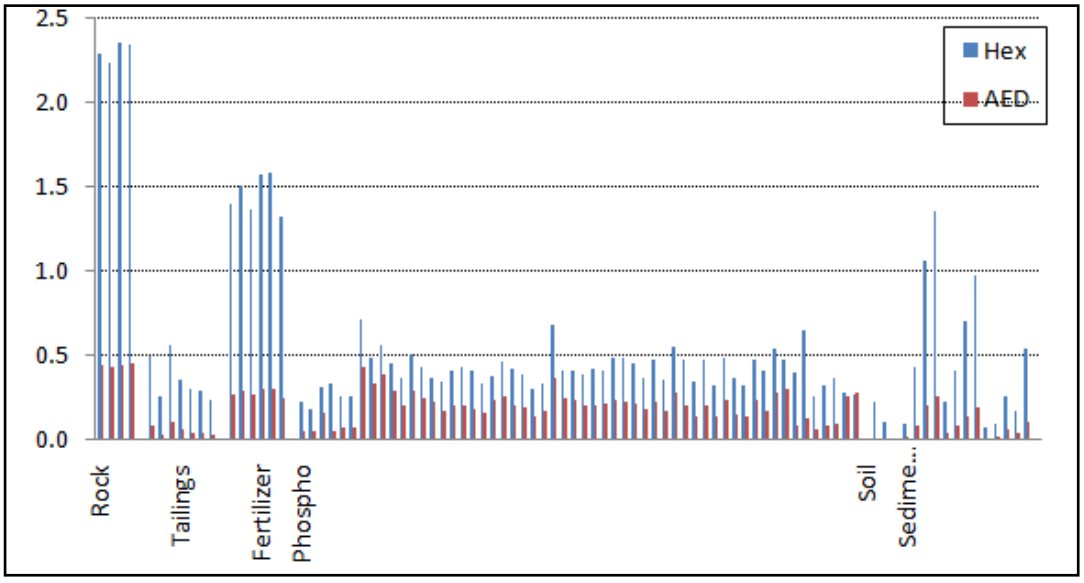


Figure 5-45: External radiation index and Annual Effective Dose (AED) of solids from the phosphate industry

From Figure 5-45 it is clear that only phosphate rock and fertilizer samples may have some radiological risk with an external hazard index greater than one. This was mainly due to the

high concentrations of ^{232}Th in these samples. The calculated AED of all samples was less than the globally prescribed dose limit of 1 mSv.a^{-1} with only a few samples exceeding the NNR dose constraint of 0.25 mSv.a^{-1}. The highest external dose of 0.45 mSv.a^{-1} is expected from phosphate rock. For fertilizer and phosphogypsum the average effective dose was 0.28 ± 0.02 and 0.20 ± 0.08 mSv.a^{-1} respectively. Some individual sediment samples also indicated some risk with H_{ex} >1 resulting in a dose > 0.25 mSv.a^{-1}. High ^{232}Th concentrations were measured in these sediment samples.

Similar to what has been concluded by Van der Westhuizen (2007) it seems from these results that regulation of the phosphate industry might not be necessary since operations will result in a dose of less than 1 mSv.a^{-1} for members of the public. According to the NNR exemption may be justified through a public safety assessment, in which case exemption above 0.25 mSv.a^{-1} can be granted where the radiation risk to individuals is considered to be low enough not to be of regulatory concern. This depends on the use of the material and will be considered by the NNR on a case-to-case basis (2.2.4).

Phosphogypsum has been viewed as a potential building material in South Africa, where the construction of low cost housing is being encouraged (IAEA, 2013). The presence of natural radionuclides in the phosphogypsum can limit its use as a building material and should be considered on a case-to-case basis based on dose assessments. The suitability for use was evaluated in 5.4. Based on the calculated gamma index [I_γ = 0.52 ± 0.14] use of phosphogypsum as BM is permitted.

5.7.4 Environmental monitoring

A summary of the results for environmental media in the vicinity of a phosphate industry are given in Table 5-35. Results were collected in the period 2012-2017. The results were discussed in detail in previous sections.

Soil and sediment

The limited results available for soil indicated no contamination. Measured concentrations were low and similar to soil from background areas. Concentrations in sediments varied with higher concentrations of especially the Th-series nuclides measured in some of the samples. Very high concentrations of the Th-series nuclides were measured in sediment from the

impounding dam on the site, with an average $^{238}U/^{232}Th$ ratio of 0.02. This can be expected, since these dams are designed to contain process water from the plant. Impounding dams are usually located onsite with restricted access to the public. Water from the dams are not released to the environment, however, overflow may result in spillage into surface water sources as have been reported in the press in an incident in 2013 (5.3.6).

Water ingestion pathway

On average the water in the surrounding environment seemed not to be impacted by the phosphate industry activities. The activity concentrations of the majority of the nuclides in ground- and surface water were < 0.1 $Bq.L^{-1}$, which was low compared to the guidance levels set by WHO for drinking water (WHO, 2011). Ingestion of water from any of these sources will result in a dose of less than 0.1 $mSv.a^{-1}$ for the adult age group and for the most sensitive age group (<1 a) it will be less than 0.25 $mSv.a^{-1}$. Sampling of the water sources coincided with the time of the spillage mentioned in 5.3.6. The results confirmed that the concern of groundwater contamination raised in the press, at least with regard to radioactivity, was unfounded. The impact on fish and other biota living in contaminated water in the area was assessed in 5.3.6 and found to be negligible.

Food ingestion pathway

Limited food samples were submitted for analysis. Concentrations of the Th-series nuclides were mostly less than MDA. The concentration of ^{238}U in fish, chicken and vegetables from the area was low compared to that of ^{210}Po. The concentration of ^{238}U in vegetables varied from 0.007-0.03 $Bq.kg^{-1}$ fresh weight, which is comparable with the UNSCEAR reference value of 0.02 $Bq.kg^{-1}$ (Table 2-3). For ^{210}Po the range was 0.025-0.36 $Bq.kg^{-1}$ (compared to UNSCEAR value of 0.05 $Bq.kg^{-1}$). The individual high values measured for some nuclides in some samples (*e.g.* ^{210}Po in P35 (meat) = 2.33±0.06 $Bq.kg^{-1}$; ^{228}Ra in P40 (lemon) =2.02±0.08 $Bq.kg^{-1}$) should be used with caution and confirmed with further analysis. The resulting dose from consumption of the analysed foodstuff was not a cause of concern since it was mostly less than 0.25 $mSv.a^{-1}$. The dose varied from 0.10 to 0.12 $mSv.a^{-1}$ for ingestion of meat and 0.008 to 0.048 $mSv.a^{-1}$ for vegetables. As already mentioned the dose for individual samples exceeding the limit should be interpreted with caution (P35=0.32 $mSv.a^{-1}$).

There seemed to be some difference in concentrations of fish collected close to the discharge point of a fertilizer plant and those of a background area. However, the concentrations were all within the range of 0.08 to12 $Bq.kg^{-1}$ for ^{210}Po in fish and seafood reported worldwide (UNSCEAR, 2000) and is was therefore concluded that no significant contamination occurred in the area and that the environmental impact of discharge into the ocean is negligible (5.2.3). The dose due to ^{210}Po from the consumption of the fish analysed in this study was estimated to vary between 0.038 to 0.34 $mSv.a^{-1}$, compared to a background dose of 0.21 $mSv.a^{-1}$. Despite the slight increase in exposure through the consumption of fish due to the fertilizer industry, the contribution is below the limit of 1 $mSv.a^{-1}$ set in ICRP. On average, human exposure associated with the ingestion of fish was not negligible, and according to the data obtained in this study for ^{210}Po, it represented up to 14% of the global average annual radiation dose from the natural radiation sources as proposed by UNSCEAR (2000).

5.7.5 Conclusions

The results presented suggested that members of the public were unlikely to receive any significant dose from the use of phosphate rocks and fertilizers. Since most of the measured concentrations in the solids were less than the 500 $Bq.kg^{-1}$ limit, it, can be expected for regulatory control to be limited to just a few basic requirements, with authorization in the form of a registration probably being the most appropriate regulatory option (as is currently done). The high concentrations occasionally measured in some of the products confirmed the need for continuous control and monitoring of the industry, especially where by-products such as phosphogypsum are utilized in agriculture or as BM. The ALARA principle implies that reasonable measures must be taken to reduce radiation doses where necessary, but considering that costs have to be weighed against the averted radiation doses.

The results showed that the concentrations in the fertilizers were of the same order of that in phosphogypsum. The expected dose based on external dose rate only, was less than 1 $mSv.a^{-1}$. The impact of the application of fertilizer to soils on plant concentrations and the resulting dose was not investigated. This should be the topic of further (transfer) studies as recommended in 5.3.7.

Activity concentrations in water from the environment around the phosphate mining industry were low and comparable to background values. Concentrations similar to background were

measured in soil from the area, whereas some sediment samples showed enhanced concentrations of Th-series nuclides. Exceptionally high concentrations were measured in sediment from the impounding dam. Although public exposure are controlled by restricted access, these areas can be of concern in future if proper measures are not taken to clean and remediate the site once operations have stopped. For example, Bezuidenhout (2015) reported a dose of up to 0.45 $mSv.a^{-1}$ at an abandoned phosphate mine, confined to the area that used to be the processing plant of the mine.

Results for food samples should be interpreted with caution, and individual high activity concentrations confirmed with analysis of more samples. A study conducted with the purpose of evaluating the dose impact from ingestion of food, should include a survey of the food habits in the area and typical consumption rates.

Studies from literature have shown that discharge of phosphogypsum and effluent waste of phosphate fertilizer plants into water may result in significantly elevated levels of radionuclides such as radium, polonium, lead and uranium in seawater, sediments and biota (especially fish, shellfish and crustaceans (2.9.2) and the practice of discharging was therefore discontinued in Europe. In many other countries (including SA) effluent is still discharged to water bodies. Although significantly elevated levels were not observed in the results presented here, further environmental monitoring in the vicinity of the discharge point is encouraged.

5.8 Radioactivity and radiation at a gold mine site

5.8.1 Background

The Witwatersrand gold fields have been extensively mined for gold for more than 100 years, resulting in many waste dumps and tailings storage facilities (TSFs) scattered around urban areas in the South African goldfields. The elevated levels of natural nuclides such as U, in these materials, may represent a radiological and chemical hazard to man and the environment. As discussed in 2.12 contamination in the area has been of concern for many years. Nevertheless, there is limited published scientific information about the radiological hazards of NORM in this area to the public.

Mining companies operate under a CoR issued by the NNR. Consequently continued monitoring of radionuclide concentrations in the environment at a specified frequency is

required as part of the public radiation protection programme of the mining operations.

The aim of this case study was to characterize a typical radiological situation in the area of gold mining operations and to estimate the potential impact of the industry on humans and the environment, using results for radioactivity analysis of different environmental media as presented in this thesis. An exposure pathway analysis was performed to estimate the exposure and dose to the public. Finally, the estimated doses were compared to reference dose rates and regulatory dose limits.

5.8.2 Study area

The study area was the South African gold mines located south-west of Johannesburg in the Gauteng region in South Africa (Figure 2-17). The area has many tailings storage facilities that have been accumulated throughout the operating history of the mines. In order to protect the interests of mining companies specific sites are not identified.

The topography of the area is relatively flat, and the vegetation is largely grassland. Livestock farming is widespread in the surrounding area. Wildlife is limited to small animals and birds. The climate is temperate, with temperatures averaging 24 ^{o}C in summer and 13 ^{o}C in winter, occasionally dipping below freezing point. Annual rainfall is about 750 mm. There are also some informal settlements residing close to the mine tailings.

Surface operations in the area include metallurgical plants, TSFs, waste rock dumps, evaporation-, storm water- and process water dams, as well as access- and up-cast ventilating shafts. Ore from shafts is crushed, milled and processed at the metallurgical plant. Processed tailings material is deposited onto a TSF.

Background water quality in the rivers and streams in the area is generally of low quality. Weathering of the sulphide masses has been the main cause of pollution along the Witwatersrand catchment area, leading to low pH surface water conditions. As a result high levels of metals and natural radionuclides have been mobilized and have been found in water and sediment from this area (see 2.12.2).

5.8.3 Radioactivity results

A summary of the results for radioactivity in solids and environmental media in the gold

mine area are presented in Tables 5-36 and 5-37.

Ores, tailings and waste rock: Most of the radioactivity in the ore ended up in the tailings; whereas the waste rock had significantly lower concentrations. With concentrations higher than the natural background U-bearing tailings deposits are a potential source of contamination. Transfer of nuclides is possible due to flow of seepage waters from the tailings pile. The concentrations in the specific tailings from this area varied from 83-668 $Bq.kg^{-1}$, which was only slightly higher than the 500 $Bq.kg^{-1}$ exemption level for NORM.

Radioactive equilibrium of ^{238}U and ^{226}Ra was observed in waste rock, as expected, since natural elution processes will have caused only minor shifts in the radioactive equilibrium. Radioactive equilibrium was also observed in the specific tailings material analysed, which will not always be the case; especially in re-processed tailings where U has been extracted, ^{226}Ra often occurs at elevated levels.

Soil and sediment: The average radionuclide concentrations in surface soils were low and similar to the worldwide background averages. Concentrations of U-series nuclides in sediment were 4-5 times higher than background soil concentrations. The ^{238}U concentration varied from about 16 -667 $Bq.kg^{-1}$, only slightly higher than the 500 $Bq.kg^{-1}$ exemption limit, but indicating contamination compared to background levels.. Since samples are often taken at locations identified from gamma surveys to have elevated gamma dose rates, the presented results are not necessarily a presentation of the average situation.

The transfer of radionuclides from sediments to water was in general low. The K_d value measured in slurry samples from the field varied from 76 -315 $L.kg^{-1}$ for ^{238}U being relatively mobile to 4000 -11000 $L.kg^{-1}$ for ^{226}Ra being rather inert. Lower K_d values were measured in leaching experiments in the laboratory (5.4.3).

Water: Water concentrations showed significant variations at various sites in the area, with groundwater of good quality. For surface water the radionuclide concentration was dominated by uranium, which varied from 13.6 – 11400 $mBq.L^{-1}$. Water of three of the nine sampling points were of good quality whilst two sampling points were clearly affected by process water from the operational site, with ^{238}U concentrations exceeding the EU radioactivity reference level of 3000 $mBq.L^{-1}$. Due to a good monitoring and control programme this water is normally not accessible to the general public for domestic use.

Water from the remaining four sites, although not exceeding radioactivity limits, exceeded the WHO limit of 30 µg.L^{-1} for chemical toxicity. Where taken from publicly accessible streams, this water might pose some risk to the public when it is taken for domestic use.

Food chain: Concentrations of Th-series nuclides were undetectable or low in all foodstuff compared to U-series nuclides. High concentration of ^{210}Pb and ^{210}Po compared to the other nuclides were found in most of the samples, but especially in vegetables and cereals, which can be attributed to deposition. ^{238}U was found at higher concentrations only in fish, which may indicate some intake of uranium by fish in water sources known to contain elevated concentrations of uranium, but it must also be noted that only two of the 11 samples analysed had high concentrations. This was also true for many of the nuclides and foodstuff where the maximum concentrations indicated in Table 5-37 was only observed for one or two individual samples. Individual high concentrations should be interpreted with caution and confirmed by sufficient additional analysis

The exception was for ^{210}Pb/^{210}Po in meat and cereal samples where several samples had concentrations greater than 1 Bq.kg^{-1}. The high concentrations found in the rye, oats, and cereal is a cause of concern. These samples were analysed as received with all plant parts included and should be considered as animal feed and used for evaluation of the secondary fodder-cattle-human pathway only, similar as what was done in 5.3.3. It is advised to analyse washed/ pepared foods. Where limits are exceeded, people should be advised not to use locally grown food.

5.8.4 Radiological public dose assessment

The site-specific data presented in 5.8.3 was used to conduct a public dose assessment for the mining operations, more specific from an "imaginary" waste facility in the area, using a source-pathway-receptor approach (Figure 2-5), as discussed in 2.3.8. The model converts radionuclide intake by receptors from sources via the various pathways into a dose.

Sources

Primary sources of interest for this assessment included radioactive effluents and discharges from the processing plants and waste residues (tailings and waste rocks). Radioactivity released from these features can accumulate in the environment, resulting in secondary sources of radiation exposure, *e.g.* deposition of contaminants on surface soils, deposition of

contaminants in surface water and transfer to sediments and spillage of contaminated mine residue on surface soil or water.

The TSF served as a source of contaminants in the following manner:

- Windblown dust emitted from the TSF contains long-lived alpha radiating isotopes (long-lived radioactive dust, LLRD), which are dispersed into the atmosphere.
- The radionuclide content of the tailings material results in the emission of radon gas.
- The inherent radiological properties of the TSF, which contains uranium, result in the continuous emission of gamma radiation.
- LLRD deposited on the upper soil layer will contribute to an external gamma radiation dose.
- Spillages will spread the tailings material over the top soil layer or where a pipeline cross a surface water body, the spread of tailings material in the water.
- Ground- and surface water activity concentrations are induced by leaching of activity from the TSF.

Exposure pathways

The main exposure pathways were through ingestion and inhalation as illustrated in Figure 2-20 and included:

- Inhalation of radon and contaminated dust.
- External gamma radiation exposure (from soil, sediment, waste residue).
- Internal exposure through ingestion of water and contaminated foodstuffs.
- Direct ingestion of contaminated solids.

Other exposure pathways such as internal exposure from incidental ingestion of water and sediment, external exposure when swimming or bathing in contaminated water, external gamma radiation during immersion in a dust cloud and external exposure to soil contaminated through irrigation with contaminated water, are also possible. However, these exposure pathways are expected to be insignificant (2.3.2).

Receptors

As a hypothetical conservative assumption, the agricultural community who occupies land

directly impacted by the gold mine industry, was considered as receptor, representing the most exposed individual situation (2.3.8). This exposure condition assumes a contribution to a total effective dose from the atmospheric, aquatic and associated secondary pathways as indicated above. These human receptors are expected to obtain all their dietary components from the local area. Similarly, contaminated surface water is their only source of water for household purposes, human consumption, and to maintain their agriculture activities.

Risk assessment and reference dose rates

Consistent with the regulatory safety standards the impact to members of the public (*i.e.* assessment endpoint) was evaluated in terms of the total effective dose incremental to background dose. A dose below 0.25 $mSv.a^{-1}$ was regarded as below the dose constraint and as a low risk only needing low priority attention in terms of optimization to keep the dose ALARA. A dose between 0.25 and 1 were regarded as below the public dose limit, but of medium risk. A dose above 1 is above the public dose limit, of high risk and needs attention to reduce the risk to the public.

Estimated dose from site specific data

Dose from exposure to inhaled radon daughters and radioactive airborne dust was not considered in the assessment. Atmospheric transfer of radon and dust emission is usually modeled by dispersion models. Literature indicates that the atmospheric pathway is important, but only close to the radon and dust sources (2.3.3). Radon concentrations in outdoor areas are largely dependent on the ^{226}Ra concentration in the solid material, *e.g.* tailings. The ^{222}Rn exhalation rate from the solid and atmospheric dispersion factors can be used to calculate the radon exposure. Based on the analytical data TSFs may therefore be an important source of radon, with much lower emission expected from waste rock. High moisture content, whether due to precipitation or deliberate wetting, decreases the potential for dust generation from a TSF.

Gamma dose rates were not measured, but calculated from the concentrations of ^{238}U, ^{232}Th and ^{40}K using equation 2.8 in 2.3.6. Gamma radiation levels in soil were low but that of sediment and tailings were elevated (6-7 times) compared to worldwide background average. Gamma dose rates for tailings were 40-400 $nGy.h^{-1}$ compared to world average of 59 $nGy.h^{-1}$ resulting in a maximum dose of 0.49 $mSv.a^{-1}$.

For the adult age group ingestion of water will not result in the international dose limit of 1 $mSv.a^{-1}$ to be exceeded. On average consumption of surface water will not result in a dose of more than 0.25 $mSv.a^{-1}$; the exception being water from the two sampling points with high radionuclide concentrations, which may result in a dose up to 0.89 $mSv.a^{-1}$. Groundwater activity concentrations were low and water was of good quality. Groundwater contamination from the TSF was not observed. Concentrations due to leaching form the TSF was not calculated, although this can contribute to poor surface water quality in the area. The concentrations in the leachate can be calculated only if information on the geometric properties of the TSF is available *e.g.* length, width, height, area, volume, density, porosity and moisture content (IAEA, 2003b). Default K_d values are used in the modelling. If higher K_d values are assumed for the tailings material then radionuclides will be retained in the tailings material, which means that less activity will be in solution (lower activity concentration in the leachate). Use of site-specific K_d values, as was attempted to determine in. 5.4.3, will very helpful to predict mobility.

For the majority of the analysed foodstuffs the estimated dose for adults was well within the "single facility" dose constraint of 0.25 $mSv.a^{-1}$; not presenting an unacceptable level of exposure. The maximum dose in Table 5-37 represents the worst-case scenario based on the highest measured value, often only for one individual sample. As shown in the table the average dose was much lower. In cases where contaminated foodstuffs are consumed, the main contributor to dose was found to be ^{210}Po, contributing 20-40%. The contribution of ^{238}U was found to be negligible compared to other nuclides, which is a consequence of the significantly lower DCF for ingestion (Figure 5-26). The only real concern was cereal, for which the average dose exceeded 1 $mSv.a^{-1}$.

Modelled dose assessment

The estimated dose for adults for the hypothetical farmer exposure condition based on the water concentrations in Table 5-37 is graphically presented in Figure 5-46. Ingestion dose was estimated using pathway models that rely on parameters such as transfer factors, concentrations ratios and K_d values to estimate concentrations. Parameters provide by the NNR licensing guide RG-002 were used in the modeled dose estimation. The aquatic pathway included the consumption of water, irradiation and ingestion of soil and secondary ingestion of contaminated food. The air pathway was not considered since no data was

available.

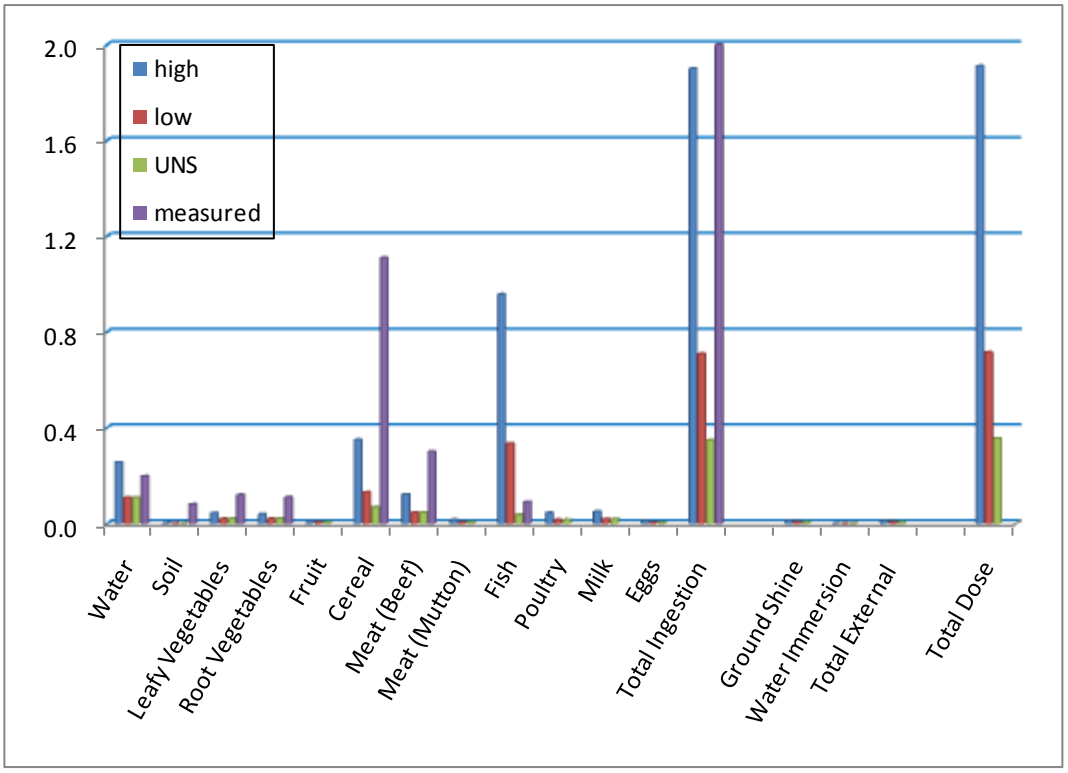


Figure 5-46: Effective dose for the Hypothetical Farmer Exposure Condition (modelled)

At first glance the results suggest that surface water from the area is not suitable for human consumption on an annual basis and most probably not suitable for release to the environment. The highest predicted ("worst-case scenario") incremental dose was estimated as 1.9 $mSv.a^{-1}$. Using a lower average water concentration, excluding the two sampling points with high concentrations (assuming that public access to this water is restricted), the dose was predicted as 0.72 $mSv.a^{-1}$. The recently updated soil-to-plant and plant-to-animal transfer factors in RG-002 seem better aligned with international values, than previous parameters in LG1032, which were at the maximum of the range of values recommended in internationally. The effect of this was clear – using LG1032 values the predicted dose was much higher - 3.4 $mSv.a^{-1}$.

Dose by pathway is shown in Figure 5-46. The contribution of external dose was insignificant compared to dose from ingestion. The highest dose was from fish (50 %), with cereal contributing 18% and consumption of water only 13%. As discussed in 5.2.3 the dose due to intake of cereal and fish will almost always dominate due to the very conservative

consumption rates assumed by the NNR for these food groups. The assumed consumption of 25 kg fish annually is based on that of a sports fisherman and is a factor 10 higher than the UNSCEAR recommended value of 2.7 kg for Africa. The amount of fish caught and consumed is, however, small compared to the amount of vegetables produced, and therefore the significance of this pathway should be negligible. Similarly the 250 kg cereal per annum is almost twice the value of 130 kg assigned by UNSCEAR (UNSCEAR, 2016). The impact on dose assuming UNSCEAR consumption rates are also shown in Figure 5-46, reducing the dose by more than half.

It should be emphasized that the hypothetical farmer exposure condition is very conservative, assuming the contaminated water is their only source of water and that all food (*i.e*. fruits, vegetables, protein, and cereals) are produced on the farm. Under this hypothesis, exposure from ingestion was most probably overestimated. In practice this is very unlikely.

The modeled dose calculated with equations 2.4-2.6 using the water concentration, as shown in Figure 5-46 was compared with the average dose calculated from the site-specific measured concentrations using equations 2.1-2.3. As can be seen from Figure 5-46 the modeled dose was about 2-3 times higher for all food, except for fish where the concentration was 10 times higher (indicating a too high bio-accumulation factor for fish in model). The other discrepancy was for cereal where the measured dose was much higher than predicted from the model. The higher dose was from high measured concentrations of ^{210}Pb and ^{210}Po (both with larger DCFs) in cereal, which can probably be contributed to deposition (atmospheric pathway), whereas only soil-plant transfer is considered in the model.

5.8.5 Conclusions

The data collected in this study shows that no member of the public is expected to be exposed to any significant dose. If release of mine effluent are controlled and access to contaminated surface water restricted, the potential effective dose received from the most likely pathway of drinking water and consuming vegetables irrigated with contaminated water is within the dose limit of 1 mSv.a^{-1} set internationally. The dose is reduced to less than the 0.25 mSv.a^{-1} dose constraint if dietary restrictions with respect to intake of fish and cereal are taken.

By definition this study has excluded some pathways of public exposure such as the inhalation of radon gas and radioactive dust. Other components of aquatic pathways that are

usually modeled are direct exposure due to swimming, boating and sunbathing on contaminated sediments. These pathways were excluded in the study since they are usually insignificant compared to other pathways. Other possible pathways are direct exposure from the contaminated irrigated lands and internal exposure from inadvertent soil ingestion. For the latter the model assumes a default value of 100 mg per day. For direct external exposure from soil for 2000 hours per year the annual effective dose was 0.05 $mSv.a^{-1}$, whereas exposure from sediment and tailings was calculated to be less than 0.49 $mSv.a^{-1}$. A few decimetres of cover placed on top of contaminated tailings may be sufficient to minimize the ambient dose rate of ^{226}Ra to natural background levels. To reduce infiltration rates and seepage from tailings, a multiple cover system is used to cap the TSF.

Based on the available results, the current radiological impact of the activities of the gold mines in the specific area does not require urgent countermeasures for soil, sediment and tailings, but the radiological impact may become important if new uses for these areas are considered, such as the integration of rehabilitated footprints into residential areas, mainly because of indoor radon risk. Guidance levels for exemption imply unrestricted use of the areas when the concentration of each individual nuclide is less than 500 $Bq.kg^{-1}$, which was the case for most of the analysed sediment and tailing samples.

It was clear that nuclide concentrations in water and foodstuffs can vary over time. Evaluation of the true extent of contamination at the various sites should therefore not be based on results obtained from a single grab sample, as was presented in some reports mentioned in the literature study. An effort should be made to obtain samples representative of a long period, as was done in the survey conducted by the DWS and licensed mines for water and soil. Frequent monitoring of all media in the area should continue.

Table 5-24: Screening results of DWS surface water samples – 2006-2017 (averages of 1200 samples)

SP	TDS	Gross Alpha ($Bq.L^{-1}$)			Gross Beta ($Bq.L^{-1}$)			α/β	Uranium $\mu g.L^{-1}$			Estimated GA from U		Quality
		Mean	UNC	Median	Mean	UNC	Median		Mean	UNC	median	GA	*Ratio	
1	159	0.026	0.022	0.023	0.150	0.010	0.136	0.22	0.341	0.284	0.313	0.009	0.3	Blue
2	248	0.041	0.030	0.036	0.172	0.093	0.160	0.28	0.939	0.625	0.830	0.024	0.6	Blue
3	471	0.054	0.035	0.055	0.418	0.132	0.408	0.16	2.11	1.28	1.85	0.053	1.0	Blue
4	809	1.16	1.07	0.81	1.34	1.15	0.87	0.85	71.1	97.8	31.9	1.80	1.6	Yellow
5	529	0.062	0.114	0.050	0.245	0.121	0.231	0.29	1.70	0.76	1.57	0.043	0.7	Blue
6	699	0.969	0.416	0.923	0.698	0.254	0.669	1.44	52.2	23.6	50.8	1.32	1.4	Yellow
7	4290	4.31	2.04	4.07	3.31	1.79	3.34	1.37	262	124	247	6.63	1.5	Yellow
8	5600	5.18	1.79	5.26	4.26	2.17	4.02	1.29	298	90	304	7.54	1.5	Yellow
9	554	0.345	0.487	0.176	0.447	0.184	0.395	0.70	17.1	26.0	7.9	0.433	1.3	Green
10	1170	1.51	0.52	1.44	0.910	0.427	0.867	1.85	75.5	20.7	75.8	1.91	1.3	Yellow
11	382	0.055	0.033	0.048	0.316	0.055	0.315	0.19	1.48	0.75	1.30	0.037	0.7	Blue
12	419	0.073	0.067	0.062	0.353	0.066	0.350	0.22	1.42	0.82	1.26	0.036	0.5	Blue
13	394	0.109	0.14	0.071	0.491	0.244	0.452	0.19	3.11	3.43	1.95	0.079	0.7	Blue
14	658	0.894	0.993	0.462	0.728	0.830	0.370	1.14	59.5	88.7	14.8	1.51	1.7	Yellow
15	653	0.847	0.428	0.81	0.593	0.202	0.556	1.44	49.6	24.6	51.6	1.26	1.5	Yellow
16	675	1.24	0.55	1.22	0.615	0.271	0.599	2.03	67.5	28.7	67.0	1.71	1.4	Yellow
17	539	0.217	0.224	0.120	0.192	0.125	0.188	0.87	10.8	12.9	5.09	0.273	1.3	Green
18	432	0.062	0.090	0.041	0.099	0.069	0.085	0.75	1.87	1.48	1.07	0.047	0.8	Blue

**ratio=estimated/measured*

Table 5-25: Screening results of DWS groundwater samples 2006-2017 (206 samples)

SP	TDS	Gross Alpha (Bq.L^{-1})		Gross Beta (Bq.L^{-1})		α/β	Uranium (µg.L^{-1})		Estimated GA from U		Quality
		Mean	UNC	Mean	UNC		Mean	UNC	GA	*ratio	
Catchment A											
1	560	0.03	0.12	0.05	0.12	0.67	0.90	0.15	0.02	0.68	Blue
2	177	0.02	0.03	0.10	0.02	0.18	0.05	0.23	0.00	0.07	Blue
3	1280	0.95	0.20	0.67	0.14	1.41	16.6	1.75	0.42	0.44	Green
4	2910	0.21	0.09	0.52	0.09	0.41	2.63	0.74	0.07	0.31	Green
5	1520	0.56	0.14	0.50	0.22	1.14	12.2	3.0	0.31	0.55	Green
6	551	0.16	0.02	0.15	0.02	1.07	2.64	0.63	0.07	0.41	Green
7	336	0.39	0.08	0.45	0.10	0.86	1.21	1.61	0.03	0.08	Green
8	1280	0.23	0.07	0.51	0.20	0.46	0.39	0.18	0.01	0.04	Green
9	1000	0.76	0.19	0.48	0.14	1.59	11.6	4.3	0.29	0.39	Green
10	136	0.13	0.06	0.31	0.07	0.42	0.22	0.30	0.01	0.04	Green
11	73	0.40	0.17	0.31	0.05	1.29	0.10	0.06	0.00	0.01	Green
12	173	0.91	0.37	0.67	0.12	1.35	2.94	5.78	0.07	0.08	Green
13	96	0.05	0.01	0.12	0.01	0.38	0.12	0.21	0.00	0.07	Blue
14	616	0.47	0.09	0.31	0.08	1.53	12.5	0.9	0.32	0.67	Green
15	454	0.36	0.33	0.26	0.19	1.39	9.13	8.55	0.23	0.64	Green
Catchment B											
1	576	0.16	0.11	0.17	0.12	0.95	1.37	1.35	6.2	0.22	Green
2	547	0.27	0.07	0.24	0.05	1.12	3.90	1.05	10.7	0.36	Green
3	229	0.05	0.11	0.08	0.08	0.65	0.01	0.26	1.9	0.01	Blue
4	515	0.20	0.11	0.15	0.04	1.30	4.70	2.46	7.9	0.59	Green
5	354	0.07	0.03	0.14	0.03	0.48	0.28	0.19	2.6	0.11	Blue
6	364	0.07	0.02	0.07	0.10	0.98	0.41	0.36	2.8	0.15	Blue
7	494	0.02	0.03	0.05	0.07	0.47	0.11	0.27	0.9	0.13	Blue

SP	TDS	Gross Alpha (Bq.L^{-1})		Gross Beta (Bq.L^{-1})		α/β	Uranium (µg.L^{-1})		Estimated GA from U		Quality
		Mean	UNC	Mean	UNC		Mean	UNC	GA	*ratio	
8	411	0.12	0.04	0.09	0.09	1.29	0.75	0.20	4.7	0.16	Green
9	266	0.02	0.01	0.05	0.03	0.35	0.00	0.31	0.7	0.01	Blue
10	535	0.08	0.02	0.22	0.31	0.37	1.62	0.49	3.3	0.50	Blue
11	559	0.05	0.05	0.09	0.03	0.56	0.33	0.61	2.1	0.16	Blue
12	989	0.88	0.18	0.65	0.14	1.36	22.7	4.5	34.7	0.65	Green
13	661	5.31	3.61	4.11	3.26	1.29	203	149	209	0.97	Yellow

Table 5-26: Summary of results for surface water from Gold mine area

Area	N	Activity concentration (mBq.L^{-1})		Gross alpha (mBq.L^{-1})		Ratios		Dose (µSv/a)		
		^{238}U	^{234}U	Measured	Calculated	238:234	238:226	< 1a	> 17a	Life AVE
GS1	8	112±46	163±61	222±187	485±171	1.47±0.16	51±63	353±140	76±33	78±29
GS2	9	956±485	874±444	1140±570	2260±860	0.92±0.04	152±92	443±92	124±33	127±34
GS3	7	1290±600	1200±540	1870±960	3470±1250	0.95±0.07	10±7	787±371	179±72	189±76
GS4	6	1190±670	1130±590	1300±80	2600±1430	0.96±0.07	260±135	460±169	150±69	149±63
GS5	5	158±78	166±64	289±260	961±175	1.11±0.19	1.07±0.66	560±66	106±21	120±12
GS6	4	5840±2410	4860±2170	6690±2320	11600±4800	0.91±0.03	178±302	1630±250	499±144	510±156
GS7	8	45±28	67±45	109±115	397±355	1.56±0.52	16±21	450±276	86±71	87±66
GS8	7	7460±3230	6450±2900	6810±2440	16300±6800	0.86±0.04	30±10	1730±700	573±241	583±249
GS9	6	2500±2640	2230±2360	2460±2490	5310±5320	0.90±0.07	40±18	830±454	238±190	250±19

Gross alpha calculated / measured = 2.36
Gross alpha measured / (^{238}U+^{234}U) = 0.69

Table 5-27: Summary of results for different types of water from NORM industries

Type of water		Activity concentration (mBq.L^{-1})							Dose (µSv.a^{-1})		Ratios				
		^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb	^{232}Th	^{228}Th	< 1a	>17a	234:238	238:226	226:210	228:232	228:226
BACKGROUND AREA															
Surface	AVE	5.2	16	20.7	4.2	7.4	3.1	6.8	173	26	3.7	2.8	1.6	2.4	3.3
(7)	STDS	4.0	11.1	10.7	3.7	9.1	2.0	8.1	128	18.5	2.0	4.0	1.6	1.7	0/9
	median	3.0	13.4	17.5	3.1	1.9	2.4	3.5	150	26	3.4	1.1	1.0	1.7	1.4
	max	11.3	38.5	43.7	10.6	25.8	6.9	24.4	440	62	6.6	11.6	4.0	5.3	13.7
	min	2.4	6.5	12.2	0.8	0.8	1.2	1.5	56	8.9	1.2	0.5	0.0	1.2	0.2
Ground	AVE	5.4	10.7	22.1	4.9	13.4	2.2	6.6	175	27	1.9	1.8	1.1	4.1	1.8
(6)	STDS	2.6	11.1	8.1	3.1	22.6	1.8	5.0	44	12	1.3	1.4	1.2	3.2	2.6
	median	6.2	6.2	22.5	6.0	3.4	1.7	4.3	160	24	1.4	1.2	0.5	3.4	1.0
	max	8.1	32.5	33.4	7.9	59.2	5.3	14.8	260	51	4.2	3.9	2.9	9.7	11.7
	min	2.1	3.1	11.2	0.7	1.7	0.5	1.9	140	18	0.7	0.4	0.1	1.3	0.3
PHOSPHATE INDUSTRY															
Surface	AVE	47.4	82.9	35.3	4.7	6.4	6.9	7.1	197	33	1.9	12	1.5	1.9	2.4
(24)	STDS	21.7	38.9	27.0	4.3	6.9	8.5	4.1	104	17	0.8	17	1.9	1.6	2.5
	median	43.6	71.0	26.8	3.2	2.9	4.6	6.7	190	32	1.7	10	0.7	1.5	2.0
	max	104	200	115	16.3	29.1	35.9	17.0	480	79	4.5	26	8	6	7.8
	min	12.7	36.4	9.0	0.02	0.6	0.7	1.1	79	13	1.1	3.5	0	0.3	0.3
Ground	AVE	43.4	105	29.5	8.2	8.3	5.1	9.5	208	35	2.6	8.0	1.8	2.6	0.9
(19)	STDS	33.2	84.5	20.2	5.9	9.3	4.6	9.3	102	15	1.0	6.7	1.4	1.6	0.4
	median	35.8	83.6	25.5	7.0	3.7	3.2	6.4	190	33	2.5	6.8	1.6	2.9	0.7
	max	147	372	89.6	21.3	31.3	16.5	36.9	440	63	4.5	20	4.9	5.9	1.4
	min	9.3	21.8	5.3	1.8	0.8	1.1	1.1	74	13	0.9	0.8	0.1	0.1	0.6
Impound	AVE	6190	5760	2650	791	658	8830	7920			0.95	12.3	4.5	1.13	26
(6)	STDS	2190	2490	1480	1050	549	4900	4780			0.11	6.8	6.5	0.08	30
	median	7030	6240	2530	341	609	7990	7540			0.96	12.1	1.81	1.12	19
MINERAL SANDS															
(10)	AVE	366	1000	37.3	116	22.3	6.3	12.6	451	110	3.1	15.9	7.3	5.7	0.8
	STDS	183	487	13.8	165	22.4	5.7	9.3	252	55	1.8	18.8	10.0	10.2	1.2

Type of water		Activity concentration (mBq.L^{-1})							Dose (µSv.a^{-1})		Ratios				
		^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb	^{232}Th	^{228}Th	< 1a	>17a	234:238	238:226	226:210	228:232	228:226
	median	356	987	32.8	37.1	11.3	3.7	9.9	341	87	2.9	6.7	4.1	2.5	0.2
	max	694	2071	56.7	485	68.8	18.3	36.9	959	205	7.8	50.9	32.7	34.3	3.5
	min	112	377	16.1	2.4	2.4	1.1	5.3	235	59	1.1	0.8	0.2	0.3	0.1
GOLD MINES															
Surface	AVE	1920	1720	73.3	79.8	12.8	13.8	12.4	735	208	1.10	59.6	11.8	1.92	1.5
(59)	STDS	2810	2470	81.6	99.2	11.0	13.6	8.22	547	201	0.33	85.4	20.0	2.36	2.0
	median	729	745	57.5	12.2	8.99	8.41	10.7	510	133	0.95	24.2	3.12	1.19	0.84
	max	11400	9970	495	370	46.9	57.4	36.1	2200	890	2.72	357	96.3	12.9	8.3
	min	13.6	35.4	14.2	1.00	1.14	0.01	0.01	140	26	0.78	0.41	0.10	0.01	0.02
Fissure	AVE	41.5	150	49.6	5.22	8.22	14.4	11.1	298	53	3.96	13.4	0.73	1.36	3.7
(14)	STDS	19.5	106	20.7	4.82	5.50	15.0	10.8	128	21	2.93	12.0	0.48	1.14	3.9
	median	34.9	91.6	46.0	3.32	5.10	7.57	7.10	285	50	2.95	10.2	0.66	0.99	1.8
	max	75.3	350	93.6	18.9	18.4	44.0	42.2	550	100	10.3	48.3	1.81	3.92	12.3
	min	18.1	46.7	24.4	1.16	2.43	1.92	1.91	120	21	1.55	2.52	0.12	0.16	0.4
Drinking	AVE	47.8	91.7	44.3	8.30	11.6	17.2	8.48	412	69	2.15	16.5	0.91	0.81	4.0
(13)	STDS	31.2	84.0	25.9	15.3	9.91	15.1	5.66	221	37	1.51	13.0	1.22	0.52	4.0
	median	46.5	89.1	39.9	2.39	7.59	19.2	6.89	431	72	1.66	13.9	0.33	0.68	3.5
	max	103	346	88.6	57.0	36.0	49.5	21.0	792	132	6.70	46.2	4.10	1.71	14.9
	min	4.61	14.4	4.88	0.93	3.59	1.75	1.48	58	10	0.98	0.82	0.04	0.12	0.60
Process	AVE	6610	5940	119	203	20.8	12.7	13.1	2120	558	0.92	33.8	17.6	1.72	0.08
(40)	STDS	3180	2880	278	84	18.9	9.83	9.36	990	232	0.09	19.2	13.4	1.71	0.06
	median	6570	5960	63.0	202	12.9	10.2	11.1	1950	580	0.90	31.2	15.8	1.10	0.05
	max	13300	12800	1800	454	86.5	39.5	53.9	5370	970	1.37	119	56.6	7.99	0.25
	min	204	280	12.8	39.7	2.52	1.44	2.22	416	69	0.82	2.54	1.33	0.27	0.01

Table 5-28: Activity concentrations in environmental media from the Wonderfonteinspruit catchment area (Bq.kg^{-1} fresh weight)

Sample	Activity ^{210}Po (Bq.kg^{-1})			Dose	Activity ^{238}U (Bq.kg^{-1})		Mass ^{238}U (mg.kg^{-1})	
	This study	Previous	UNS	mSv.a^{-1}	This study	Previous	This study	Hamman
Water	0.00035±0.00035	-	-	0.00025	0.614±0.020	-	0.049	0.057±0.043
	0.0165 ± 0.0030	-	-	0.012	0.795±0.052	-	0.064	-
Sediment	103 ± 12	730 ± 20[(1)]	-	-	311± 9	1290±30[(1)]	25.1	45.3±30.0
	215 ± 21	270 ± 20[(2)]	-	-	1040± 30	934±14[(2)]	83.9	-
	94.6 ± 10.7	-	-	-	191 ± 6	-	15.4	-
Soil in wetland	179 ± 18	-	-	-	717 ± 21	-	57.8	117.0±87.7
Soil next to dam	88.4 ± 11.2	-	-	-	410 ± 12	-	33.1	110.4±84.5
Cattle feed	5.36 ± 0.05	5.64 ± 0.36[(3)] 9.55 ± 0.93[(3)]	-	0.090	1.27 ± 0.07	-	0.10	40.10±87.2
Feed (background)	-	5.98 ± 0.63[(3)]	-	-	-	-	-	4.04±1.40
Meat	3.32 ± 0.80	0.115-0.250[(3)]	0.015[(4)]	0.120	0.634± 0.025	-	0.051	1.58±0.82
	5.07 ± 0.44	-	-	0.183	0.0419±0.0042	-	0.003	-
Meat (Reference)	-	-	-	-	-	-	-	0.014
Meat (Control)	-	-	-	-	-	-	-	0.05±0.00
Liver	52.1 ± 3.3	13.1 ± 0.75[(3)]	-	1.88	0.100 ± 0.006	-	0.008	5.07±9.05
Liver (Reference)	-	-	-	-	-	-	-	0.026
Liver (Control)	-	-	-	-	-	-	-	0.04±0.01
Bone	2.53 ± 0.84	-		-	0.581 ± 0.133	-	0.047	0.60±0.22
Milk	0.0830 ± 0.0418	0.162± 0.075[(3)]	0.005[(4)]	0.012	-	-	-	-
Milk (Background)	0.0127 ± 0.0037	-	-	0.002	-	-	-	-

(1) NNR, 2007; (2) Ramathlape *et al*, 2010; (3) Table C-4; (4) UNS, 2000 (5) Hamman, 2012

Table 5-29: Summary of results for soil, tailings and waste rock samples) [Activity in Bq.kg^{-1}; Dose in mSv.a^{-1}]

	n	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{228}Ra	^{228}Th	^{40}K	Ra_{eq}	H_{ex}	D	AED
SOIL Baseline												
B1	11	19.0±5.7	18.2±6.7	71.7±10.7	19.4±6.1	19.2±7.1	20.7±7.2	109±40	-	-	-	-
B2	3	17.9±7.2	14.1±4.5	23.2±4.9	9.78±3.7	11.9±5.0	11.8±4.7	39.1±11.3	-	-	-	-
B3	8	10.2±5.7	6.70±3.4	15.8±5.8	8.15±6.9	7.84±6.68	6.87±6.1	47.3±43.2	-	-	-	-
B4	8	10.6±3.4	9.50±3.1	15.5	5.76±1.9	8.66±3.0	7.81±2.9	70.3±23.2	-	-	-	-
B5	7	33.3±9.9	33.9±15.2	100±32	55.4±20.2	59.2±25.1	59.4±23.2	67.2±25.4	-	-	-	-
B6	5	38.5±12.0	24.1±13.0	40.9±11.5	18.7±6.8	19.8±8.7	21.4±7.1	272±205	-	-	-	-
AVE		21.1	18.6	54.5	20.7	21.5	21.6	97.1	53.5	0.14	24.2	0.03
STD		12.4	13.4	34.4	19.5	21.0	21.0	98.9	41.3	0.11	18.3	0.02
SOIL: Mineral Sands												
MS1	7	38.1±30.1	34.6±23.3	89.5±7.8	46.4±4.7	38.7±35.0	37.3±34.8	442±240	135	0.36	62.4	0.08
SOIL: Gold mining industry												
GM1	12	41.0±5.1	49.7±19.2	84.1±28.2	22.4±3.6	22.2±6.3	25.1±3.9	220±79	-	-	-	-
GM2	5	34.2±8.6	34.8±9.8	-	17.3±1.3	21.6±3.4	22.2±8.3	142±37	-	-	-	-
GM3	7	38.1±7.4	35.8±15.1	66.2±27.1	16.5±1.5	18.4±5.3	17.4±5.8	61.8±21.2	-	-	-	-
Average gold mines												
AVE		38.9	42.6	77.0	19.7	21.0	22.2	157	8.28	0.22	38.1	0.05
STD		6.9	17.5	28.5	3.9	5.6	6.3	91	22.8	0.06	10.8	0.01
Range all soil samples												
		3.0-87.5	2.1-94.3	8.9-119	2.3-128	1.5-111	1.4-108	6.2-734	-	-	-	-
World Average												
		35(17-60)	-	-	30 (11-64)	-	-	400(140-800)	370	-	59	0.07
TAILINGS Gold mines												
AVE	49	338	349	467	23.3	23.9	23.7	195	395	1.07	1.82	0.22

	n	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{228}Ra	^{228}Th	^{40}K	Ra_{eq}	H_{ex}	D	AED
STD		160	185	245	8.53	14.5	9.35	74	195	0.53	90	0.11
MIN		82.5	60	70.2	9.37	1.95	7.53	96	85.9	0.23	39.9	0.05
MAX		668	819	901	42.6	60.3	40.2	405	867	2.34	399	0.49
WASTE ROCK Gold mines												
AVE	32	36.9	34.8	73.9	15.1	18.5	15.2	354	82.5	0.22	39.4	0.05
STD		17.3	20.5	47.0	5.09	7.23	5.35	127	23.4	0.06	10.8	0.01
MIN		15.6	5.83	11.7	8.76	5.47	5.16	139	44.3	0.12	21.0	0.03
MAX		90.7	84.0	175	30.0	37.6	32.7	813	147	0.40	68.1	0.08

Table 5-30: Summary of results for sediment samples

	n	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{228}Ra	^{228}Th	^{40}K	Ra_{eq}	H_{ex}	D	AED
Baseline												
B1	12	16.2±3.87	15.7±3.9	-	21.1±10.8	24.3±14.1	23.6±12.2	214±143	-	-	-	-
B2	4	41.0±30.1	28.6±30.7	33.8±29.8	20.9±12.9	19.6±14.9	19.3±14.7	62.8±27.7	-	-	-	-
B3	4	20.7±18.0	20.3±19.9	27.3±22.1	17.3±17.8	21.1±20.6	19.6±18.9	210±239	-	-	-	-
B4	4	7.96±3.3	8.59±2.1	12.5±7.4	9.89±6.2	11.6±4.8	10.5±5.6	95.1±86.3	-	-	-	-
AVE		19.7	17.5	24.5	18.6	20.9	20.0	168	57.0	0.15	26.3	0.03
STD		16.7	14.9	21.9	11.9	14.3	13.1	150	35.6	0.09	16.4	0.02
Phosphate												
P1	2	155±35	662±162	770±9	5190±860	3060±60	5260±2500	340±42	-	-	-	-
P2	4	29.5±8.7	44.8±21.2	63.2	291±192	11±61	249±172	111±67	-	-	-	-
P3	6	41.8±35.3	45.5±33.6	82.0	70.9±64.7	80.4±34.8	93.3±72.3	187±107	-	-	-	-
P4	3	33.5±28.4	43.9±47.1	280	30.9±23.0	-	25.3±11.8	433±245	-	-	-	-
Mineral Sands												

	n	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{228}Ra	^{228}Th	^{40}K	Ra_{eq}	H_{ex}	D	AED
MS1	5	59.0±51.0	53.7±45.3	109±98	57.1±50.3	55.6±63.8	64.2±54.2	311±398	-	-	-	-
MS2	2	33.2±1.6	28.3±6.6	48.5±15.7	61.7±5.74	85.9±1.57	82.1±10.8	899±55.6	-	-	-	-
MS3	2	462±61	456±30	451±40	4390±1420	5380±1270	5540±1160	660±724	-	-	-	-
Average phosphate and mineral sands (excluding impounding)												
AVE		41.6	45.5	107	105	74.1	106	366	216	0.58	95.3	0.12
STD		33.2	32.9	92	131	51.8	114	333	914	0.52	82.3	0.10
Gold mines												
GM1	7	145±27	216±72	61.8	53.5±7.4	61.1±14.0	55.3±14.5	684±92	-	-	-	-
GM2	6	158±85	123±60	132±104	26.4±9.5	34.1±7.3	32.5±14.0	185±62	-	-	-	-
GM3	6	95.9±37.7	135±90	70.6±26.5	35.3±12.4	56.4±27.9	47.0±13.8	213±177	-	-	-	-
GM4	5	439±139	230±112	170±44	16.1±3.8	23.0±7.7	18.0±8.9	170±69	-	-	-	-
GM5	7	25.1±5.4	27.8±9.9	-	12.7±4.5	16.5±9.5	17.2±7.3	112±85	-	-	-	-
GM6	4	217±129	385±326	300±260	37.1±5.9	47.8±29.5	50.3±16.8	250±164	-	-	-	-
GM7	5	33.9±8.6	34.8±9.9	-	17.3±4.5	21.6±9.5	22.2±8.3	142±37	-	-	-	-
AVE		156	155	161	28.4	38.7	34.3	283	229	0.62	106	0.13
STD		150	153	140	15.9	22.9	19.0	230	181	0.49	84	0.10
Range all sediment samples												
		5-667	2-777	7-776	3-5842	3-6280	4-7020	5-1170				
Range all sediment samples (excluding impounding dams)												
		5-667	2-718	7-553	3-552	3-169	4-484	5-938				
World Average												
		35(17-60)			30 (11-64)			400(140-800)	370	-	59	0.07

Table 5-31: Comparison of results for cement samples obtained by instrumental and radiochemical techniques; Activities in Bq.kg^{-1}

Sample	Thorium-232 Radiochemical			Thorium-232 Instrumental			Thorium-228 Radiochemical			Thorium-228 Instrumental			Polonium-210 Radiochemical			Lead-210 Instrumental		
CEM 1	22.1	±	3.4	13.4	±	1	15.6	±	2.8	19.5	±	4.6	13.5	±	2		<	140
CEM 1	19.7	±	2.6	18.2	±	1	26.9	±	3.1	22.2	±	5	15.9	±	2		<	120
CEM 1	21.5	±	2.9	23.8	±	1.2	25.6	±	3.2	36.4	±	6	14.3	±	2.7		<	140
CEM 1	39.1	±	4.8	34.3	±	1.6	48.3	±	5.3	43.1	±	7.1	47.7	±	4.2		<	130
CEM 1	15.3	±	2.2	11.1	±	0.9	15.1	±	2.1	14.8	±	2.7	59.9	±	4.4		<	120
CEM 1	17.8	±	2.3	17.9	±	1.1	19.5	±	2.3	25.7	±	3.7	15.4	±	2.3		<	78
CEM 1	20.1	±	3.3	11.5	±	0.9	18.7	±	3.1		<	20	18	±	3.4		<	130
CEM 1	15	±	2.9	15.4	±	0.9	34.4	±	4.3	14.7	±	4	18.7	±	2		<	130
CEM 1	31.9	±	4	19.6	±	1.1	34.7	±	4.1	33.4	±	5.3	15.2	±	1.7		<	130
CEM 1	19.6	±	2.6	14.3	±	0.9	21.9	±	2.7	17.3	±	2.9	25.8	±	3.5		<	130
CEM 1	26.7	±	3.4	19.5	±	1.2	32.5	±	3.9	13.9	±	3.4	14.0	±	2.3		<	110
Gypsum	9.98	±	1.96	4.34	±	0.67	13	±	2.2	21.4	±	7.1	42.7	±	3.6		<	120
Gypsum	14.3	±	3.4	12.1	±	0.8	18.1	±	4.1	9.37	±	4.24	105	±	6		<	180
Gypsum	6.03	±	2.46		<	4.2	17.7	±	4.2		<	23	113	±	10	132	±	34
Gypsum	35.9	±	3.5	36.5	±	1.7	27.9	±	3.1	40.9	±	7.1	7.1	±	1.9		<	160
Gypsum	25.5	±	3.4	20	±	1.1	35.8	±	3.9	28	±	3.6	20.6	±	3.7		<	120
Slag	65.2	±	4.6	67.6	±	3.4	76.5	±	4.9	73.8	±	11	16.7	±	2.1		<	140
Slag	84.2	±	5.2	71.2	±	3	95.1	±	5.5	95.5	±	8.8	9.41	±	2.12		<	150
Slag	90	±	4.9	78.5	±	3.2	88.3	±	4.8	97.1	±	8.3	11.8	±	2.3		<	150
Concrete	69	±	6	28.5	±	1.5	47.8	±	5.2	25.9	±	4.2	15.2	±	2.2		<	110
Concrete	93	±	5.8	64.1	±	2.8	99.2	±	6.1	62.9	±	6.3	81.7	±	6.5	67.6	±	23
Concrete	44.4	±	3.9	33	±	1.7	49.3	±	4	35.9	±	4.9	20.6	±	4.5		<	110
Concrete	46.9	±	5.2	26.4	±	1.5	60.2	±	5.8	25.3	±	4.3	29.5	±	4.1		<	130

Sample	Thorium-232 Radiochemical			Instrumental			Thorium-228 Radiochemical			Instrumental			Polonium-210 Radiochemical			Lead-210 Instrumental		
Fly-ash	166	±	14	161	±	6	175	±	14	177	±	11	192	±	10	148	±	33
Fly-ash	178	±	12	164	±	6	186	±	12	173	±	13	236	±	12	181	±	35
Silica Fume	2.8	±	1.25	2.72	±	0.56	6.05	±	2.1		<	30	121	±	7		<	200

Table 5-32: Summary of results for samples from the building industry: Activity concentrations and radium equivalent activities (Bq.kg^{-1})

	Bricks	Cement	Ceramic	Concrete	Gypsum	Fly-ash	Phospho gypsum	Plaster board	Sand	Slag	Silica Fume
n	7	11	1	11	68	30	57	3	1	4	1
^{238}U	53.1-142	5.03-38.3	779±15	23.7-59.6	4.96-322	98-246	3.63-69.6	-	28.9±5.6	-	< 6.1
^{230}Th	-	16.6-98.4	-	42.3-85.6	24.3-110	-	-	-	-		28.8±3.8
^{226}Ra	57.7-157	10.5-56.1	710±18	24.9-74.1	**29.9-836**	35-237	**52.9-153**	67.7-92.5	96.8±5.1	132±23	**47.4±8.7**
^{210}Pb	-	-	817±57	67.6-181	45-217	63-320	64-165	-	225±29		< 200
^{210}Po	-	13.5-59.9	-	15.2-81.7	7.1-113	-	-	-	-		**121±7**
^{232}Th	19.8-29.8	15-39.1	200±3	22.8-93	4.87-164	11.0-212	4.04-116	-	9.49±1.83	77±12	2.82±1.25
^{228}Ra	20.4-31.8	11.2-40.6	180±13	26.3-75.6	**6.3-531**	87.5-260	**16-464**	52.2-85.8	12.6±4.1		**57.5±13.6**
^{228}Th	19.8-36	15.1-48.3	166±10	30.1-99.2	4.2-331	20-254	25.9-471	75.1-95.3	5.50±1.53		6.05±2.12
^{40}K	117-236	84.5-362	<130	42.4-189	40-109	50-438	39-195	73-191	54.6±21	193±76	599±79
Ra_{eq}	117±26	67±27	996	125±25	214±123	370±114	151±39	197±27	115	256±34	98
I_γ	0.41±0.09	0.24±0.1	3.4	0.43±0.12	0.73±0.42	1.3±0.4	0.52±0.14	0.68±0.1	0.39	0.9±0.1	0.37
^{226}Ra/^{238}U	1.01	**1.48**	0.91	1.13	**6.2**	0.96	**6.2**	-	**3.6**	1.03	**3.9**
^{228}Ra/^{232}Th	1.04	0.88	0.90	1.00	**2.6**	1.18	**5.3**	-	1.3	**1.47**	**20.5**

**Using Ra-228 and not Th-232 in Leningrad formula: Ra_{eq} = 347±210 for gypsum; 383±164 for phosphogypsum*

Table 5-33: Summary of results for solids from the mineral sands and zircon industry [Activity in Bq.kg^{-1}; Dose in mSv.a^{-1}]

Product	n	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{228}Ra	^{228}Th	AED
HMC, products, tailings	11	4510±1810	4020±1530	2890±2180	2430±1130	2550±1260	2550±1260	1.20±0.51
Ilmenite	6	203±119	170±94	322±121	476±282	410±232	413±246	0.12±0.07
Gypsum	3	280±95	240±122	400±190	979±319	699±258	831±345	0.21±0.09
Slag	4	44±12	37±11	<120	63±21	68±28	66±19	0.02±0.01
Quartz	4	3230±990	3190±1240	1840±1350	1230±430	1310±451	1260±380	0.75±0.25
Fumed silica	2	2270±1610	6130±750	6370±2350	105±74	136±58	833±65	1.03±0.11
Zirconia	4	4860±690	2180±770	<75	224±32	719±71	375±116	0.43±0.12
Zircon	6	7870±1620	7540±2200	4750±3770	4790±1180	5740±2120	5480±2030	2.34±0.73
Monazite	9	3910±2050	4980±2920	4950±2890	56100±30500	81200±58300	77300±54100	12±9

Table 5-34: Summary of results for solid samples from the phosphate industry (Activity in Bq.kg^{-1}, AED in mSv.a^{-1})

Product	Data	n	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{228}Ra	^{228}Th	Ra_{eq}	AED
Phosphate rock	D-10	4	122-137	97-131	100-214	483-527	459-534	517-594	830-875	0.43-0.46
Phosphogypsum	D-5	55	3.63-69.6	53-153	64-165	4.04-70	16-464	26-471	70-265	0.03-0.14
									*96-831	*0.05-0.43
Fertilizer SSP	D-10	3	85-98	55-90	79-100	316-327	233-313	311-343	508-558	0.27-0.29
Fertilizer MAP	D-10	3	215-202	36-60	<110	343-410	<120	270-327	490-586	0.25-0.30
Scale in plant	D-10	3	7-232	15-229	5280-7640	35-2450	51-643	36-1050	111-3528	0.06-1.82
Tailings and waste	D-10	7	11-91	13-76	<130	13-92	31-114	8.3-100	88-183	0.03-0.11
Soil	D-8	3	12.7	4.6	9.52	10.2-19.8	12.2	12.4	41-83	0.01
Sediment	D-7	13	5.75-92	12.7-100	63-280	7.02-552	29.9-164	17-484	27-502	0.015-0.26
Sediment **	D-7	2	155±35	662±162	770±9	5190±860	3060±60	5250±2490	8110±1390	4.2±0.7

**using ^{228}Ra and not ^{232}Th in calculation; **from impounding dam*

Table 5-35: Summary of results for water and food products from the phosphate industry (Activity in mBq.L^{-1} (water), Bq.kg^{-1} wet weight (food) and Dose in mSv.a^{-1})

Product	Data	n	^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Po	^{232}Th	^{228}Th	Dose
WATER										
Surface water 1	D-12	7	46.2±29.9	85.5±32.4	39.0±35.8	3.5±3.4	4.4±4.9	7.2±8.3	5.5±2.9	0.013-0.070
Surface water 2	D-12	6	46.8±17.3	83.8±26.3	63.3±92.9	4.6±3.9	1.9±2.8	8.1±14.0	5.9±4.9	0.016-0.079
Surface water 3	D-12	6	63.7±10.7	109±54	41±20	7.4±6.1	5.2±6.8	5.8±6.1	9.4±4.4	0.022-0.046
Surface water 4	D-12	4	30.0±7.3	47.1±7.7	20.0±8.6	3.4±2.8	4.7±5.0	6.3±4.3	8.1±4.2	0.017-0.049
Borehole 1	D-12	5	23.6±13.4	67.3±31.1	22.2±12.6	16.6±4.0	6.0±5.6	5.8±4.9	14.5±13.1	0.024-0.063
Borehole 2	D-12	5	40.4±17.9	96.2±47.6	37.3±33.6	2.9±0.7	6.7±8.7	6.2±4.1	10.1±12.1	0.013-0.057
Borehole 3	D-12	5	80.4±83.2	77.3±59.1	45.7±44.7	6.8±3.4	3.1±1.9	8.9±15.9	8.0±3.8	0.022-0.095
Borehole 4	D-12	6	56.9±22.2	183±108	40.2±20.5	5.7±1.9	2.4±2.0	10.7±12.8	5.5±1.5	0.017-0.061
Impounding dam	D-12	6	6180±2190	5760±2490	2750±1480	791±1050	658±549	8830±4900	7920±4780	
FOOD										
Fish 1	D-4	7	0.013-0.198	-	-	<0.56	0.28-1.48	-	< - 0.549	0.038-0.076
Fish background	D-4	9	0.066-0.112	-	-	<0.72	0.63-3.17	<		0.032-0.21
Fish discharge point	D-4	5	0.037-0.157	-	-	<	2.21-6.60	<	<	0.13-0.34
Crab/Crayfish	D-4	2	0.066-0.112	-	-	0.702	8.1-10.8	<		0.33-0.46
Chicken/Meat	D-4	5	0.011-0.078	-	-	<	0.18-0.98	<		0.10-0.12
Vegetables	D-4	5	0.007-0.03	-	-	<	0.025-0.36	<		0.008-0.048

Table 5-36: Summary of results for solid samples from the gold mining industry (Activity in Bq.kg^{-1}, AED in mSv.a^{-1})

Product	Data	n	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{228}Ra	^{228}Th	Ra_{eq}	AED
Soil	D-8	24	38.9±6.9	42.6±17.5	77.0±28.5	19.7±3.9	21.0±5.6	22.2±6.3	38.1-135	0.03-0.08
Sediment	D-7	40	156±150	155±153	161±140	28.4±15.9	38.7±22.9	34.3±19.0	33.8-811	0.02-0.46
Waste rock	D-9	32	36.9±17.3	34.8±20.5	73.9±47.0	15.1±5.09	18.5±7.23	15.2±5.35	44.3-147	0.03-0.08
Tailings	D-9	49	338±160	349±185	467±245	23.3±8.53	23.7±14.5	22.2±9.35	86-867	0.05-0.49

Table 5-37: Summary of results for water and food products from the gold mine industry (Activity in mBq.L^{-1} (water), Bq.kg^{-1} wet weight (food) and Dose in mSv.a^{-1})

Product	Data	n	^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Po	^{232}Th	^{228}Th	Dose
WATER										
Surface	D-13	59	1920±2810	1720±2470	73.3±81.6	79.8±99.2	12.8±11.0	13.8±13.6	12.4±8.2	0.022-0.890 (0.197)
Surface *	D-13	44	648±659	618±595	73.2±78.1	51.4±74.5	7.3±10.1	14.4±13.9	12.4±8.1	0.026-0.218 (0.121)
Ground	D-13	14	41.5±19.5	150±106	49.6±20.7	5.22±4.82	8.22±5.50	14.4±15.0	11.1±10.8	0.021-0.100 (0.053)
Drinking	D-13	13	47.8±31.2	91.7±84.0	44.3±25.9	8.30±15.3	11.6±9.91	17.2±15.1	8.48±5.66	0.010-0.132 (0.068)
Process	D-13	40	6610±3180	5950±2880	119±278	203±84	20.8±18.9	12.7±9.83	13.1±9.4	0.069-0.970 (0.557)
FOOD										
Fish	D-4	11	0.13-**3.02**	-	-	0.35-**4.38**	0.21-0.99	<	0.03-0.64	0.012-0.48 (0.09)
Meat	D-4	11	0.014-0.045	-	-	0.32-0.33	0.12-**3.87**	<	<	0.062-0.75 (0.30)
Leafy	D-4	12	0.004-0.289	-	-	0.39-0.92	0.09-**1.12**	0.06-0.40	<	0.017-0.39 (0.12)
Root	D-4	12	0.058-0.714	-	-	0.51-0.98	0.23-**2.11**	0.01-0.20	0.02-0.20	0.097-0.16 (0.11)
Cereal	D-4	16	0.004-0.096	-	-	<	0.47-**2.6**	0.040.32	0.02-0.37	0.008-1.8 (1.11)

**excluding sampling point GS6, GS8; Dose – average in brackets*

Chapter 6 CONCLUSIONS AND RECOMMENDATIONS

In this chapter the specific aims of the study are reviewed to present an overview of the major findings of this study. Conclusions are added to those already made in all other chapters. Recommendations for further work are also given.

6.1 General conclusions

The objective of the study was to investigate how radiometric techniques can support NORM industries to comply with regulations in order to minimize the radiological impact on humans and the environment. The focus of the presented work was on the analytical techniques, measurement and the results obtained, but also gave some indication of the radiological impact of NORM industries in South Africa, how they contribute to radioactivity in the environment and how this can be accurately measured and assessed.

In general it can be concluded that most of the results presented in the case studies for NORM industries indicated insignificant risk to humans and the environment. However, some "hot-spots" were identified, which may be of concern. Further monitoring and evaluation of radiological risk in these areas are recommended.

6.2 Radio analytical techniques

In line with the main objectives of the study the implementation of suitable radiometric techniques were investigated and advantages and limitations discussed. Attention was paid to the required sensitivity of the measurement to obtain meaningful results. Since cost effectiveness is clearly an important factor in the choice of analytical methods, and the cost of analysis often increases with the sensitivity required, the analytical capability only needs to be sufficient for comparison with a level as appropriate. Adequate confidence in the results of the analysis is ensured if samples are analysed at an accredited laboratory, such as RadioAnalysis.

Radioactivity in the samples used in the study were analysed using radiometric techniques including gross alpha/beta counting, non-destructive techniques such as NAA and gamma spectrometry, as well as alpha spectrometry. The method performance parameters indicated suitability of the implemented methods for quantification at levels well below internationally

accepted limits. Radiochemical separations, followed by alpha spectrometry, were required for quantification of some nuclides in order to reach the required level of sensitivity.

The results demonstrated that it was adequate to perform gross alpha-beta counting for screening of the total radioactivity, but that it had limited value for determining the actual radioactivity content in samples. Screening results was used to detect trends in data and to give an indication of the radionuclide composition, which was useful in deciding upon subsequent analytical steps. The radiochemical methods were adequate for determination of individual nuclides of interest at a level of 0.005-0.01 $Bq.L^{-1}$ with a precision and accuracy of better than 20%, which met the demand for more sensitive radiometric techniques for lower maximum limits in radioprotection regulations. Since these methods are complex, time-consuming and costly, the determination of gross alpha/beta activities is recommended for screening purposes.

In most ores, the natural decay series are often in equilibrium. In such cases, any radionuclide within the chain can be the target of the analysis. As was shown in some of the case studies, equilibrium between the nuclides within the decay series may be disturbed as a consequence of physical and chemical processes in the extraction of minerals and concentrates from the ore. Accordingly, it was important to analyse the individual radionuclides of these series and not only the parent nuclides. The analytical methods summarized in 4.12 were demonstrated to be suitable for analysis of the solid samples. The behaviour of the volatile elements ^{210}Pb and ^{210}Po in some of the industrial processes were difficult to evaluate due to the high detection limit of the gamma spectrometry technique used for analysis of solid samples.

It was demonstrated how incorrect and insensitive analytical methodology could result in incorrect conclusions, usually leading to over-estimation of the dose and impact of the industry. The use of broad energy gamma spectrometry for measurement of ashed samples greatly improved the LOD of the instrumental techniques for analysis of foodstuff. However, to prevent overestimation of dose due to a high LOD, nuclides such as ^{230}Th and ^{210}Po had to be analysed by radiochemical separation after microwave digestion.

Development of a “Best Practise Document” for NORM industries, including sampling methodology and analysis, is recommended. Analysis should always be done with the objective in mind *e.g.* is full nuclide analysis necessary or will screening provide sufficient information? Unfortunately the high cost of radionuclide analysis does not always allow

sufficient samples to be collected and analyzed to provide adequate statistical confidence in the results. However, any conclusions based on limited data and single grab samples must always be interpreted with caution.

6.3 Radioactivity at NORM industries in South Africa

Analytical data for environmental samples obtained from routine monitoring programmes of NORM industries were used to evaluate the potential impact of the industries in South Africa by application in several case studies. The ERICA tool was used to assess the radiological risk to biota, but the main emphasize was on the impact to humans. For this purpose the pathways of internal ingestion and external gamma dose radiation were considered, as well as some secondary pathways such as consumption of meat and milk of cattle grazing on contaminated crops.

Solids from NORM industries

It was not the intention of this study to do an in-depth radiological impact assessment of NORM material. The case studies provided merely served the purpose to illustrate the proposed analysis and evaluation protocols. Samples submitted by industries, radiation protection specialists and other interested parties were used in this study.

It must be emphasized that the activity concentrations may differ from batch to batch and that the materials chosen in some of the case studies may not be representative of materials obtained from other similar NORM industries in South Africa. It is therefore advisable to monitor the radioactivity levels of materials from any new source.

The results presented for solids gave an indication of the distribution of natural radionuclides associated with solids from different NORM industries in SA. In general, results obtained were comparable to studies undertaken in other countries. As long as activity concentrations remained below 500 $Bq.kg^{-1}$, the reference dose level of 1 mSv per year was not exceeded. Higher activity concentrations observed in solid samples from some industries *e.g.* mineral sands was found to be of limited concern to the public.

Based on the results presented in this study for selected samples of building materials and constituents used in the manufacture of cement, it was concluded that the industry can be exempted from nuclear regulatory control in South Africa, even though some raw material

(slag, fly ash) exceeded the recommended exemption levels for exposure. It was found that the materials analysed was safe for use as construction material and do not present a significant radiation risk. The results presented for selected samples from the phosphate industry also suggested that it was unlikely for any member of the public to receive a significant dose from the use of phosphate rocks for fertilizer production.

Essential basic data were provided for radiological risk assessment of Coal Fired Power Plants (CPPs), which are not currently regulated in South Africa. Since the activity concentrations in fly ash and coal samples were all lower than the 500 $Bq.kg^{-1}$ exemption limit set by the NNR, it was found not to be a source of alarm. Natural radioactivity in coal samples was not significantly higher than in soils and rocks and of the same order of magnitude as in other parts of the world, whereas fly ash showed some enrichment, again similar to the trend observed in worldwide studies on coal and ashes. Utilization of fly-ash as an additive in cement should be possible without any special restrictions based on the regulations dealing with building material in the European directive.

Environmental media

The results for environmental media showed elevated concentrations compared to the baseline data in some areas. However it is the opinion of the author that the situation in some regions has approved compared to values reported in literature studies and that industries are controlling releases and taking care of the environment.

Measured soil concentrations from all areas were similar to background, whereas some sediment samples showed enhanced concentrations. In the phosphate industry concentrations of the Th-series nuclides in sediment from the impounding dam was high. Although not of concern at the moment due to restricted access, these areas can be of concern in future if proper measures are not taken to clean and remediate the site once operations have stopped. On average the concentrations in sediment and tailings samples from the specific gold mine area investigated did not exceed the 500 $Bq.kg^{-1}$ exemption level and no urgent countermeasures are required. The radiological impact may become important if new uses for these areas are considered, such as the integration of rehabilitated footprints into residential areas, mainly because of indoor radon risk. Guidance levels for exemption imply unrestricted use of the areas when the concentration of each individual nuclide is less than 500 $Bq.kg^{-1}$, which was the case for most of the analysed sediment and tailing samples.

Data on the radiological quantity of various water sources in SA were presented, and the water quality evaluated with reference to South African national standards and international limits. The results presented are important since data on radioactivity in drinking water in SA is relatively scarce. In water impacted by mines the ratio of $^{234}U/^{238}U$ was found to be equal to one, whereas in environmental groundwater the concentration of ^{234}U was found to be higher than ^{238}U up to a factor three. Measurement of only ^{238}U was shown to result in an underestimation of the total U activity in these water samples with observed disequilibrium. However, for surface water sources from the DWS study future radiological assessment may only require determination of the chemical concentration of uranium, based on the correlation found between the U concentration and gross activity.

The bottled water analysed was radiologically safe and posed no significant hazard to the consumer. For the majority of DWS water sources the screening results indicated good or ideal quality water, with only some radioactive "hot spots" indicated for which future monitoring should include nuclide specific analysis. Dose assessment based on nuclide specific analysis of environmental surface- and groundwater showed that the radiological quality of most of the sources was good resulting in a dose of less than 1 $mSv.a^{-1}$ if consumed. Water from six sites exceeded the NNR dose constraint of 0.25 $mSv.a^{-1}$ and might have health effects to the most sensitive age group (infant) if used for domestic purposes. The quality of water from mining- and NORM industries varied, with fairly high activities measured in some surface water samples from the gold mine areas, indicating a possible radiological health risk from ingestion of this water, which was clearly impacted by process water. However, for the majority of sources from other industries the results indicate insignificant levels of public exposure and suggest only limited radiological impact of the industrial activities on communities in the area. Even if no intervention is required, in terms of the ALARA principle, mines and other industries should continue to limit the discharge of water containing unacceptable levels of radioactivity.

For the majority of analysed foodstuffs it was concluded that the industrial activities did not have a significant impact; there were however some exceptions which should be further investigated. The estimated dose for adults was well below the "single facility" dose constraint of 0.25 $mSv.a^{-1}$. For many samples where the dose limit was exceeded it could be explained by either poor sensitivity of the analytical technique resulting in high LODs, assumption of equilibrium for some nuclides with high DCF that were not measured (*e.g.*

^{230}Th and ^{210}Po) or unrealistic high consumption rates used in the dose estimation. The high activity concentrations measured in some samples cannot be ignored since it might indicate contamination in some areas. More work has to be done to determine the impact of the specific NORM industries. The activity concentrations of ^{210}Po in food confirmed that ingestion of food is an important route for intake of this nuclide.

For the gold mine area that showed some increased concentrations of radionuclides in water and foodstuff, it was concluded that no member of the public is expected to be exposed to any significant dose. If release of mine effluent is controlled and access to contaminated surface water restricted, the potential effective dose received from the most likely pathway of drinking water and consuming vegetables irrigated with contaminated water is within the internationally set dose limit of 1 mSv.a^{-1}. If dietary restrictions with respect to intake of fish and cereal are taken the dose is reduced to less than the 0.25 mSv.a^{-1} dose constraint.

6.4 Dose assessment models

A caustic approach is used in dose assessment models, whereby values are selected so as to deliberately overestimate exposure. Overestimation due to conservative assumptions are usually not communicated to the public, leading to unnecessary concern, *e.g.* is it reasonable to assume that residents will obtain all their regular drinking water from a contaminated sources close to a mine residue deposit? As shown in the case studies the choice of modelling parameters can have a huge impact on the results. Discrepancies were observed between measured and modelled value. The parameters suggested for use by the NNR for assessments were in most cases found to be conservative.

It is recommended that site-specific parameters are collected where possible and that the values in RG-002 are adjusted accordingly. The ability of the radio analytical laboratory to provide accurate and reliable data at the required sensitivity level in a timely fashion is essential for this purpose. For example, enough experimental data for dry-wet ratios for food were presented in this thesis to be used to update the RG-002 values. There is also a need for studies on radionuclide transfer to specific plants grown in the areas of the NORM industries since there is a lack of data for transfer factors relevant for SA (RG-002 uses IAEA derived values). These studies should be conducted under controlled experimental conditions in collaboration with concerned farmers in affected areas. Until specific data becomes available for SA a more accurate approach will be to measure the activity concentrations in biota rather

than to use default values in models to predict the activity concentrations.

Another important parameter in models predicting environmental behaviour of natural nuclides is the K_d value. The case study presented showed good comparison of the measured K_d with theoretical values, but more detailed experimental work is required. The study confirmed higher mobility of U compared to Ra, Pb and Th and confirmed that uranium in solids is bio-available and can be leached under acidic conditions.

6.5 Radiological impact on biota

At the international level, the ICRP has established a framework for radiological assessment and protection of biota. National guidance in this regard is still lacking in South Africa. To facilitate the implementation of the ERICA tool for evaluating the potential radiological impact on biota in proximity to NORM industries in South Africa, more research is required. This will require extensive sampling and radioactivity measurement of biota and environmental media to address current data gaps.

Some aspects of the application of modelling tools for dose assessment to biota were presented in the case studies. Hopefully this will initiate some scientific effort in this regard and support activities of the planned radio-ecology study group under direction of the NNR. For application of the ERICA tool measurement of environmental media and biota from the local environment will be required to reflect the South African situation, which is not necessarily addressed by defaults organisms in the model. The support of the radio analytical laboratory is important for this.

6.6 Regulations

NORM industries in South Africa are well regulated, operating under a Certificate of Registration issued by the NNR, and optimizing practises to keep dose ALARA. Industries are assuming responsibility and control releases to the environment. The results presented suggested that it was unlikely for any member of the public to receive a significant dose from any of the NORM industries, since most of the measured concentrations in the solids were less than the 500 $Bq.kg^{-1}$ exemption level. The high concentrations measured in some of the products confirmed the need for continuous control and monitoring of the industry, especially where by-products are utilized elsewhere. The most appropriate regulatory option remains authorization in the form of a CoR. Under this condition the authorized industry conducts

routine plant operations in a manner aimed to limit exposure in the workplace, protect the environment and keep dose to the public below levels of concern.

Where the dose constraint of 0.25 $mSv.a^{-1}$ was exceeded, it must be kept in mind that dose constraint is not dose limit, and exceeding the dose constraint does not represent non-compliance with regulatory requirements. According to the ICRP principle of optimisation doses should be kept ALARA, but always keeping in mind the economic and social impact. NORM industries that cannot be ignored from a regulatory protection point of view should be identified, but it must be noted that inappropriate selection of criteria could result in many industries being regulated without any benefit in terms of reduced radiation risk. The current exemption level in SA is lower than the internationally recommended value of 1000 $Bq.kg^{-1}$. This more restrictive conservative level may restrict and complicate international trade, for which an international harmonized approach is required. The ultimate decision for exemption should be the 1 mSv dose criterion and not the activity concentrations in the material *per se*.

In the European Union, all listed NORM industries is subject to notification, including cement production and coal fired power plants. These industries are not currently regulated in SA. Implementation of regulations to the building industry should be carefully considered, since it can result in unnecessary work for the regulator and have financial implications for manufacturers. As per the international trend, restrictions should not be applied to the use of any building material, without considering the ventilation rates and dilutions when mixing and preparing the final building material such as cement. High concentrations of radon inside buildings are not normally expected in South Africa due to the warm climate and high ventilation rates. If regulations similar to the EU-BSS are to be imposed on the building industry in South Africa, cost effective techniques for the measurement of activity concentrations will be required to support the building industry in the determination of the ACI. Measurement may especially be required in case of the "risk" material *i.e*. slag and fly ash. As demonstrated in this thesis our laboratory has the capability to perform such measurements.

According to international legislation exemption values (of 1000 $Bq.kg^{-1}$) do not apply to drinking water, foodstuffs and existing residues in the environment, and separate standards and guides exist for these materials. There are currently no specific standards in SA for radioactivity in food and drinking water. As shown in the results for water samples,

regulations are not always easy to implement and may be interpreted in many ways. DWS guidelines are fairly strict and limit dose to < 0.1 $mSv.a^{-1}$ for ideal quality water. It is recommended for evaluation of water sources to be aligned with international WHO or EU-BSS standards.

6.7 Recommendations

The focus of any radiological assessment should be on the radiation exposure induced by an industry, above natural background radiation. Knowledge of the environmental conditions prevailing at proposed mining sites before start of operations is therefore essential. Unfortunately there is a lack of baseline data for many of the NORM industries in SA. It is therefore important that a baseline radiological survey of a site is conducted before commencement of any new projects, which may have a potential radiological impact on the environment, to assess the site's existing environment.

Generally there is a lack of published data on radioactivity resulting from NORM industries in South Africa. Results in the public domain are scarce, especially in case of commissioned research by companies or consultants. Information from similar studies conducted in other countries worldwide is much more freely available. In the opinion of the author SA authorities should encourage a more open approach and allow presentation of results from radiological studies and public impact assessments on worldwide platforms. In particular the issue of data confidentiality is interpreted very differently by various government departments. Because of the sensitivity of the topic of radioactivity, the results in the thesis had to be presented in a very neutral manner. The few cases where data was presented with an open approach were only where samples were received from independent parties (*e.g.* farmers, universities).

There are often sensational claims in the press with regard to radioactive contamination in the environment, which are not necessarily accurate. Unfortunately, since data are not available and/or easily obtainable there is not always enough factual information available to proof the opposite. NORM industries can "clear" the air by being more open about results obtained. Public access to similar data as presented in this thesis will help to provide more clarity and transparency. Even where contamination is real, the public has the right to be informed and to be provided with scientific data.

No database on natural radioactivity in the environment in SA is currently available and data of Southern Africa in international databases compiled by UNSCEAR and the IAEA are very scarce. In this regard the study conducted by the DWS as presented in the thesis, are of much value in adding to a national radioactivity database. Due to budget limitations monitoring programmes similar to that of the DWS are not conducted nationally for food.

Although the author does not disagree with the general findings about the occurrence of contamination in some areas, it was my impression that some of the published reports tend to focus on isolated investigations of selected sites with "hot spots" of pollution, thereby adding to public concern. In some of these reports the published results were based on a single measurement only, which might well have been explained by inaccurate measurement or measurement with an inappropriate insensitive technique, as discussed in the thesis. I fully agree with the opinion of Winde (2013) that "serious misjudgement of associated risks can occur from wrong data with serious implications on consumers". With regard to the Wonderfontein Spruit catchment area newspaper articles claimed, for example, "that thousands of cattle had to be shot because of pollution, that exposure to dust while driving through the area could lead to cancer and that extreme levels of U were found in vegetables grown in the area". Not all of these reports were based on scientifically sound results. For example, when quoted by activists and the press it was never mentioned that the reports were based on a very small data pool. To suppress unrealistic fears it is important that enough scientific data are published and available in the public domain.

In this regard it should again be emphasized that no evaluation should be based on results from a single grab sample, but that an effort should be made to obtain samples representative of an extended period, as was done in the NRMP of the DWS. Therefore the author has cautioned in this thesis where single results were presented that it should be interpreted as giving an indication of the true assessment only.

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