Determination of tritium (^3H) and radiocarbon (^{14}C) levels in groundwater using alpha/beta spectrometry

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I would also like to thank my family and friends for their support and words of encouragement throughout my study.

ABSTRACT

With the current state of water scarcity in Mahikeng due to the low water levels, increasing population and increased demand for fresh water supply, it is therefore crucial to ensure the sustainability and availability of the available water resources such as groundwater (borehole) by making sure that these resources are protected and well-managed. Hence it is important to study water quality, contamination and flow dynamics. In this study, the levels of tritium and radiocarbon were determined using the Perkin Elmer Ultra low liquid scintillation counter 2000.

The mean activity concentrations for groundwater samples with analysed for tritium in different villages in Mahikeng were as follows; 3.61 ± 0,01 Bq/L for samples from Dibate, 386 ± 0.01 Bq/L for sample from Lokaleng and 1.83 ± 0.02 Bq/L for samples from Moletsamongwe, Lekung, Airport view and Seweding. The mean activity concentrations for groundwater samples with analysed radiocarbon in different villages in Mahikeng were as follows; 0.59 ± 0.01 Bq/L for samples from Dibate, 0.83 ± 0.01 Bq/L for sample from Lokaleng and 1.38 ± 0.02 Bq/L for samples from Moletsamongwe, Lekung, Airport view and Seweding. Out of the 30 samples analysed for radiocarbon, 2 of the samples were below the minimum detectable activity (0.37 Bq/L).

For groundwater samples analysed for ^{3}H, samples from Dibate village had a mean annual effective dose average of 0.05 μSv/y, 0.05 μSv/y for samples from Lokaleng village, while samples from Moletsamongwe, Lekung, Airport view and Seweding had an average of 0.02 μSv/y. The annual effective dose for ^{14}C groundwater samples from Dibate village had an average of 0.25 μSv/y, Lokaleng village had an average of 0.37 μSv/y and the average annual effective dose for ground water samples from Moletsamongwe, Lekung, Airport view and Seweding was 0.58 μSv/y. The lifetime cancer risk for mortality and morbidity in adults was also evaluated and the values for this study were lower than the radiological cancer risk limit of 1.63×10^{-3} set by the United Nations Scientific Committee on the Effects of Atomic Radiation.According to the radiological values recommended by the World Health Organization and other international organizations, these results were within the permissible limits and show that consumption of the studied groundwater by humans does not pose any health risks in terms of tritium and radiocarbon.

This is the first study of tritium and radiocarbon in groundwater consumed in the studied villages in Mahikeng, therefore this will provide a valuable baseline study for future researchers and water resource management experts in Mahikeng.

Key terms Groundwater; Radioactivity; Lifetime cancer risk; Cancer mortality and morbidity; Annual effective dose; Human consumption; Tritium; Radiocarbon; Radio-pollution.

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LIST OF ABBREVIATIONS

AED	Annual Effective Dose
Bq/L	Becquerel per litre
CARST	Centre for Applied Radiation Science and Technology
CPM	Counts per Minute
CPS	Counts per Second
DC	Dose Coefficient
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
DPM	Disintegrations per Minute
DPS	Disintegrations per Second
GPS	Global Positioning System
HEA	Hypothetically Exposed Adult
HTO	Hydrogen Tritium Oxide
ICRP	International Commission of Radiological Protection
LD	Limit of Detection
LSC	Liquid Scintillation Counting
LT	Lifetime average
LTCR	Lifetime Cancer Risk
MCA	Multi-Channel Analyser
MDA	Minimum Detectable Activity
OBT	Organically Bound Tritium
PSA	Pulse Shape Analyzer
UNSCEAR	United Nations Scientific Committee on the Effects of Atomic Radiation
USEPA	United States Environmental Protection Agency
WCR	Water Consumption Rate
WHO	World Health Organization

CHAPTER 1 INTRODUCTION AND PROBLEM STATEMENT

1.1 Introduction

The Earth consists of about 30% arid or semi-arid region, where there is a low rainfall. In these regions, groundwater is often the only water source that is reliable but due to the low rainfall, these environments may be subjected to intermittent surface runoff. Arid/ semi-arid regions may become more drier due to the ongoing drought and extreme weather conditions in many parts of the world including South Africa (Herczeg and Leaney, 2011). As a result, developing countries like South Africa, tend to face scarcity of good drinking water. An estimated 884 million people in the world especially in developing regions still do not get their drinking water from approved sources.

With the rapid increase in South African population, the need for clean water is also escalating. Some places, like towns/cities in the North West province are already facing the issue of water shortages because of extreme weather conditions such as warmer temperature and lack of rainfall (Mussá et al., 2015) . The North West Province of South Africa gets most of its water from ground water resources. However, groundwater quality is greatly affected by natural processes and man-made activities. These two factors can affect the groundwater negatively which could lead to the shortage of available clean water. For the social and economic development of the semi-arid parts of South Africa, one of the most important and critical aspects is water resource. The lack of enough distribution network and weak treatment facilities together with high evapo-transpiration, which exceeds precipitation, are a few of other challenges to achieving the developmental target of providing potable water supply (Abubakar and Adekola, 2012).

Water is essential to humanity because it plays a major role in human activities including drinking, industrial, agriculture and recreational purposes. It is therefore a priority to supply the population with clean water, whether the water is surface or groundwater, because the quality of water supply can affect the human health (Olorunfemi et al., 2013). Health due to water quality is determined by many factors which may include financial status, ecological conditions like access to adequate sanitation and safe drinking water supplies, behavioural change and availability of health services (Nkamare et al., 2012).

Groundwater has a history of neglect and unsustainable utilization in South Africa. Despite the latest developments in policy, and the importance of groundwater as a strategically significant resource on which many rural areas rely, water management in South Africa remains largely dependent on the surface water systems. The protection of water resources in South Africa is often neglected. This is supported by numerous pollution occurrences and failure to deal with the serious acid mine water drainage (AMD) question. Protection measures were developed but these approaches were not implemented at a national scale (Pietersen et al., 2011).Groundwater source is threatened because it flows slowly through the subsoil, hence the anthropogenic activities impact may affect the groundwater for a long time. This means that the pollution which happened decades ago may still threaten water quality at present and, in some cases, will continue to do so for several generations (Enyoh et al., 2018).

South Africa generally, has unpredictable rainfall, high evaporation rates and low conversion of rainfall to runoff. It is a semi-arid country and her average rainfall of about 464 mm per year is well below the world average of about 860 mm per year (Charity et al., 2018). This means that, South Africa is a water stressed country, where demand is fast approaching available supply. This, combined with the rising water consumption, is placing increasing demands on the nation's existing water resources. As the country is slowly reaching the limit of surface water availability, and the demand for groundwater increases, sustainable groundwater management is necessary to ensure that the use of this resource is economically efficient and environmentally sustainable.

Since 1994 most rural communities have been served from groundwater. More than 80% of rural communities in KwaZulu-Natal and North West provinces are getting their water from groundwater sources, and the same goes for more than 50% of rural communities in the Eastern Cape. This access to groundwater is one of the critical factors ensuring sustainable livelihoods in many of these communities (Pietersen et al., 2011). Groundwater has great potential to serve even more communities in those areas where large bulk water infrastructure does not exist, and arid conditions prevail. The importance of a clean and safe ground water source to the North-West province, can never be over emphasized. The North-West province consists mainly of a rural population. This fragile part of the community depends entirely on groundwater as means of livelihood. In many cases, ground water represents the only source of water at their disposal. Furthermore, many rural communities in the North West province depend on groundwater as a sole source of domestic water (Van Wyk et al., 2012).

The North West province, being generally an arid province, with all these water resource constraints, has four districts, such as Ngaka Modiri Molema, Dr. Ruth Mompati, Bojanala Platinum and Dr. Kenneth Kaunda. Ngaka Modiri Molema consist of five local municipalities which are Mahikeng, Ratlou, Ramotshere Moiloa, Ditsobotla, and Tswaing. Mahikeng local municipality is a category B municipality in Mahikeng, situated in the Ngaka Modiri Molema district (Lolwana, 2017). Borehole water is commonly used in the rural areas of Mahikeng which are without municipal water supply. Hence, Mahikeng, is one of several towns in South Africa whose residents especially in rural areas, depend on groundwater resources (Palamuleni and Akoth, 2015).

Mahikeng is the capital city of the North West Province of South Africa with a population growing at a rate of 4.3 % (Materechera, 2018). It is one of the largest and most important groundwater-dependent towns in South Africa. Mahikeng's water demand is about 50 ML/day (18.3 Mm^3/a). About 20 ML/day (7.3 Mm^3/a) of this water comes from the Setumo Dam, on the Molopo river to the west of Mahikeng. Groundwater from the Molopo Eye spring and from boreholes in the Grootfontein aquifer supply the other 30 ML/day (11 Mm^3/a) - roughly 20 ML/day (7.3 Mm^3/a) from the spring and 10 ML/day (3.7 m^3/a) from the boreholes (Cobbing, 2018). Water services are essential to the wellbeing of Mahikeng communities and as such, providing these services requires adequate planning on the part of the relevant authorities to optimise delivery. Even though municipal councils have executive and administrative authority over clean water service, in providing the community with clean water, problems are still arising regarding the management of water purification and cost recovery systems of the Mahikeng local municipality (Mleya, 2016).

When a groundwater body is polluted, the pollution could last for decades, or centuries, because the natural processes of thorough-flushing are so slow. Solutes are transported by the bulk movement of the flowing groundwater, through a process called advection. When a small volume of solute, either a contaminant or an artificial tracer, is released into an aquifer it will spread through advective transport (solute moving with the average velocity of the water) (Konikow, 2011). Furthermore, there is a considerable degree of physico-chemical and chemical interdependence between the water and the containing material.

There are global concerns that the usage of water above permitted limits could result to dire health consequences and o address this concern, water samples are should be analysed and measured against a range of health and non-health based physico-chemical standards. Most of these standards are based on the World Health Organization (WHO) (Adeniyi et al., 2016). The interest in groundwater quality studies, flow dynamics and contamination is increasing because knowing these aspects is crucial for managing and protection of water resources. There are hydraulic connections between water components, which is why it is essential for these studies to be done correctly because the results can affect the next water resource (Mahlangu et al., 2020)

1.2 Environmental Tracers

Environmental tracers make it possible to assess the internal dynamics of a groundwater system and to study the quantity of timescales associated with groundwater flow. The importance of being able to have an understanding and characterizing the sustainability of groundwater as a water supply source for the human race, is increasing along with the population growth and climate change. Environmental tracers that are used for groundwater age determination, can also be used to determine whether shallow aquifers are susceptible to anthropogenic contamination (Banks et al., 2021). Environmental tracers that originate from the atmosphere are broadly used for geographical recharge localization to aquifers and to quantify its average value. The most commonly used atmospheric tracers are chloride and water stable isotopes such as tritium and radiocarbon, which are analysed in this study (Custodio and Jódar, 2016).The interpretation of environmental tracers can provide an integrated estimate of the flow velocity between two given locations, for instance, between a recharge zone and a discharge zone, or between a contaminant source and potential receptors. ^{39}Ar, ^{14}C, ^{36}Cl, ^{2}H, ^{3}H , may be classified under the category of environmental tracers that have an estimable initial activity concentration and a known rate of decay or fractionation (Turnadge and Smerdon, 2014) .

Radioactive and stable isotopes have become powerful tools in the last few decades, they are usually used in groundwater hydrogeology as natural tracers to help solve many issues, such as groundwater management and the exposure of groundwater aquifers to contamination. Evaluation of different isotope composition can be applied to obtain information about the behaviour of the groundwater aquifer, like the origin of the groundwater, the mixing properties and dynamics, the age distribution as well as aquifer processes occurring within the geological structure (Palcsu et al., 2021). It is important to understand water circulation with isotope tracers for the purpose of sustainable exploration of geothermal resource. The tritium radioisotope with a half-life of 12.32 years, is a direct tracer of water movement and is a constituent of water molecule (in the form of HTO) (Chatterjee et al., 2019). In groundwater, tritium is treated as an indicator of radionuclide release from nuclear activities. Tritium concentrations are different in the atmosphere and in the hydrosphere, generally because of atmospheric transport and/or regional man-made sources like nuclear facilities, chemical industries, heating systems that use wood or industries that produce tritium light sources like airport runway lights, luminous dials, gauges and wrist watches, which give off tritium and cause local contamination (Affolter et al., 2020).

Tritium mostly enters the water cycle in the form of tritiated water (HTO). Natural tritium is produced by cosmic radiation that interacts with nitrogen in the upper atmosphere (Juhlke et al., 2020). Tritium an ideal environmental tracer because it can be rapidly transported through environmental pathways and taken up by organisms. During metabolic activities, a portion of the HTO incorporates into the organic molecules, including plant structural material or soil organic matter (Kamath et al., 2019).

The common presence of DIC (Dissolved Inorganic Carbon) has led to the widespread use of radiocarbon (^{14}C) to estimate residence times of groundwater in regional aquifers. Radiocarbon’s ubiquitousness and long half-life of 5730-years, makes it a perfect environmental tracer for different timescales (Han and Plummer, 2016). It is sensitive on both the timescales of thousands of years and recent decades because it is an excess isotope from the 20th century bombing (Seltzer et al., 2021). Cosmic particles lead to the formation of radiocarbon and it is then distributed across numerous compartments in the Earth system. Subsequently, knowing the accurate levels of past ^{14}C makes it possible for new discoveries and provides connections across broad research areas. Thus radiocarbon (^{14}C), as a result of its production in the atmosphere and subsequent dispersal through the carbon cycle, is a key tracer for studying the Earth system (Heaton et al., 2021).

The production of radiocarbon in the atmosphere via the interaction between energetic neutrons created by cosmic radiation and atmospheric nitrogen is continuous. The equilibrium between cosmic ray production and the natural decay process in the atmosphere is relatively constant over time. Upon the death of photosynthetic tissues, carbon exchange with the atmosphere stops and the ^{14}C concentration of dead organic matter is reduced as time passes. Given their geological age, carbonates from sedimentary rocks have effectively a zero ^{14}C concentration. Low ^{14}C concentrations are also observed in other inorganic carbon sources, such as dissolved inorganic carbon (DOC). The ^{14}C concentrations in the hydrological environments are naturally lower than atmospheric levels (Larsen et al., 2018).

In this study, these two tracers were be used to investigate the extent of pollution of groundwater (borehole) from the rural villages in Mahikeng in order to establish the extent of water pollution.

1.3 Groundwater quality assurance

The development and growth of the country's economy is highly dependent on the access to reasonable quantity and quality of water. Regular monitoring of drinking water quality is very important to the public health of developing nations like South Africa, as the majority of the citizens in rural and sub-urban communities depend on individual boreholes and wells for drinking water. Natural sources (wells and boreholes) are increasingly used as drinking water sources in rural areas (Owamah et al., 2021) like the studied villages in Mahikeng. Groundwater quality monitoring helps in- preventing water pollution, monitoring groundwater management plan design and groundwater security. Groundwater systems are very compound, involving various hydrogeological conditions, numerous formation mechanisms, and diverse influencing factors. All must be carefully considered in groundwater quality research (Li, 2016).

Groundwater contamination is a widespread environmental problem, such that it needs long-term monitoring. Groundwater has a large storage capacity and is less subjected to pollution therefore, it has become an important water source for agricultural, municipal, and industrial purposes. Amongst other aspects, human activities pose a threat to groundwater quality. Groundwater requires more attention when it comes to monitoring because although groundwater is less susceptible to pollution compared to surface water, it is difficult to monitor it since it is trapped beneath the ground surface and it is threatened by increased man-made activities (Abioye and Perera, 2019). Usually, quality of groundwater depends on the existence and concentrations of several chemical components, which influenced by the recharge and geological characteristics of the aquifer. A number of trace elements derived from erosion also contaminates groundwater and weathering of rocks, wastewater discharges, mines, agricultural activities, leakage into the groundwater supplies from heavily contaminated areas, and geothermal waters. Even though some trace elements are essential for the human body, high intakes of these elements may result in hostile health effects like; shortness of breath, cancer, hypertension, vascular disease, lung disease, gastrointestinal bleeding, neurological disorder and reproductive effects (Bodrud-Doza et al., 2020).

Humans and other living organisms are at risk if they consume contaminated water (Belle et al., 2021). Good quality water supply is essential for the economic development of a country because water quality is considered the primary indicator of good health. Polluted water threatens human health and productivity (Mpenyana-Monyatsi and Momba, 2012). The increasing population in sub-Saharan Africa (SSA) depends on groundwater for the majority of domestic water supply; therefore, it is of great importance for communities in Africa to gain access to safe and reliable water. This will help in the development of the health status and livelihoods for low-income communities in Africa (Lapworth et al., 2017).

One of the major concerns when it comes to groundwater is contamination by trace elements. Therefore, the use of groundwater as a potential and reliable alternative, depends on the concentration of trace elements, which gets dissolved from the aquifer-bearing rocks through complex hydro -geochemical process. Hence, it is vital to understand these processes considering both current and future possibilities before considering groundwater as a reliable water resource (Gorelick and Zheng, 2015). It is important to analyse the hydro-geochemical characteristics of the aquifer in different seasons in order to demonstrate the mechanism of groundwater evolution in any aquifer system and to understand how groundwater quality changes over time. A lot of methods are presently available to monitor the hydro-geochemical processes responsible for groundwater contamination (Saraswat et al., 2019). These groundwater monitoring programmes are needed to detect trends in contaminant concentrations, to identify elevated and natural baseline concentrations, and to differentiate between anthropogenic and natural sources. The most direct environmental tracers for groundwater dating are tritium and radiocarbon (Morgenstern and Daughney, 2012).

1.4 Problem statement

Water is important for life on Earth, therefore having safe and clean water should be the main concern for sustainable development. Groundwater is a great resource of drinking water, but it appears to be vulnerable to radionuclide pollution. It is also often withdrawn for agricultural, municipal, and industrial uses by constructing and operating extraction wells; however, these human activities are also the main factors of groundwater environmental pollution (Postigo and Barceló, 2015).

Anthropogenic activities affect the water sources on which we all depend. Groundwater is constantly being put under pressure because of the economic developments, emerging needs of the population, and its improper use as a resource. The negligence of handling groundwater has led to the rise in the scarcity of clean drinking water in present time due to water pollution problems (Soni et al., 2020). Negative impacts can vary from the sedimentation caused by poorly built roads during exploration through to the sediment, and disturbance of water during mine construction. The interconnection between different water resource components is defined using isotope studies. In order to ensure that water resource components are available and sustainable they need to be protected and managed correctly, hence the studies on water quantities, flow dynamics, quality, and contamination are important. These water resources have been negatively affected by the population growth, development of the country and a changing climate and the increased demand for fresh water (Mahlangu et al., 2020).

With Africa being the second driest continent worldwide, after Australia. The continent as a whole suffers from what we call acute water scarcity problems, which is the insufficiency or inaccessibility of safe water supplies to the communities. Acute water scarcity problems include water stress which is defined as the inability to meet the water demand of the population and water shortage which involves not having enough quantity of water for a specific biophysical process (Naik, 2017) .South Africa is one of the countries in Africa whereby water scarcity and access to clean water supply is a major concern. Hence the importance and criticality of groundwater as a source of water to fulfil the needs of the human race and provide a long-term water-supply to the growing population should be exaggerated. Groundwater is increasingly being threatened as a result of the emergence of various contaminants that are due to both natural and anthropogenic activities, and the detection of biological agents in the groundwater sources of developed and developing countries (Kurwadkar, 2017). Water management is generally important to ensure the wellbeing and security of humans. In South Africa some of the challenges regarding water management include the lack of rainfall, physical resources that are limited, poor stagnant economies and a fast growing population. Poor rural communities with no access to clean water and proper sanitation are the most affected by these challenges (Molobela and Sinha, 2011).

Currently, the Mahikeng water consumption exceeds the required supplies, meaning water recycling is necessary. This means in order to protect the health of the population in Mahikeng, water treatment must be a priority (Mathuthu and Olobatoke, 2016). It is important for groundwater to be screened and analysed for contaminants such as tritium and radiocarbon to ensure the health and safety of the residents who depend on it for basic needs. Pesticides, heavy metals, and leaching potential of various organic and inorganic contaminants from waste products residuals that are poorly managed might be some of the emerging contaminants. Mining effluent can also have a severe effect on the quality of the country's water resources. Mines can release water into the environment under carefully controlled conditions, but sometimes there are unplanned discharges, for example, seepage from dams or high rainfall, which then releases polluted effluent into rivers and streams (Haggard et al., 2015). Climate change has also attributed to water shortages and droughts in some areas and floods in others around the globe.

This study will provide knowledge on how radioactive isotopes (tritium and radiocarbon) are used as environmental tracers to study the extent of groundwater pollution. The production of tritium and radiocarbon in the atmosphere and how these radioisotopes are incorporated in the hydrological cycle will be reviewed in chapter 2.The radiological impact of tritium and radiocarbon in the environment and in humans will also be reviewed in the literature review in chapter 2.For the purpose of this study, 30 groundwater samples will be collected from 6 villages around Mahikeng, the Perkin Elmer, Quantulus 1220 ultra-low-level liquid scintillation counter will be used to run the samples. The obtained results will then be analysed to determine/calculate the activity concentrations of tritium and radiocarbon in groundwater samples. From the calculated concentrations, the annual effective dose and the lifetime cancer risk to the members of the public can be determined. This will help fulfil the aim and objectives of the study, which are outlined below.

1.5 Research aims and objectives

1.5.1.1 Aim

The aim of this research was to determine the levels of tritium (^{3}H) and radiocarbon (^{14}C) in the groundwater of selected villages of Mahikeng, using the Perkin Elmer ultra-low liquid scintillation counter 2000.

1.5.1.2 Objectives

The objectives were to:

- Analyze tritium (^{3}H) and radiocarbon (^{14}C) activity in the groundwater,
- Estimating the annual effective dose rates (AED) due to ^{3}H and ^{14}C in groundwater,
- Estimate the lifetime cancer risk (LTCR) to the members of the public due to these isotopes.

CHAPTER 2 LITERATURE REVIEW

This chapter focuses on how tritium and radiocarbon are formed and how they are incorporated into the environment. This chapter also discuss the radiological impact of these radioisotopes and how these impacts are assessed. The focus of the study was to determine the levels of tritium (^{3}H) and radiocarbon (^{14}C) in groundwater samples, hence groundwater and isotope hydrology were reviewed.

2.1 Tritium and radiocarbon

Tritium and radiocarbon are both naturally occurring radioactive isotopes which are as a result of cosmic rays interacting with atmospheric gases. Both decay as beta emitters. They are produced in small quantities in the upper atmosphere and are then incorporated into water molecules and, therefore, are present in rainwater and surface recharge to aquifer systems. ^{3}H is produced in the upper atmosphere through the reaction of $^{14}N(n,^{3}H)^{12}C$ and ^{14}C is produced through the reaction of $^{14}N + n \rightarrow ^{14}C + ^{1}p$ (Fig.2-1) (Van Rooyen, 2021). Both tritium and radiocarbon can be used to trace and date groundwater, calculate rates of water circulation in the hydrologic cycle, and assess how long a specific groundwater source has been stored out of contact with them before laden recharge. Such a study is called isotope hydrology. The two isotopes are ubiquitous in the environment and in all biological systems, and thus quickly integrated into numerous cycles of the geosphere and biosphere. In the environment, tritium is present in all the five parts of the geosphere, including atmosphere, hydrosphere and lithosphere, the biosphere and the anthroposhere (Eyrolle et al., 2018) .

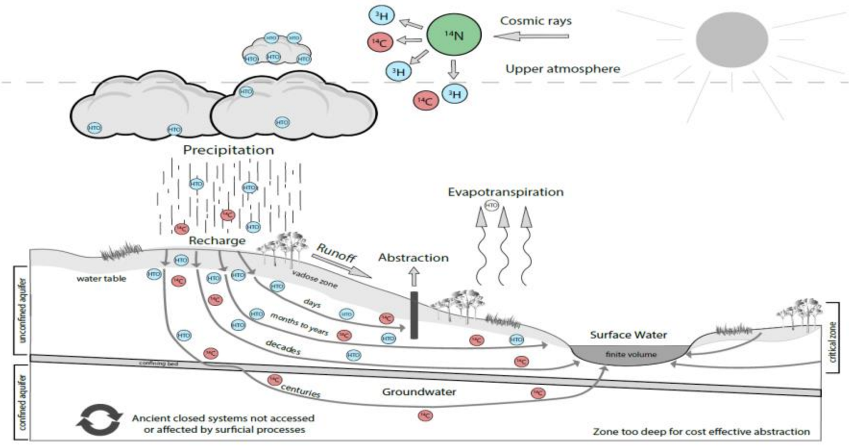

Figure 2-1: Tritium and radiocarbon in the hydrological cycle (Van Rooyen, 2021).

2.1.1.1 Tritium

Tritium (^{3}H), which is a radioactive isotope of hydrogen, consists of one proton and 2 neutrons and has a natural abundance of 0.0001%.Tritium is one of the three naturally occurring isotopes of hydrogen, whereby the other two are stable isotopes are protium (^{1}H) with one proton and a natural abundance with 0.028% and deuterium (^{2}H) which is the most abundant one with one proton, one neutron and a natural abundance with 99.972%. Tritium has a half-life of 12.3 years, and it has maximum energy of 18 keV, and an average energy of approximately 6 keV. As shown if Fig.2-2, tritium decays to ^{3}He via beta decay ($^{3}H \rightarrow {}^{3}He + \beta^{-} + \text{Energy}$). Tritium units (TU) are used to express the values of ^{3}H. One TU of sample has $^{3}H/^{1}H$ ratio which is equals to $1/10^{18}$ (Keesari et al., 2014). Tritium does not interact with the aquifer materials during movement through the porous media and is considered conservative, which makes it different from other geochemical tracers of groundwater pollution (Zuber et al., 2011). Its activity in water sample can be measured at low level. For these reasons, tritium is commonly used to study the extent of groundwater pollution (Sankoh et al., 2021).

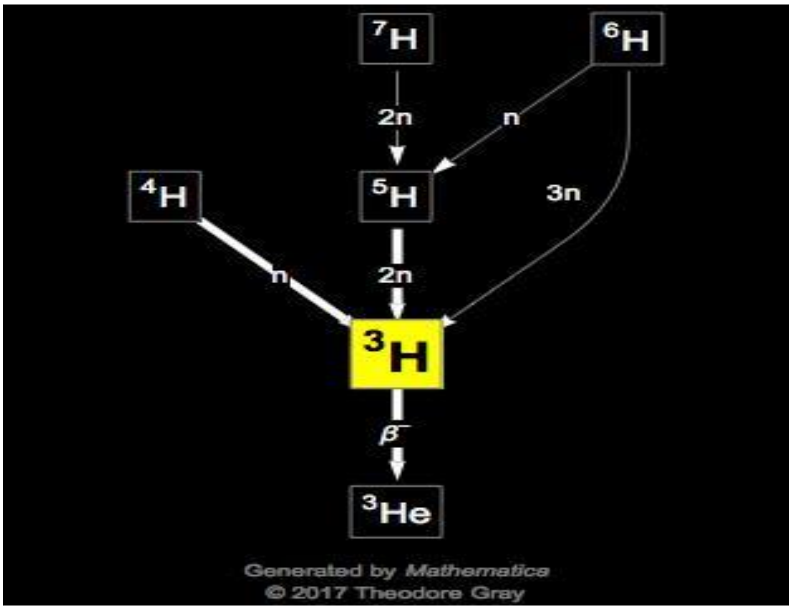

Figure 2-2: Tritium decay chain adapted from (RESEARCH, 2014).

The table below summarizes the radiological characteristics of tritium:

Table 2-1: Radiological characteristics of tritium (Phillips and Castro, 2014).

Radionuclide	**Decay mode**	**Decay energy (keV)**	**Half Life (years)**	**Decay constant**	**Activity conversion**
^{3}H	β^- to He-3 (100%)	$\beta_{Max} =$ 18 keV $\beta_{AVG} =$ 6 keV	12.32 Y	0.06 y^{-1}	1Bq/L = 8.47TU = 27pCi/L

2.1.1.1.1 Tritium transfer from the atmosphere to groundwater

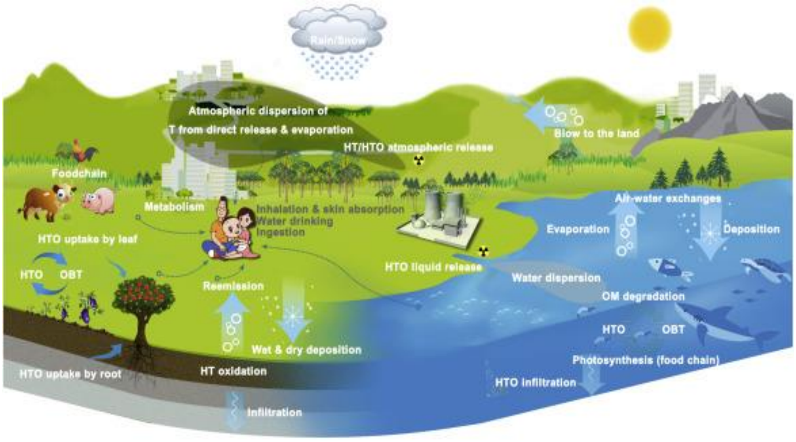

Figure 2-3: Tritium transfer in terrestrial environments, adapted from (Nie et al., 2021).

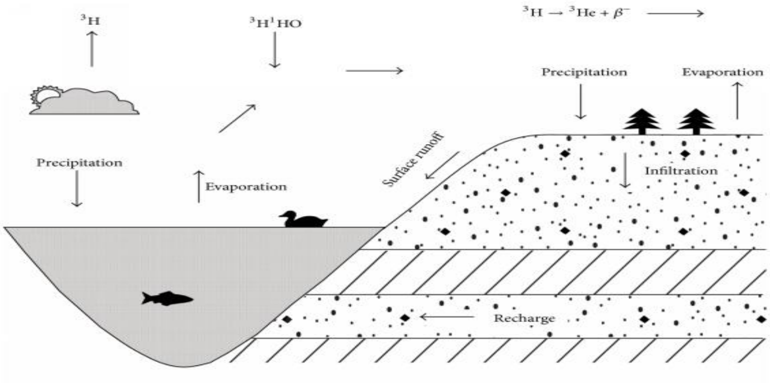

Figure 2-4: Tritium in the groundwater flow system, adapted from (Cidzikienė et al., 2014).

Tritium is found at a very low concentration compared to the commonly stable hydrogen isotope (^1H) with a natural $^3H/^1H$ ratio of 10^{-18}, which is equal to 1 tritium unit (TU) or a specific activity of 0.118 Bq/L of water. Just about two thirds of the natural production occur in the stratosphere.Tritium is the radioactive isotope of hydrogen, it is naturally produced mainly by the interaction of cosmic radiation with atmospheric gases (cosmogenic origin) (Affolter et al., 2020). It occurs in the upper atmosphere when fast neutrons interact with nitrogen from the reaction; $^{14}N(n,^{3}H)^{12}C$ (Cidzikienė et al., 2014). It can be transferred from atmosphere to the environment through diffusion; which is the movement of tritium from an area of high concentration to an area of low concentration, and isotopic exchange; which is a chemical reaction in which the atoms of a given element interchange between two or more chemical forms of this element. For example, in tritiated water, occurs when a tritium atom from one water molecule changes places with a hydrogen atom from an adjacent water molecule (Kostyukevich et al., 2018).

In the atmosphere, tritium combines with water molecules by firstly colliding with oxygen (O_2) to form a relatively stable radical HO_2, then the radical reacts with ozone (O_3), after a photochemical decomposition reaction to form HTO/^{3}HHO (Commission, 2014). As shown in Figure 2-3, tritiated water is precipitated out of the atmosphere to the environment together with ordinary water as rain or snow. HTO is then deposited into soil water through infiltration and from soil water into groundwater through vertical infiltration as shown in Figure 2-4.

^{3}H is a potential candidate for dating groundwater recharged over the last 50–100 years. Due to the production of ^{3}H, during atmospheric nuclear tests, the ^{3}H input function in rainfall has a distinct peak in the 1950s–1960s. This “bomb ^{3}H pulse” has been utilized to trace the flow of water recharged during this period. Most commonly ^{3}H presence in groundwater is interpreted as modern recharge (Keesari et al., 2017). However complete analysis of drinking water radionuclide-pollution is done by also incorporating radiocarbon in the analysis of radioactivity from ground water as modern recharge.

2.1.1.2 Radiocarbon

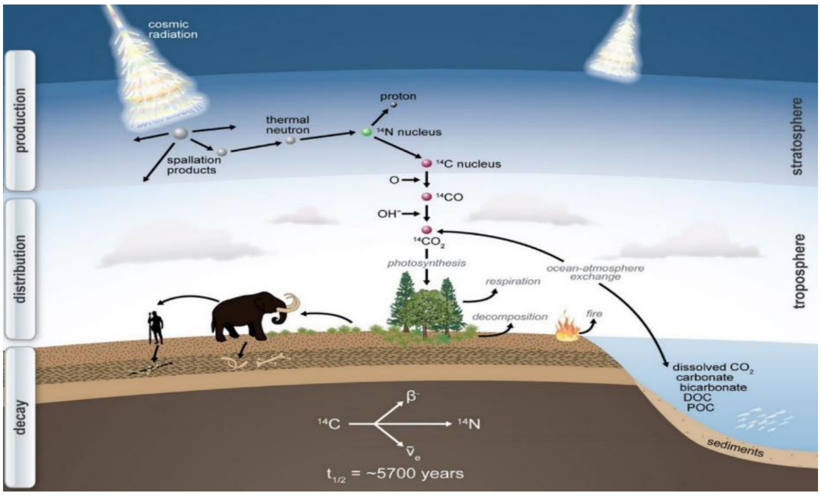

Figure 2-5: The formation of ^{14}C in the upper troposphere and stratosphere (Schuur et al., 2016).

Carbon exists as three isotopes. The most common carbon-12 (^{12}C) with 6 protons and 6 neutrons, carbon-13 (^{13}C) with 6 protons and 7 neutrons. ^{12}C and ^{13}C represents almost all of carbon's natural abundance with 98.89% and 1.109%. Then there is carbon-14 (^{14}C) or radiocarbon, 6 protons and 8 neutrons, which is only found naturally in trace amounts.The formation of the radioisotope ^{14}C is the result of cosmic ray neutron bombardment of ^{14}N in the upper troposphere and stratosphere; ($^{14}N + n \rightarrow {^{14}C} + {^{1}p}$) which yields a $^{14}C/^{12}C$ isotopic ratio of 1×10^{-12}. This ratio was disturbed by anthropogenic activities and hence the atmospheric ^{14}C was rapidly increased during the nuclear bomb tests. As seen in the Figure 2.5 above, after the formation of ^{14}C, it is oxidized to ^{14}CO and then to $^{14}CO_2$, and it is then transferred to the atmosphere, the ocean, and the terrestrial biosphere, via photosynthesis, respiration and decomposition. ^{14}C is very difficult to remove due to its long half-life of 5730 years, and a maximum energy of 0.156 MeV and an average energy of 0.049 MeV (Prăvălie, 2014). However, ^{14}C has also been produced in all types of reactors via neutron-induced reactions with isotopes of carbon, nitrogen, and oxygen (Osman et al., 2016).

Figure 2.6 and Table 2.2 below show the decay chain of radiocarbon and its radiological characteristics.

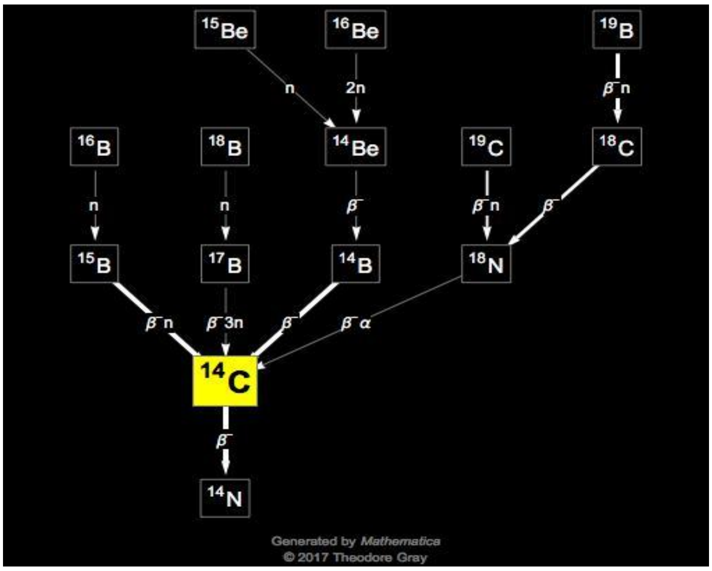

Figure 2-6: Radiocarbon decay chain adapted from (Research, 2014).

Table 2-2: Radiological characteristics of radiocarbon

Radonuclide	**Decay mode**	**Decay energy (keV)**	**Half Life (years)**	**Decay constant**
^{14}C	Decays to ^{14}N through β	βMax = 156 keV βA= 49 keV	5730 Y	3.84 x 10^{-12} s^{-1}

2.1.1.2.1 Radiocarbon transfer from the atmosphere to the environment

As shown in Figure 2-5, cosmic rays lead to the production of thermal neutrons which react with (^{14}N) in the upper troposphere/lower stratosphere to produce radiocarbon (^{14}C) (Olsen et al., 2017). Once ^{14}C is produced, it is rapidly integrated into the atmosphere as CO and then oxidized to CO_2. Carbon-14 is incorporated in the carbon cycle of continental hydro-systems where the main forms are organic carbon dissolved organic carbon (DOC). ^{14}C it makes its way into the environment in the form DOC through photosynthesis, and the carbon cycle (Jull and Burr, 2015).

During infiltration, major part of carbon enters groundwater through soil CO_2, however chemical and biochemical reactions can modify the initial ^{14}C content of groundwater along flow paths (Aggarwal et al., 2009). After recharge, a process whereby the instability of the ^{14}C nucleus eventually destroys this isotope, DIC (Dissolved inorganic carbon) becomes isolated from the carbon source and ^{14}C decays with time. A number of physical and chemical processes may affect the ^{14}C content of DIC in groundwater. The reaction of dissolved CO_2 with carbonate minerals with no ^{14}C activity (dead carbon) is one of the most important processes; this results in increased DIC concentrations and hence ^{14}C dilution in groundwater. This carbon is defined as the carbonate carbon source, as shown in the Figure 2-7 below (Wang et al., 2020).

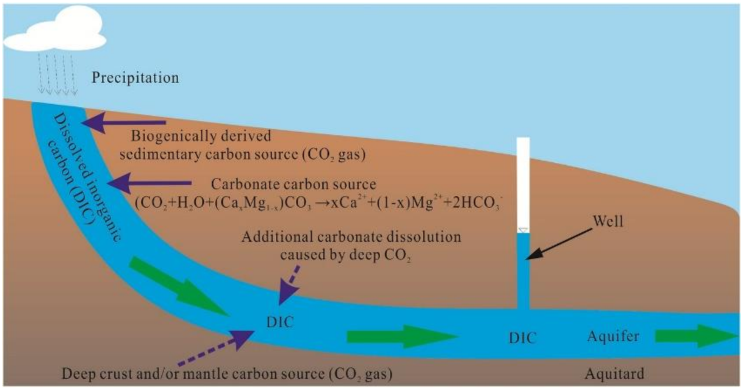

Figure 2-7: Groundwater flow and carbon cycle in an aquifer, adapted from (Wang et al., 2020)

2.2 Groundwater

As shown in Figure 2-9, Rainfall is a result of water evaporating from the ocean and land surfaces, then held temporarily as vapour in the atmosphere, and falls back to earth's surface as precipitation. Surface water is the filtrate of precipitation and melted snow, called runoff. Where the average rate of precipitation surpasses the rate at which runoff soaks into the soil, evaporates, or is absorbed by vegetation, bodies of surface water such as streams, rivers, and lakes are formed. Groundwater is water that penetrates the Earth's surface, slowly percolating downward into aquifers (Muro Gorostiaga, 2015). Groundwater is the water that has filled in the pore space between particles, gravels, and rock fractures that make up the earth (Nie et al., 2021).

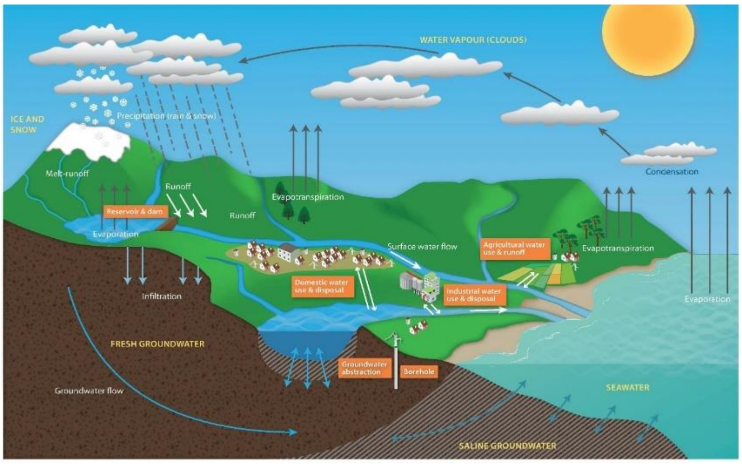

Figure 2-9: Groundwater cycle (Saskia Nowicki, 2020)

Water resources are impacted by different human pressures, such as overexploitation, contamination, changes in land use and climate patterns worldwide. Retaining the good chemical status of groundwater is good practice with respect to its use for human consumption, but also with respect to the requirements of ecosystems dependence on groundwater as an important component of the sustainable development programmes. An indispensable element of the groundwater resources management are predictions of the effects that the anthropogenic pressures exert on groundwater quality (Wachniew et al., 2016).

2.2.1.1 Isotope hydrology

Isotope hydrology is a field of geochemistry and hydrology that uses stable isotopes and radioisotopes to evaluate surface and groundwater age, origins. In this field, the isotopes are used as environmental tracers to study and understand the processes within the atmospheric hydrologic cycle. Isotopes are the most direct and powerful tools available to estimate the age, vulnerability and sustainability of water resources. Naturally occurring radioactive isotopes found in water, such as tritium, radiocarbon and noble gas radioisotopes, are used to estimate groundwater age (Ortega and Gil, 2019).Environmental isotope hydrology is a relatively new field of investigation based on isotopic variations observed in natural waters. These isotopic characteristics have been established over a broad range and time scale. Isotopes of hydrogen and oxygen are ideal geochemical tracers of water because their concentrations are usually not subject to change by interaction with the aquifer material. They are currently referred to as the ‘DNA’ of water bodies because they can respond sensitively to changes in the environment and trace these changes effectively (Ette et al., 2017). Using environmental tracers such as tritium and radiocarbon to study groundwater depends on variations in the concentration of chemical species with time. These variations may be due to changes in recharge concentration of a tracer, radioactive decay of a tracer within the subsurface, or production of a tracer within the subsurface (McCallum et al., 2014).More on environmental tracers in isotope hydrology was discussed in chapter 1,section 1.3 of this study.

2.2.1.2 Groundwater recharge

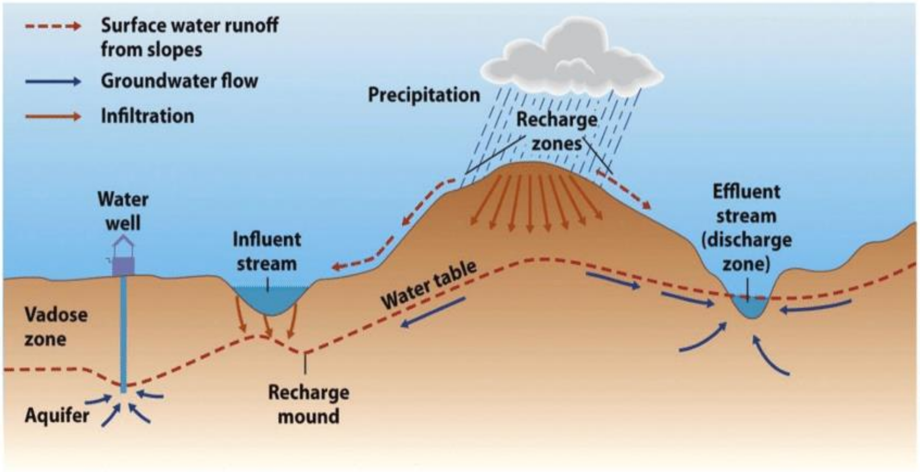

Figure 2-10: Groundwater recharge, figure adapted from (Mahadeo, 2018) .

Groundwater recharge is simply defined as a hydrological process where water moves downwards from surface water to groundwater, it is usually a brief process controlled by factors such as climate change, land use, and soil characteristics. It is important to quantify groundwater to determine whether the groundwater is suitable for public, industrial, or agricultural uses. Climate change, changes in land and water use, including agriculture and drainage may alter groundwater recharge processes (Santos et al., 2017). Figure 2-10 shows the cycle of ground water recharge. There are three recharge mechanisms which are direct, indirect and localized recharge, whereby direct recharge is defined as infiltration of atmospheric precipitation through the unsaturated zone to a ground water body, indirect recharge is percolation to the water table through riverbeds and localized recharge is the accumulation and infiltration of precipitation in surface water bodies, through the unsaturated zone to a groundwater body (Epting et al., 2021).

Groundwater recharge information is beyond scientific interest as it provides a better understanding of the groundwater resource and management strategies. Understanding the proper geological context can also provide criteria for water management in South Africa. In arid/semi-arid regions such as the Southern African region , groundwater resource play a tactical role in various economic sectors (Abiye, 2016).The application of isotopic tracers to analyse groundwater is one of the fast paced technological areas, whereby the use of isotopic measurements to help interpret groundwater ages, flow paths, and recharge areas, is being utilized. There are a number of studies about application and theories this technique because it has become popular and of late, the techniques based on the heat or chemical isotopic tracers are becoming important in the estimation of groundwater recharge (Islam, 2016).

2.2.1.3 Groundwater age

Groundwater age is defined as the time between when groundwater was recharged into the subsurface environment system until it was sampled (Kumar, 2019).The exposure of the groundwater source (well/borehole) to contamination can be predicted by groundwater age. The key to understanding groundwater contaminant trends is through geochemistry, groundwater age and the assessment of contaminant loads independently. Groundwater travel time and distribution can be derived from tracer concentrations (Visser et al., 2013). Radiocarbon and tritium are used to estimate the age and circulation of groundwater (Bhandary et al., 2015) .

Groundwater age can also be used to map groundwater renewability and to describe resource attributes, thus facilitating the sustainable use of groundwater resources (Chen et al., 2017). Radiocarbon and tritium are important radioactive isotopes for groundwater dating. The ^{3}H isotope is often used for determining whether modern recharge exists, while ^{14}C is suited for dating old groundwater. The combination of ^{3}H and ^{14}C enables an accurate determination of groundwater age in aquifers (Guo et al., 2019).

The concept behind the use of environmental tracers to determine aspects of groundwater age is that there is some variation in a chemical compound over time. This may be due to variations in recharge concentrations, radioactive decay, and production of a compound in an aquifer system or a combination of these factors. By knowing how these concentrations vary with time (and hence age), a measured concentration of such a compound can be related to groundwater age (McCallum et al., 2015).

2.2.1.4 Residence time

Groundwater *residence time* is the time taken by the water molecules to travel from the recharge area to the discharge area of the aquifer (Kumar, 2019). Groundwater residence time tracers have been used in many cases such as the assessment of the extent of contamination in groundwater, groundwater flow rate, paths and processes calculating the mean residence time of groundwater (Lapworth et al., 2018).This information is important in order to determine whether the use of groundwater is sustainable. It is important to know and understand the groundwater flow paths and residence times for the sustainable management of any aquifer. Environmental tracers such as ^{14}C and ^{3}H have been used extensively to determine the sources of groundwater and residence times (Batlle-Aguilar et al., 2017).

Radioisotopes with short half-lives are uniquely positioned to provide information on recent recharge processes and hence can be used to track the impact of modern climate change on groundwater systems (Cartwright et al., 2020). Modern recharge can occur over a period of weeks in shallow alluvial aquifers to decades and older in deeper confined systems or in aquifers with low hydraulic conductivity. Tritium has been identified as an ideal residence time indicator of modern processes because it is dominantly a function of atmospheric processes and typically not produced underground along groundwater flow paths (van Rooyen et al., 2020) .

Qualified monitoring and risk assessment requires the mean residence time of groundwater because it helps develop hydrogeological concepts of groundwater bodies that are reliable. Short mean residence time indicates that the groundwater is exposed to contamination, which compromises its value as a source of drinking water, agricultural and industrial use. Modern water with a residence time from 1 to 60 years can be measured by $^{3}H/^{3}He$. Old waters (hundreds to thousands years) can be measured by ^{14}C and ^{39}Ar (Kralik, 2015) .

2.3 Radiological impact of these radioisotopes on the environment

ALARA (as low as reasonably achievable) is a radiation safety principle for reducing doses and releases of radioactive material by using all reasonable methods. In principle, no dose should be acceptable if it can be avoided or is without benefit. Therefore, the impact of radionuclides is studied and assessed because of interest in the effects of its radioactivity to humans and the environment, the transport, uptake, and health impact of these radionuclides released to the biosphere. Tritium and radiocarbon are assessed because they both tend to move freely through biological systems.

2.3.1.1 Radiological impact of tritium

Tritium reacts with hydrogen or water molecules very fast and due to this reason; it is very mobile and ubiquitous in all the parts of the environment. It is found in gaseous forms (HT, CH_3T), liquid form (HTO), as well as associated with naturally occurring organic compounds (Organically Bound Tritium - OBT) (Nie et al., 2021). HTO follows the whole water cycle and the water mass dynamics because it is the main form of tritium in the environment. As a result, it is generally encountered in various components of the hydrosphere including atmosphere, rivers, groundwater, etc. (Ducros et al., 2018).

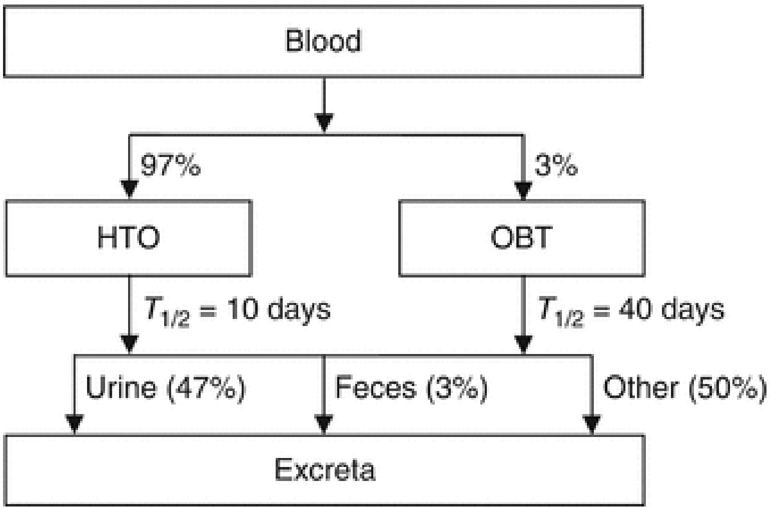

Figure 2-8: Tritium in the human body, adapted from (Bundy et al., 2012).

Tritium is a low-energy beta emitter ($\beta_{AVG=}$ 6 keV), and it has a low radiotoxicity. The most found form in the biosphere is tritiated water and the main exposure route is ingestion. As a low-energy beta (β)-emitter, tritium poses a health risk only if internalized (Niel et al., 2019). Tritium is uniformly distributed through all biological fluids within 1–2 h and the average half-life of TFWT (Tissue Free Water Tritium), in humans is about 10 days (the same as water). Large liquid intake (3–4 L/day) could reduce effectively average half-life of TFWT in a human body by a factor of >2, as tritium is easily flushed from the human body. OBT (Organically Bound Tritium) has a biological half-life of 40 days (Wang et al., 2020), as shown in Figure 2-8.

Tritium(^3H) gas readily oxidizes to form tritiated water molecules ($^1H^3H^{16}O$) and can subsequently enter biological pathways, becoming part of the organic molecules inside tissues and cell.Tritium must enter the nucleus/cell to damage DNA and/or produce other biological effects because the average pathway length of tritium β-particles in water/tissues is not long, with an average pathway length of 0.56 µm in water (Guéguen et al., 2018). Besides the ionizing effects of β-rays emitted from tritium, in-situ transmutation of tritium into helium and enrichment of water in DNA hydration shell plays a role on the enhancement of the effects of tritium on DNA (Radiation, 2011). Moreover, DNA damages bear responsibility for producing irreversible effects such as carcinogenesis, thus analysis of DNA damage is critical to evaluate genotoxicity, which has correlation with cancer induction (Quan et al., 2019).

2.3.1.2 Radiological impact of radiocarbon

The quantitative process of estimating the effect of the release of radionuclides to the biosphere on humans is known as radiological assessment. Radiocarbon (^{14}C) is one of the most important contributors to the radiation dose (Rizzo et al., 2019). It is a low energy beta emitter and even large amounts of this isotope pose little external dose hazard to persons exposed. The beta radiation barely penetrates the outer protective dead layer of the skin of the body. The major concern is the possibility of an internal exposure because the main carbon-14 exposure path to humans is ingestion (Norris, 2018). Carbon is metabolized fast and much of the radionuclide is exhaled in the form of radioactive carbon dioxide. The metabolism and kinetics of ^{14}C in the human body follow those of stable carbon. At equilibrium (i.e., ^{14}C is in isotopic equilibrium with stable carbon in different environmental compartments) more than 99% of the dose contributed by ^{14}C comes from the ingestion pathway (D'Souza et al., 2019).

Because of the relatively long half-life and biological effects of radiocarbon, a radiological assessment on the impacts of this radioisotope is important for radiation protection (Kocsis et al., 2021).It is important to evaluate the potential for radiological health risk due to the increase of carbon-14 in the environment and in humans because it involves considerations related to somatic and genetic effects. The effects of this ^{14}C radioactivity on humans are given by the International Commission on Radiological Protection, ICRP. According to this authority, a standard person has a ^{14}C equilibrium activity of 3,500 Bq, and the biological half- life is 40 days (van der Plicht and Beijers, 2011) .

2.3.1.3 Ingestion of these radionuclides

Water and food ingestion are one of the main processes contributing to the internal exposure of the human body to ionizing radiation. . Radioactive particles ionize nearby atoms in the body once ingested, and they travel through cells or other material. A useful alternative in evaluating the effective dose due to internal exposure of the body to ionizing radiation by drinking water and consuming food is by determining the concentration of radionuclides in water and food (Pintilie-Nicolov et al., 2021), which is one of the objectives of this study. There are two groups which classify the health effects in humans due to ionizing radiation: deterministic and stochastic effects. The deterministic effects are health effects of ionizing radiation, whereby the severity of the effects depend on exposure time and dose. It has a threshold of doses, which means exposure to radiation only causes effects when it's above the threshold level (Matsumoto et al., 2021).Stochastic effects are the effects which occur when a high radiation dose is received, the severity of the effects does not depend on absorbed dose and there is no threshold dose (Bolus, 2017).

Tritium is associated with radiological risk only if it is absorbed on ingested by the human body, emitted β-particles can cause radiation damage to the human body through internal exposure especially after the ingestion of tritiated organic molecules (Bondareva et al., 2022). Ingestion includes ingestion of contaminated plant products, animal products, and drinking water. HTO could be transferred into OBT via photosynthesis and finally ingested by people (Lyu et al., 2016). Tritium can exist in several forms, such as gaseous (HT, HTO, organic molecules), liquid (HTO or organic molecules in solution) or OBT, which can become incorporated into living organisms (vegetables, animals, humans). Tritium can be incorporated into animal tissue or fluids, by consumption of tritiated water and food. The incorporation as water or organic molecules depends on the form of the tritium ingested (Baglan et al., 2013). Since tritium is a low energy β emitter with a half-life of 12.3 years, it causes high ionization density within a relatively small volume of matter. As a result, if enough tritium is ingested, the energy deposited could lead to health complications. Ionizing radiation can affect cells and, if the DNA is left unrepaired, potentially have an effect on individual health or reproductive fitness (Gagnaire et al., 2020).

The ^{14}C is released mainly in the form of carbon dioxide into the atmosphere and as bicarbonate into environmental water. Environmental ^{14}C existing in the form of carbon dioxide or bicarbonate will be readily incorporated into the terrestrial and aquatic plants by photosynthesis and subsequently transferred to animals by feeding. The ^{14}C incorporated into these plants and animals will be also transferred to humans as food he distribution of radiocarbon in the body(van der Plicht and Beijers, 2011).In ICRP publication 134 (ICRP,2017) (Occupational Intakes of Radionuclides: Part 2) ,it is stated that the fractions of ingested or inhaled activity lost by exhalation, urinary excretion, and faecal excretion depends on the nature of the carbon compound taken into the body . In Publication 30 (ICRP, 1981) and Publication 68(ICRP,1994), it is assumed in that inhaled or ingested ^{14}C-labelled compounds are distributed instantly and uniformly throughout all organs and tissues of the body, where they are retained with a biological half-time of 40 days (ECKERMAN, 2017).

2.4 Radiological hazard assessment

The emission of ionizing radiation from various radioactive substances/radioisotopes in drinking-water may result in radiological exposure. Such hazards are rarely of public health significance, and radiation exposure from drinking water must be assessed alongside exposure from other sources to evaluate the safety of drinking-water relating to its radionuclide content (Osterc and Stibilj, 2011). The development of cancer due to exposure to ionizing radiation is not an immediate effect. It may take quite a few decade years to develop if it develops at all. In this study, the activity concentration, annual effective dose rates and lifetime cancer risk were evaluated to assess the effects of exposure from tritium and radiocarbon to humans.

2.4.1.1 Estimation of radionuclide concentrations, annual effective dose rates and lifetime cancer risk

Food is known to contain natural and artificial radionuclides that, after ingestion, contribute to an effective internal dose.Average radiation doses to various organs of the body also represent an important pathway for long-term health considerations. The potential harmfulness of radionuclides is based on their long half-lives and chemical behavior (Van et al., 2019). Average radiation doses to various organs of the body also represent an important pathway for long-term health considerations. The potential harmfulness of radionuclides is based on their long half-lives and chemical behavior(Amin and Ahmed, 2013).

Activity concentrations

Activity concentrations were measured using the direct method through liquid scintillation counting with the PerkinElmer® Wallac 1220 Quantulus (Ultra Low-Level Liquid Scintillation Spectrometer). The direct method allows for the groundwater samples to be mixed directly with the Ultima Gold uLLT cocktail, so in this case, the groundwater samples were filtered then mixed with the cocktail in preparation for counting. The spectrometer was equipped with 3 trays, each of which can contain 20 samples for a total of 60 vials. A total of 30 samples were analyzed for 240 minutes, 3 cycles each. The background activity, which must be measured every time the type and/or batch of the scintillating liquid is changed, was also analyzed in the same time frame (La Verde et al., 2021) . High efficiency for the detection of low energy beta particles and a low and stable background are needed for obtaining accurate measurements any counting system because the specific activity of natural water samples is so low.The count rate for standard solutions are used to estimate the counting efficiency and it is essential for determination of tritium/radiocarbon activity concentration in water samples .(Sudprasert et al., 2022).Therefore in this study, the efficiency was determined using the internal standard method whereby two commercial standards with known activities were used. The commercial standards were counted through liquid scintillation counting, the count rate (cps) was obtained and the following formula was used to obtain the efficiency:

$$\text{Efficiency} = \frac{Count\ rate}{standard\ activity}$$

After calculating the efficiency, the activity concentrations were calculated in Becquerel per liter (Bq/L) using the following equation:

$$A\ (Bq/L) = \frac{Rs - Rb}{\mathcal{E}\ x\ Vs}$$

Annual effective dose rate estimation

Effective dose means the quantification of radiation exposures to human body .The radiological quality of the drinking water is useful especially for the environmental studies for the health of the general public caused by internal radiation hazard from the radioisotopes in groundwater. The acceptable AED recommended by ICRP for the radioactive materials in drinking water is approximately 1 mSv per year, while the AED recommended by WHO from the consumption of drinking water for an adult is 0.1 mSv per year. The annual effective dose rate estimation is essential for monitoring the dose of radioactive materials consumed by humans in water per year (Al-Bedri, 2021).The radionuclide concentration estimated using the equation above, allows for the estimation of the annual effective dose rate because activity is one of the key factors in calculating the AED. The calculation used here:

$AED\ \left(\frac{\mu Sv}{y}\right) = AS\ \left(\frac{Bq}{L}\right) x\ DC\ \left(\frac{\mu Sv}{Bq}\right) x\ WCR\ \left(\frac{L}{Y}\right)$, considers the dose received by a hypothetically exposed adult (HEA) positioned at specific sampling sites. The HEA is defined as an adult member of the public who receives the greatest induced dose from all sources. This person is assumed to remain at this location 24 hours per day, 365.5 days of the year. According to the guidelines for drinking water, set by the World Health Organization, 2011 edition at Switzerland, Geneva (WHO, 2011). It is assumed that a standard person consumption of drinking-water is approximately 2 L/day which is approximately 731 L/Y. Calculating the annual whole-body dose rate from ingestion of drinking water requires three key factors: the radionuclide concentration in water samples (Bq/L), the dose coefficient for the radionuclides (µSv/Bq), the rate at which water is consumed (L/y). The dose coefficients according to ICRP are 1.8×10^{-11} Sv/Bq / (1.8×10^{-5} µSv/Bq) for ^{3}H (triatiated water) and 5.8×10^{-10} Sv/Bq / (5.8×10^{-4} µSv/Bq) for ^{14}C (Masuda, 2021).

Lifetime cancer risk to members of the public

The lifetime risk of developing cancer is the probability that a person will be develop or die from cancer over the course of their lifetime. The lifetime cancer risk is determined for both the morbidity rate, which is the probability of being diagnosed with cancer and the mortality rate which is the number of deaths which could occur in a particular population due to cancer .The lifetime risk is widely used as a popular measure of how widespread cancer is in a particular population (Ahmad et al., 2015).For the purpose of this study, the average life expectancy at birth for males and females in North-West , was estimated at 58.6 years for males and 65.0 years for females, provided they consume 2L of water for 365.5 days. The following equation was used to determine the lifetime cancer risk due to ingestion of groundwater samples containing tritium and radiocarbon:

$$LTCR = AS\; x\; WCR\; x\; LT\; x\; CRC.$$

The radiological cancer risk limit set by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) is 1.63 x 10^{-3}.

2.5 Liquid scintillation counting

Liquid scintillators allow for dissolution of the sample to avoid typical counting problems associated with sample self-absorption, attenuation by detector windows, and backscattering. LSC uses an organic scintillation fluid to convert energetic emissions from the sample to measurable light, therefore there is a limit to the amount of sample material that can be incorporated into each measurement. The organic fluid has a limited ability to mix with aqueous samples, and turbidity in the mixture can cause quench effect at certain mixing ratios (Kang et al., 2020).

The main advantages of LSC methods in measurements of low-energy beta activities like tritium are its speediness, sensitivity and simplicity, low detection limits that can be achieved, conveniently even for determination of natural tritium concentration. One main problem of liquid scintillation spectroscopy in general, is quench effect present in samples which can alter detection efficiency and thus affect the value of the obtained activity concentrations. However, reliable results can be assured if corrections of possible quench occurrence are established for each method, instrument, take place (and additional equipment (LS cocktail and vial used, for example), and laboratory conditions in which sample preparation and their counting (Jakonić et al., 2014).

2.5.1.1 Calibration of 1220 Ultra-Low LSC

In this instrument, the background of the detector is automatically reduced by means of a passive shield (made of lead, cadmium and copper) and an active shield (based on mineral oil scintillate) around the vial chamber. The liquid scintillation counter is calibrated by both CPM / DPM counting mode and spectrum plot mode (Varlam et al., 2011), whereby, external radiation source is used to calibrate extinction level in CPM / DPM counting mode, and Spectrum plot mode is used to analyze the spectrum of external radiation source. In CPM / DPM counting mode, numerous samples can be measured by single calibration regardless of its higher background while it is costly, and more time is required to analyze multiple samples using spectrum plot mode (Noha et al., 2015). There are two methods that can be used to establish the counting efficiency in LSC samples: an internal standard method—with known activity added to a sample, and an external standard method—based on the calibration curve.

The internal standard method is commonly used to establish counting efficiency due to the low-level radioactivity (Gudelis and Gaigalaitė, 2021). In this study, two commercial standards with known activities, tritium standard (253400.00 DPM 3H) and a radiocarbon standard (123600.00 DPM 14C) from Perkin Elmer were used. Pulse shape analysis (PSA) is an important function of Liquid Scintillation Counting which discriminates alpha from beta radiations and directs them separately into alpha or beta multi-channel analyzers (MCA).The optimum PSA is usually determined by the generation of cross-over plots, where a pair of pure alpha and beta emitters is essential (Feng et al., 2014). PSA calibration is done to find out the optimum setting where there is equal and minimum spillover of alpha pulses into the beta MCA and beta pulses into alpha MCA (Çakal et al., 2015). For the purpose of this study, PSA calculation/settings were not required because the instrument was set to analyze for radiocarbon and tritium directly and in separate protocols.

Pollutants in surface water and groundwater may be present naturally due to geochemical processes taking place in aquifers or anthropogenic activities. Naturally occurring radioactive isotopes present in water, such as tritium radiocarbon are used to study the extent of groundwater pollution. This chapter covered the behaviour of these radioisotopes in the environment, how they are formed in the atmosphere and their radiological impact in humans and the radiological assessment due to tritium and radiocarbon, some concepts in isotope hydrology were also discussed. The next chapter covers research methods used in this study.

CHAPTER 3: METHODOLOGY

This section describes the methodology which was used for the research project. It was important to have an understanding of the research methodology in order to provide a stractured approach to the research process.

3.1 Research method

Selecting the research method is important for what conclusions can be made about levels of tritium and radiocarbon in groundwater. It was also important to choose research methodology that is within the limits of what the research can do. This research method was a way to systematically solve the research problem and help in interpreting the findings of other research studies.

3.2 Study location

This study was done around 6 villages, in Mahikeng, which is in the North-West province of South Africa. Mahikeng is 1290 m above sea level, with a local semi-arid climate. During the year there is little rainfall. The temperature here averages 18.5 °C | 65.3 °F. The annual rainfall is 571 mm | 22.5 inches.

About 66% of the samples were collected in Dibate and Lokaleng, therefore they are the main villages for sample collection.

Dibate, is a small rural village, next to Mmabatho, located in Ngaka Modiri Molema district municipality, North-West, South Africa. The village history dates to 1899 (Hlatshwayo, 2017). Lokaleng is a rural village which is situated in Molopo, North West, South Africa. See Figure 1. Lokaleng village falls under ward 6 of Mahikeng local municipality, it is a small, disadvantaged village, which lacks basic services from the municipality (Benecke and Verwey, 2019), such as clean water supply.

3.2.1.1 Sample collection

Groundwater/borehole water samples were collected in October 2020 around the rural villages located in Mahikeng namely Dibate, Lokaleng, Moletsamongwe, Lekung, Airport view and Seweding. The water samples were collected by allowing the water from the borehole pump to flow directly into the sample bottle, then the bottle cap was replaced carefully. The water samples were collected in 500 mL polyethene bottles and were carried to the laboratory at the Centre for Applied Radiation Science and Technology (CARST) at North West University, Mafikeng campus. Precautions were taken not to introduce contaminants to the water samples.

A total of 30 samples were collected. The samples were grouped into 3 sets, the first set was group A, 10 samples (S1-S10) from Dibate , the second set was group B, 10 samples (S11-S20) from Lokaleng village and the third was group C, 10 samples (SM1-SM10) from Moletsamongwe, Lekung , Airport view and Seweding , located near Mmabatho unit 14 and Lokaleng village. The samples were collected at different locations (households) within the villages, separated by a distance of 5 km.

Global positioning system (GPS) was used to record the exact locations of the research samples in terms of the elevations above mean sea level, longitude and latitude. The GPS offers precise positioning and navigation of the sample points so that accurate maps of the sampling locations can be plotted.

The Figure below shows the GPS sampling points.

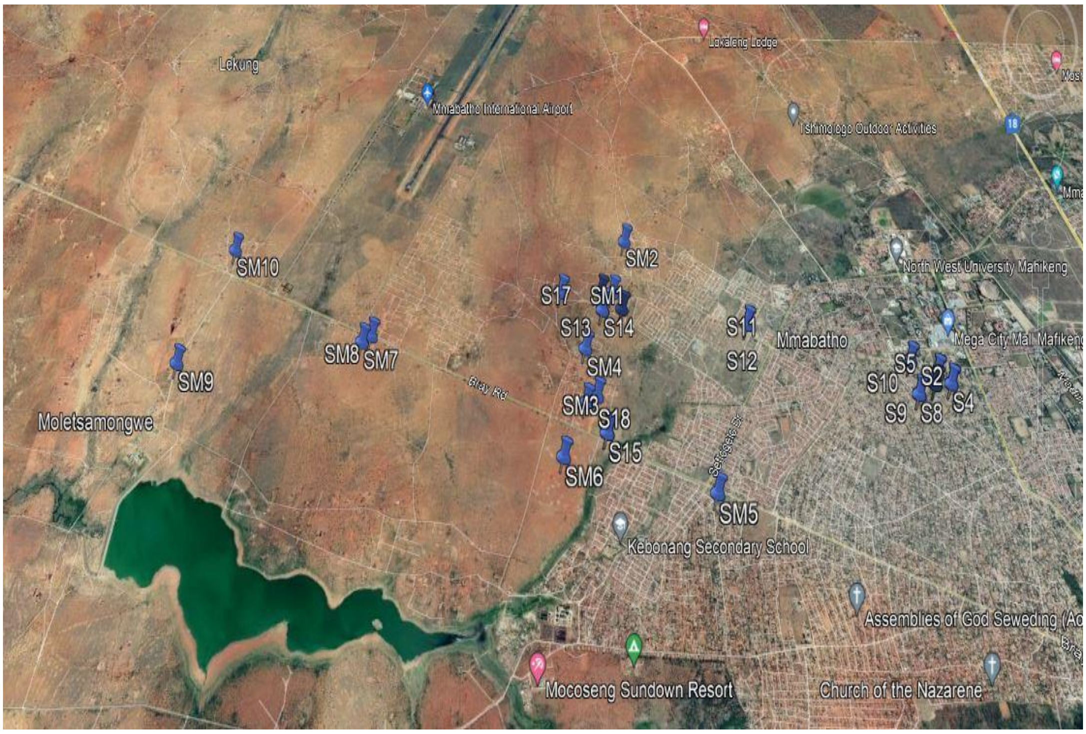

Figure 3-1: Map of study location.

3.3 Sample preparation with LSC

All the water samples were filtered using 90 mm filter papers, 413 batch no; prior to analysis with the LSC. 10 ml of the filtered water samples were placed in 20 ml polyethylene vials and then mixed with the organic solvent (Ultima Gold uLLT) from Perkin Elmer, at a ratio of 10 ml to 10 ml (1:1). 30 samples were prepared and placed between two photomultiplier tubes in the spectrometer of the LSC for analysis. The windows were fixed to channels 1–1024.

3.3.1.1 Equipment

Figure 3-2: Perkin Elmer 1220 ultra-low-level liquid scintillation counter at CARST (NWU).

The Perkin Elmer, Quantulus 1220 ultra-low-level liquid scintillation counter, was used for determination of the activity of tritium which is a low energy beta emitter and radiocarbon which is a high energy beta emitter (Lin et al., 2020). Two protocols were created for both radiocarbon and tritium, the configuration selected for radiocarbon was ^{14}C (high energy beta) and the configuration for tritium samples was ^{3}H (low energy beta). The acquired spectra for the 2 protocols were open and analysed using the Easy View (EV) software on the equipment. This instrument has its own background reduction system around the vial chamber, which consists of both an active and passive shield. The detection system converts incident radiation energy into fluorescence in an organic scintillator with a linear energy response and has advantages due to its sensitivity and reproducibility. Organic scintillators are preferred for alpha/beta spectroscopy because of their hydrogen content (Nikolov et al., 2013).

3.4 Analysis of the levels of tritium (3H) and radiocarbon (14C) in groundwater

Liquid scintillation counter uses a spectrum plot mode which uses an internal radiation source and a cpm/dpm counting mode which uses an external radiation source. It is usually used to analyse ultra-low level tritium. (Hou and Dai, 2020). The 30 sample vials were loaded on the auto sampler and a Run initiated after normal procedure. The samples were counted for 720 minutes (240 minutes x 3 cycles each). The spectra were evaluated by the computer software programme 1224-534 Easy View, which is a Windows 95, 98 NT 4.0 spectrum analysis software for Quantulus raw spectrum display and processing (Faurescu et al., 2019). Raw data was saved on the PC hard disk or a network drive and was later processed off-line with EASY View spectrum analysis software. 1224-534 EASY View displays up to 6 spectra simultaneously and allows spectral arithmetic, radioactive decay measurements in disintegration per minute (DPM) and counts per minute (CPM), statistical analyses, and radiocarbon age dating. Calculations are done in an Excel type spreadsheet and the spreadsheet is saved in Excel formats. Easy View has automatic summing of cycled and/or Spectrum subtraction (ÖZÇAYAN and ASLAN, 2021). The results were presented in counts per second (CPS).

The following formula was used to calculate the activity concentrations

$$A\ (Bq/L) = \frac{Rs - Rb}{\mathcal{E}\ x\ Vs} \qquad (1)$$

Where A—the activity concentration of $^{3}H/^{14}C$ (Bq/L), Rs—the sample count rate (cps), Rb—background count rate (cps), Ɛ-the calculated efficiency, Vs- sample volume (20 m1 = 0.02L)

Determination of the efficiency

For the determination of the detector efficiency, the calibrated standards activity was counted.

Tritium and radiocarbon standards that were readily prepared from Perkin Elmer (DPM ^{3}H) with an activity of 253400.00 DPM, which is equivalent to 4223.33 Bq and (DPM ^{14}C) with an activity of 123600.00 DPM, which is equivalent to 2060.00 Bq, both dated (10 October 2013) were used. To get the new activities of the standards today (the date of sample analysis), the radiation pro calculator (http://www.radprocalculator.com/Decay.aspx) was used. The new activity for tritium standard (DPM ^{3}H (Perkin Elmer) on the 1st of July 2021 was 2735.02858 Bq and the new activity for the radiocarbon standard (DPM ^{14}C (Perkin Elmer) on the 25th of June 2021 was 2058.07902 Bq. These activities were used to estimate the efficiency.

Efficiency = $\frac{Count\ rate}{standard\ activity}$

The following equation was used:

$$\mathcal{E} = \frac{Rst-Rb}{Ast} \qquad (2)$$

Where Rst is the tritium/radiocarbon standard count rate (cps), Rb is the background aliquot count rate, in counts per second (cps), and Ast is the activity of the tritium/radiocarbon standard. The calculated efficiency for tritium was 0.61 = 61% and 0.92= 92% for radiocarbon.

Determination of MDA

The MDA was evaluated using the Currie formula (Currie, 1968), (Nikolov et al., 2013).

$$MDA\ (Bq/L) = \frac{Ld}{\mathcal{E}\ x\ tb\ x\ V} \qquad (3)$$

$$Ld\ counts = 2.71 + 4.65\sqrt{Rb\ x\ tb} \qquad (4)$$

L_d —detection limit, R_b—background count rate (cps), t_b—counting time of the background sample (s) which was 720 minutes (240 minutes x 3). Ɛ - is the efficiency calculated in equation (2) and V - is the volume of the sample, which was 0.02 L (20 ml).

$$MDA\ (Bq/L) = \frac{2.71 + 4.65\sqrt{Rbx\ tb}}{\mathcal{E}\ x\ tb\ x\ V} \qquad (5)$$

The MDA values were calculated to be 0.58 Bq/L for tritium samples and 0.33 Bq/L for radiocarbon samples. The calculated MDA(s) corresponded with the ones obtained from radiation pro calculator at 95% confidence level (http://www.radprocalculator.com/Decay.aspx).

Determination of AED

The following equation was used to estimate the annual effective dose (Njinga et al., 2016).

$$AED\ (\mu Sv/y) \ = \ AS\ (Bq/L)\ x\ DC\ (\mu Sv/Bq)\ x\ WCR\ (L/Y) \qquad (6)$$

Where, AED - annual effective dose, A_S -activity concentration, DC -dose coefficient, WCR -the rate of the water consumption rate per year.

Lifetime cancer risk

The following equation was used to estimate the lifetime cancer risk associated with the consumption of groundwater containing tritium and radiocarbon (Dizman and Mukhtarli, 2021).

$$LTCR \ = \ AS\ x\ WCR\ x\ LT\ x\ CRC \qquad (7)$$

Where, LTCR is the lifetime cancer risk, As is the activity the radionuclide in water samples (Bq L^{-1}), WCR is the water consumption rate (731 L y^{-1}) of adults, LT is average lifetime (year) for individuals; according Statistics South Africa release (Mid-year estimates 2020) (Release, 2021), the average life expectancy at birth for males and females in North-West in 2016-2021, was estimated at 58.6 years for males and 65.0 years for females .

CRC is cancer risk coefficient given by EPA (EPA, 1999), (Council, 2014) in mortality and morbidity. For ^{3}H (triatiated water), the mortality CRC is (9.44×10^{-13} Bq^{-1}) and the morbidity is ($1.37 \text{ x } 10^{-12}$ Bq^{-1}) and for ^{14}C the mortality CRC is ($2.89 \text{ x}10^{-11}$ Bq^{-1}) and the morbidity is ($4.20 \text{ x } 10^{-11}$ Bq^{-1}).

The method and calculations discussed in this chapter were used to obtain the results, analyse them and fulfil the aim and objectives of this study, in the following chapter, the results obtained in this study are presented in tables and figures and a discussion of the results is provided

CHAPTER 4: RESULTS AND DISCUSSIONS.

In this section, the results for the activity concentrations, Annual effective dose rate, and lifetime cancer risk of the studied radionuclides (^{3}H and ^{14}C) are presented and discussed. The quality of drinking in South Africa is managed and monitored based on policies and regulations from international standards such as the World Health Organization (WHO), (Rivett et al., 2013) , therefore the results were compared to the international standards.

The following tables and figures summarize the activity concentrations in the analysed groundwater samples with tritium and radiocarbon. One (1) of the groundwater samples from Dibate (group a) analysed for radiocarbon were below the MDA, hence the results were omitted from the tables and graphs

4.1 Determination of activity concentrations

Equations (1) and (2) were used to determine the activities of tritium and radiocarbon in drinking ground water samples. Figures 4-1 - 4-6 and Tables 4-1 and 4-2, shows all the activity concentrations result from this study.

Table 4-1: Tritium Activity concentrations for groundwater samples

Radioisotope	**Sample ID**	**Crate(cps)**	**Cerror (cps)**	**Activity (Bq/L)**	**Activity error**
^{3}H	Standard	1663.35	0.35		
^{3}H	Background	0.10	0.00		
^{3}H	SM1	0.13	0.00	2.46	0.03
^{3}H	SM2	0.13	0.00	2.34	0.03
^{3}H	SM3	0.12	0.00	1.75	0.02
^{3}H	SM4	0.12	0.00	1.86	0.02
^{3}H	SM5	0.11	0.00	1.22	0.02
^{3}H	SM6	0.12	0.00	1.54	0.02
^{3}H	SM7	0.12	0.00	1.85	0.02

^3H	SM8	0.12	0.00	1.39	0.02
^3H	SM9	0.13	0.00	2.43	0.02
^3H	SM10	0.12	0.00	1.50	0.02
^3H	S1	0.14	0.00	3.23	0.00
^3H	S2	0.15	0.00	4.34	0.01
^3H	S3	0.15	0.00	3.90	0.01
^3H	S4	0.15	0.00	3.87	0.01
^3H	S5	0.14	0.00	3.73	0.01
^3H	S6	0.14	0.00	3.53	0.01
^3H	S7	0.14	0.00	3.46	0.01
^3H	S8	0.13	0.00	2.90	0.00
^3H	S9	0.14	0.00	3.25	0.00
^3H	S10	0.15	0.00	3.91	0.01
^3H	S11	0.15	0.00	4.05	0.01
^3H	S12	0.15	0.00	4.35	0.01
^3H	S13	0.14	0.00	3.71	0.01
^3H	S14	0.15	0.00	3.93	0.01
^3H	S15	0.15	0.00	4.28	0.01
^3H	S16	0.14	0.00	3.77	0.01
^3H	S17	0.14	0.00	3.74	0.01
^3H	S18	0.14	0.00	3.38	0.01
^3H	S19	0.15	0.00	3.93	0.01
^3H	S20	0.14	0.00	3.46	0.01

The following Figures (4-1 to 4-3) shows the activity concentrations from the drinking groundwater samples analysed for ^3H.

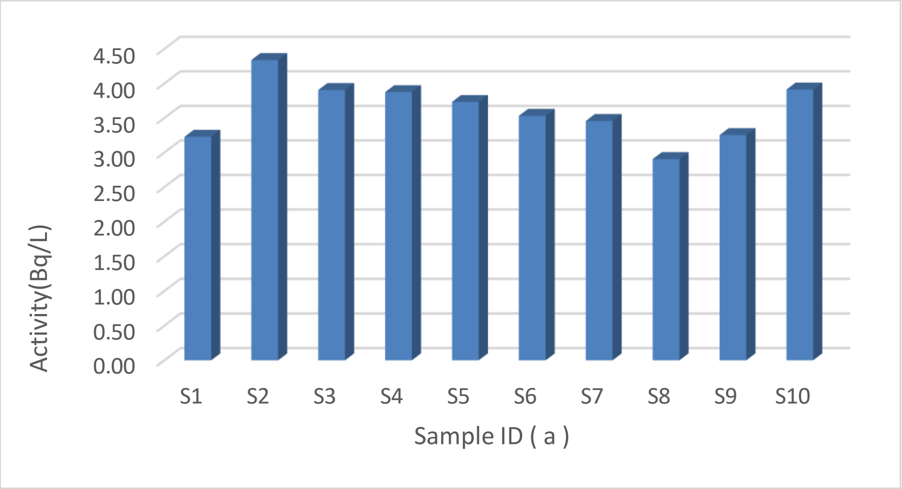

Figure 4-1: Tritium activity concentrations for groundwater samples collected from Dibate village.

Figure 4-1 summarizes the results for tritium samples (S1-S10) collected from Dibate village, Mahikeng. The activity concentrations ranged from 2.90 ± 0.002 Bq/L to 4.34 ± 0.01 Bq/L, with an average of 3.61 ± 0.01 Bq/L.

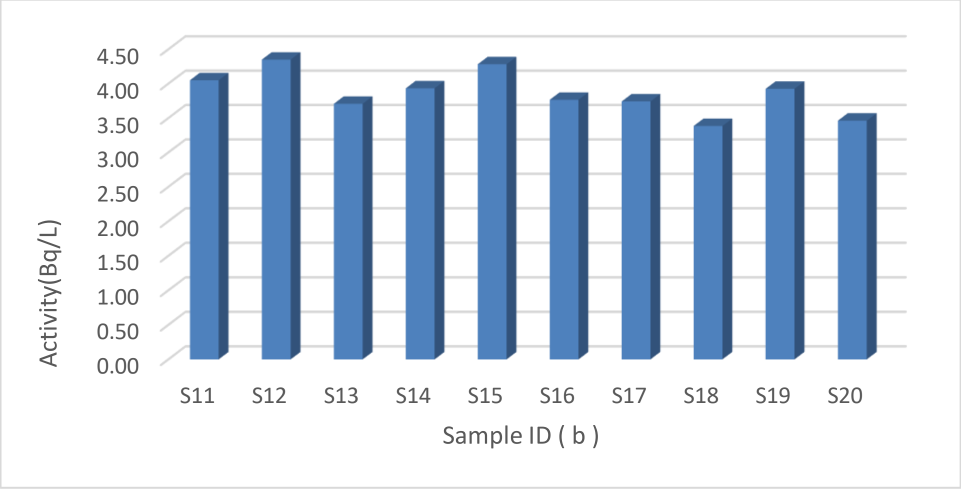

Figure 4-2: Tritium activity concentrations for groundwater samples collected from Lokaleng village.

Fig 4-2 show the results obtained from the tritium samples (S11-S20) collected from Lokaleng village in Mahikeng, the activity ranged from 3.46 ± 0.01 Bq/L to 4.34 ± 0.01 Bq/L.

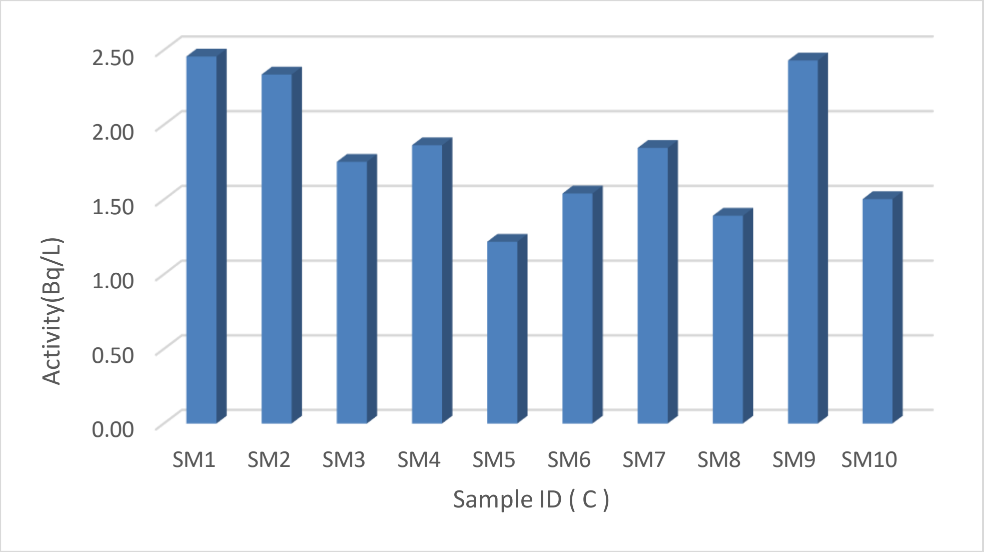

Figure 4-3: Tritium activity concentrations for groundwater samples collected from Moletsamongwe, Lekung, Airport view and Seweding.

It can be observed from Figure 4-3 that samples SM1 – SM10 have lower activity concentration for tritium. Their average was 1.83 ± 0.02 Bq/L. These samples were from Moletsamongwe, Lekung, Airport view and Seweding villages in Mahikeng.

Table 4-2: Radiocarbon activity concentrations for groundwater samples with radiocarbon.

Radioisotope	**Sample ID**	**Crate(cps)**	**Cerror (cps)**		
^{14}C	**Standard**	1884.70	0.37		
^{14}C	**Background**	0.07	0.00	**Activity(Bq/L)**	**Activity error**
^{14}C	SM1	0.11	0.00	1.86	0.03
^{14}C	SM2	0.11	0.00	1.72	0.02
^{14}C	SM3	0.10	0.00	1.39	0.02
^{14}C	SM4	0.10	0.00	1.61	0.02

^{14}C	SM5	0.09	0.00	0.90	0.01
^{14}C	SM6	0.10	0.00	1.13	0.02
^{14}C	SM7	0.10	0.00	1.30	0.02
^{14}C	SM8	0.10	0.00	1.25	0.02
^{14}C	SM9	0.10	0.00	1.18	0.02
^{14}C	SM10	0.10	0.00	1.42	0.02
^{14}C	S1	0.08	0.00	0.57	0.01
^{14}C	S2	0.09	0.00	0.73	0.01
^{14}C	S3	0.08	0.00	0.51	0.01
^{14}C	S4	0.09	0.00	0.63	0.01
^{14}C	S5	0.09	0.00	0.72	0.01
^{14}C	S6	0.08	0.00	0.44	0.01
^{14}C	S7	0.08	0.00	>MDA	>MDA
^{14}C	S8	0.08	0.00	0.49	0.01
^{14}C	S9	0.08	0.00	>MDA	>MDA
^{14}C	S10	0.09	0.00	0.68	0.01
^{14}C	S11	0.09	0.00	0.84	0.01
^{14}C	S12	0.09	0.00	1.08	0.02
^{14}C	S13	0.09	0.00	0.92	0.01
^{14}C	S14	0.08	0.00	0.34	0.01
^{14}C	S15	0.10	0.00	1.30	0.02
^{14}C	S16	0.09	0.00	1.11	0.02
^{14}C	S17	0.09	0.00	0.64	0.01
^{14}C	S18	0.08	0.00	0.52	0.01
^{14}C	S19	0.09	0.00	0.97	0.01
^{14}C	S20	0.09	0.00	0.91	0.01

The following Figures 4-4 - 4-6 show the activity concentrations from the drinking groundwater samples analysed for ^{14}H.

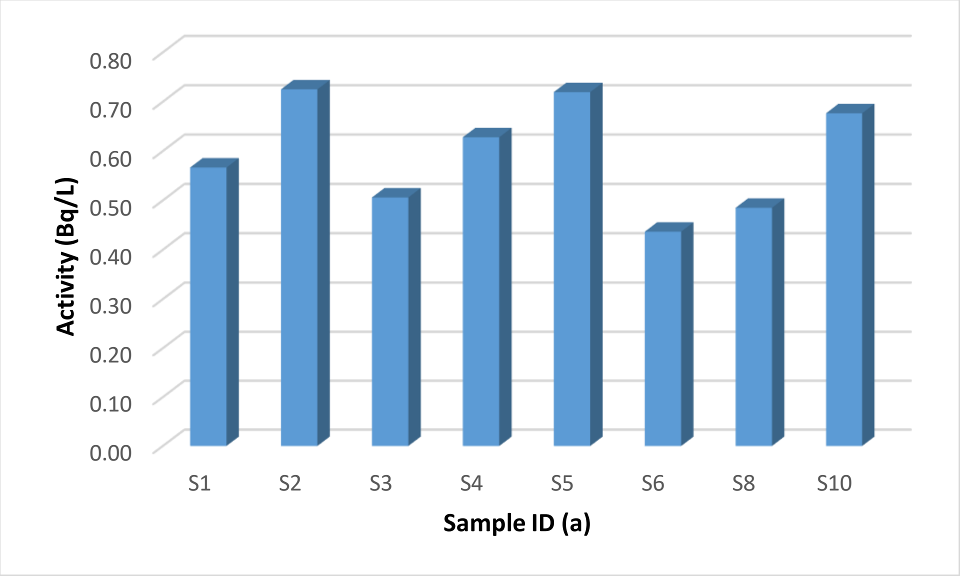

Figure 4-4: Radiocarbon activity concentrations for groundwater samples collected from Dibate.

Figure (4-4) shows the results obtained for radiocarbon samples (S1-S10) collected from Dibate village, Mahikeng. The activity concentrations ranged from 0.44 ± 0.01 Bq/L to 0.73 ± 0.01 Bq/L, with an average of 0.59 ± 0.01 Bq/L.

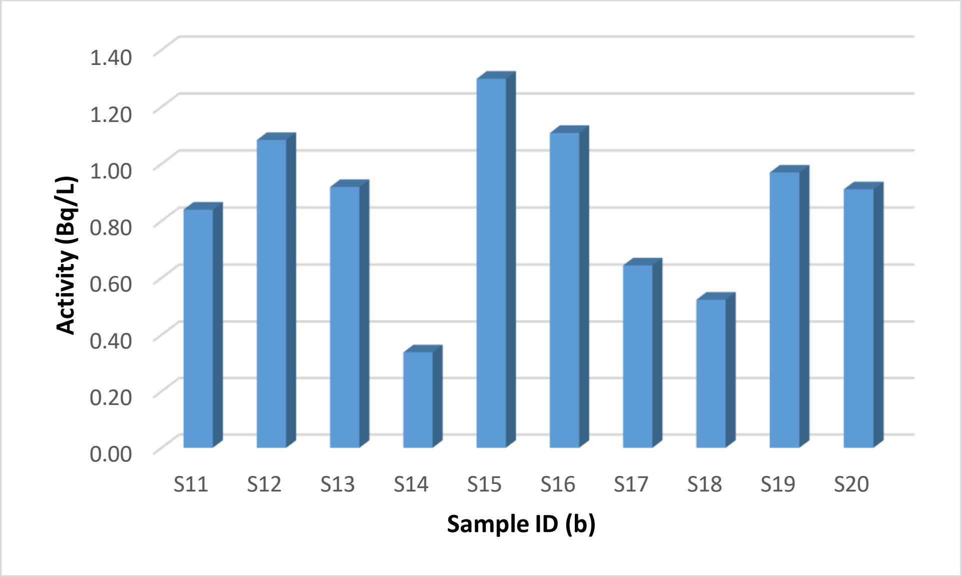

Figure 4-5: Radiocarbon activity concentrations for groundwater samples collected from Lokaleng.

Figure 4-5 shows the results taken from the radiocarbon samples (S11-S20) collected from Lokaleng village in Mahikeng had an average activity concentration of 0.86 ± 0.01 Bq/L, the activity ranged from 0.34 ± 0.01 Bq/L to 1.29 ± 0.02 Bq/L.

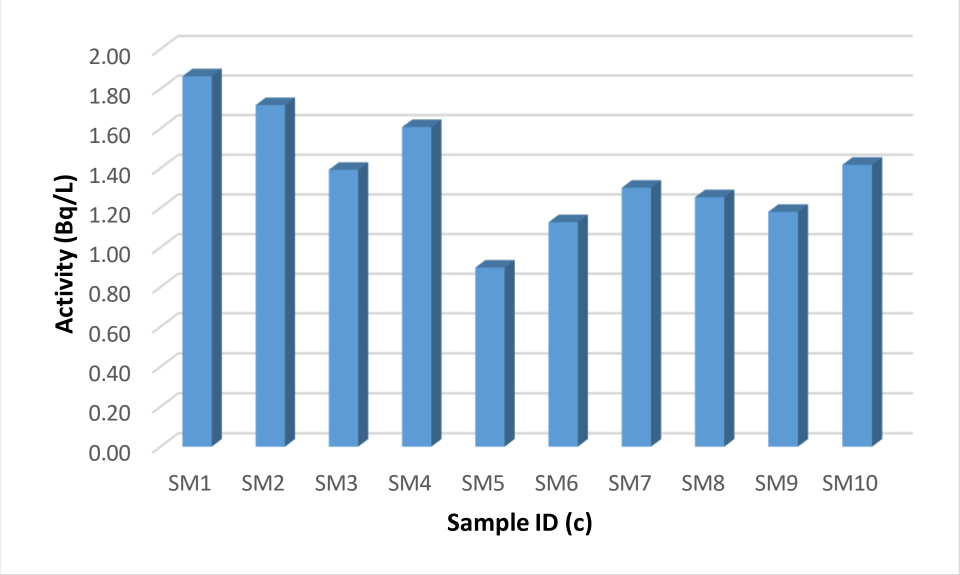

Figure 4-6: Radiocarbon activity concentrations for groundwater samples collected from Moletsamongwe, Lekung, Airport view and Seweding.

The highest activity concentration in the data set was SM1 with 1.86 ± 0.03 Bq/L, shown in Figure 4-6 from the samples collected from Moletsamongwe, Lekung, Airport view and Seweding villages. Samples SM1-SM10 have an average activity concentration of 1.38 ± 0.02 Bq/L.

4.1.1.1 Annual effective dose rates

The following tables and figures summarize the annual effective dose rates for groundwater samples with tritium and radiocarbon.

Table 4-3: Annual effective dose rate for groundwater samples with tritium.

Sample ID	**Activity(Bq/L)**	**AED(µSv/y)**
SM1	2.46	0.03
SM2	2.34	0.03
SM3	1.75	0.02
SM4	1.86	0.02
SM5	1.22	0.02
SM6	1.54	0.02
SM7	1.85	0.02
SM8	1.39	0.02
SM9	2.43	0.03
SM10	1.50	0.02
S1	3.23	0.04
S2	4.34	0.06
S3	3.90	0.05
S4	3.87	0.05
S5	3.73	0.05
S6	3.53	0.05
S7	3.46	0.05
S8	2.90	0.04
S9	3.25	0.04
S10	3.91	0.05
S11	4.05	0.05
S12	4.35	0.06
S13	3.71	0.05
S14	3.93	0.05
S15	4.28	0.06
S16	3.77	0.05
S17	3.74	0.05
S18	3.38	0.04
S19	3.93	0.05
S20	3.46	0.05

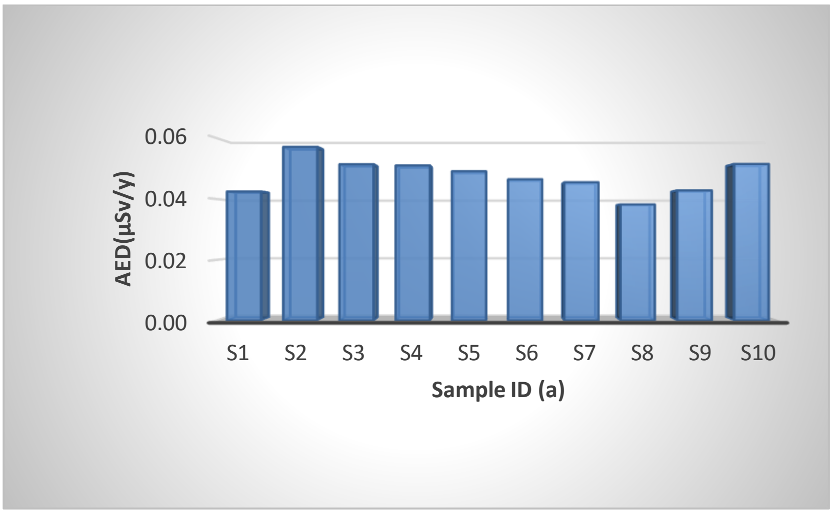

Figure 4-7: Annual effective dose rate for tritium in groundwater samples collected from Dibate village.

As shown in Figure 4-7 the estimated annual effective dose rate (AED) for ^{3}H groundwater samples from Dibate village range from 0.04 μSv/y to 0.06 μSv/y with an average of 0.04 μSv/y. S8 show the lowest dose rate while S2 show the highest dose rate. The difference in the dose rates are due to the difference in activity concentrations, S8 was found to have the highest AED while S2 had the lowest.

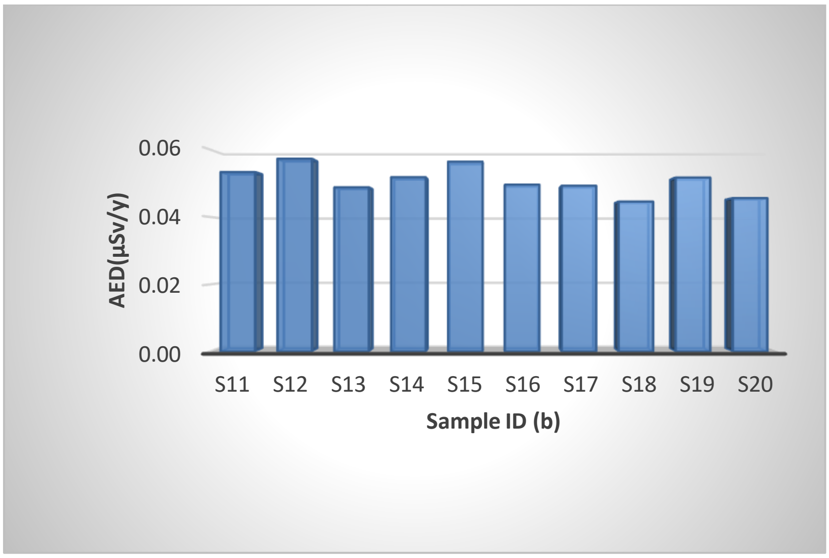

Figure 4-8: Annual effective dose rate for tritium in groundwater samples collected from Lokaleng village.

Figure 4-8 show the estimated AED for ^{3}H groundwater samples collected from Lokaleng village, the results range from 0.04 µSv/y to 0.05 µSv/y, with an average AED of 0.05 µSv/y. S12 was found to have the highest AED while S15 had the the lowest.

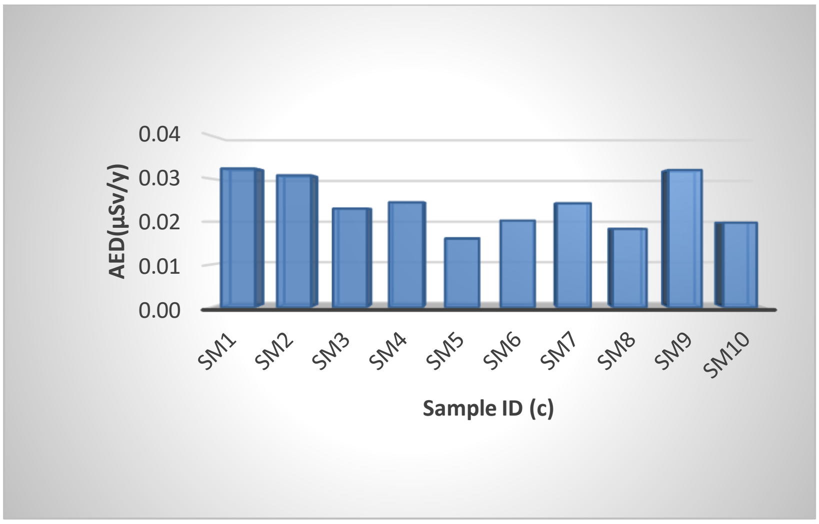

Figure 4-9: Annual effective dose rate for tritium in groundwater samples collected from Moletsamongwe, Lekung, Airport view and Seweding.

Figure 4-9 show the AED for ground water samples from Moletsamongwe,Lekung, Airport view and Seweding. The results range from 0.01 µSv/y to 0.03 µSv/y, with an average of 0.02 µSv/y. SM1 was found to have the highest AED while SM5 had the lowest.

Table 4-4: Annual effective dose rate for groundwater samples with radiocarbon.

Sample ID	Activity(Bq/L)	AED(µSv/y)

SM1	1.86	0.79
SM2	1.72	0.73
SM3	1.39	0.59
SM4	1.61	0.68
SM5	0.90	0.38
SM6	1.13	0.48
SM7	1.30	0.55
SM8	1.25	0.53
SM9	1.18	0.50
SM10	1.42	0.60
S1	0.57	0.24
S2	0.73	0.31
S3	0.51	0.21
S4	0.63	0.27
S5	0.72	0.31
S6	0.44	0.19
S8	0.49	0.21
S10	0.68	0.29
S11	0.84	0.36
S12	1.08	0.46
S13	0.92	0.39
S14	0.34	0.14
S15	1.30	0.55
S16	1.11	0.47
S17	0.64	0.27
S18	0.52	0.22
S19	0.97	0.41
S20	0.91	0.39

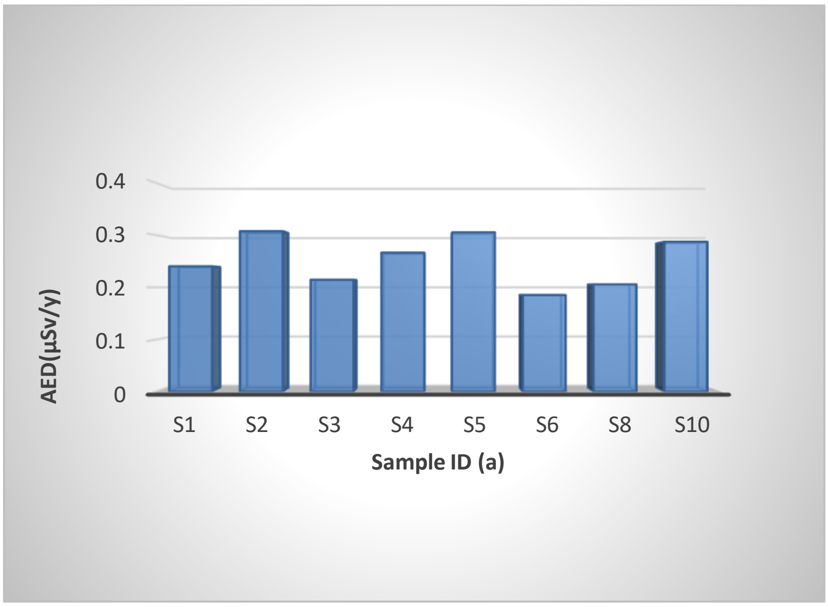

Figure 4-10: Annual effective dose rate for radiocarbon in groundwater samples collected from Dibate.

Figure 4-10 show the annual effective dose rate (AED) for ^{14}C groundwater samples from Dibate village, the dose rates ranged from 0.18 µSv/y to 0.31 µSv/y with an average of 0.25 µSv/y. S2 was found to have the highest AED while S6 had the lowest.

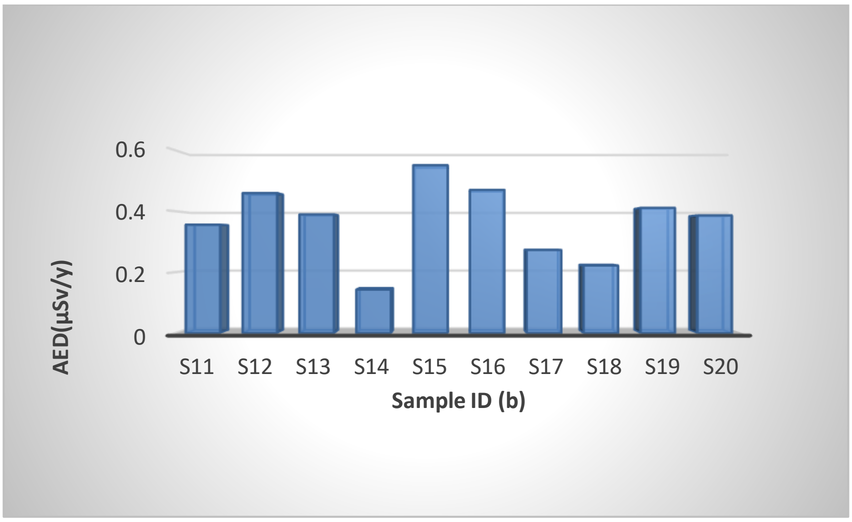

Figure 4-11: Annual effective dose rate for radiocarbon in groundwater samples collected from Lokaleng.

Figure 4-11 shows the estimated AED for ^{14}C groundwater samples collected from Lokaleng village, with the dose rates ranging from 0.14 µSv/y to 0.55 µSv/y, with an average AED of 0.37 µSv/y. S15 was found to have the highest AED while S14 had the lowest.

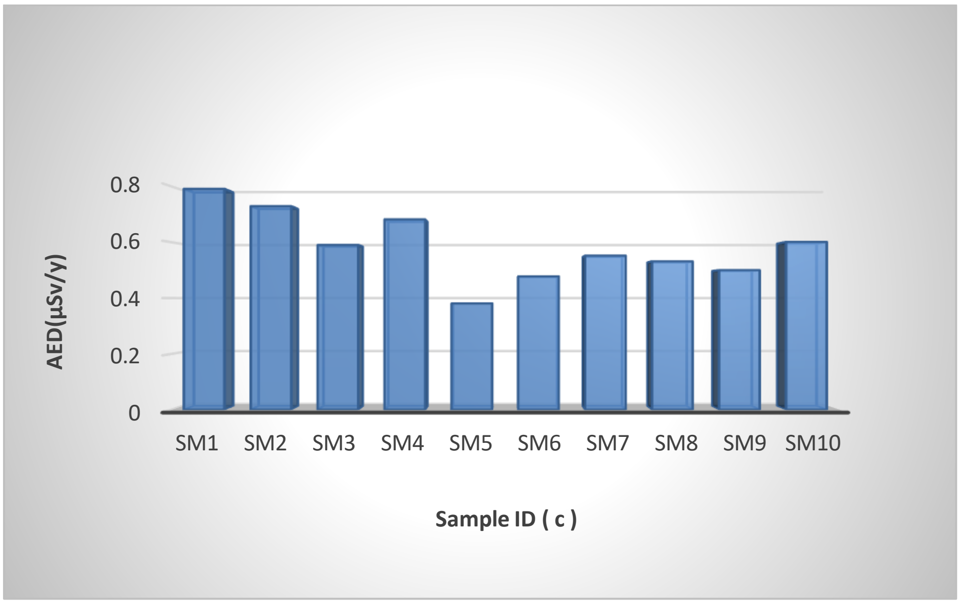

Figure 4-12: Annual effective dose rate for radiocarbon in groundwater samples collected from Moletsamongwe, Lekung, Airport view and Seweding.

Figure 4-12 shows the AED for ground water samples from Moletsamongwe, Lekung, Airport view and Seweding. The results range from 0.48 µSv/y to 0.79 µSv/y, with an average of 0.58 µSv/y. SM1 was found to have the highest activity concentration while SM5 had the lowest.

The following table and figures shows the lifetime cancer risk LTCR mortality and the morbidity for males and females in the studied areas. The clustered bar graph represents mortality while the stacked line graph represents morbidity.

Table 4-5: Estimated lifetime cancer risk (LTCR) for tritium in groundwater samples.

Sample ID	Activity (Bq/L)	**Mortality**		**Morbidity**	
		Men	**Women**	**Men**	**Women**
SM1	2.46	9.94E-08	1.10E-07	1.44E-07	1.60E-07
SM2	2.34	9.45E-08	1.05E-07	1.37E-07	1.52E-07
SM3	1.75	7.09E-08	7.86E-08	1.03E-07	1.14E-07
SM4	1.86	7.54E-08	8.36E-08	1.09E-07	1.21E-07
SM5	1.22	4.92E-08	5.46E-08	7.15E-08	7.93E-08
SM6	1.54	6.23E-08	6.91E-08	9.04E-08	1.00E-07
SM7	1.85	7.46E-08	8.28E-08	1.08E-07	1.20E-07
SM8	1.39	5.63E-08	6.24E-08	8.17E-08	9.06E-08
SM9	2.43	9.83E-08	1.09E-07	1.43E-07	1.58E-07
SM10	1.50	6.08E-08	6.74E-08	8.82E-08	9.78E-08
S1	3.23	1.30E-07	1.45E-07	1.89E-07	2.10E-07
S2	4.34	1.75E-07	1.95E-07	2.55E-07	2.82E-07
S3	3.90	1.58E-07	1.75E-07	2.29E-07	2.54E-07
S4	3.87	1.57E-07	1.74E-07	2.27E-07	2.52E-07

S5	3.73	1.51E-07	1.67E-07	2.19E-07	2.43E-07
S6	3.53	1.43E-07	1.58E-07	2.07E-07	2.30E-07
S7	3.46	1.40E-07	1.55E-07	2.03E-07	2.25E-07
S8	2.90	1.17E-07	1.30E-07	1.70E-07	1.89E-07
S9	3.25	1.32E-07	1.46E-07	1.91E-07	2.12E-07
S10	3.91	1.58E-07	1.75E-07	2.30E-07	2.55E-07
S11	4.05	1.64E-07	1.82E-07	2.38E-07	2.64E-07
S12	4.35	1.76E-07	1.95E-07	2.55E-07	2.83E-07
S13	3.71	1.50E-07	1.66E-07	2.18E-07	2.41E-07
S14	3.93	1.59E-07	1.76E-07	2.31E-07	2.56E-07
S15	4.28	1.73E-07	1.92E-07	2.51E-07	2.79E-07
S16	3.77	1.52E-07	1.69E-07	2.21E-07	2.45E-07
S17	3.74	1.51E-07	1.68E-07	2.20E-07	2.44E-07
S18	3.38	1.37E-07	1.52E-07	1.99E-07	2.20E-07
S19	3.93	1.59E-07	1.76E-07	2.30E-07	2.56E-07
S20	3.46	1.40E-07	1.55E-07	2.03E-07	2.25E-07

Figures 4-13, 4-14 and 4-15 show the LTCR mortality and morbidity for groundwater samples analysed for tritium.

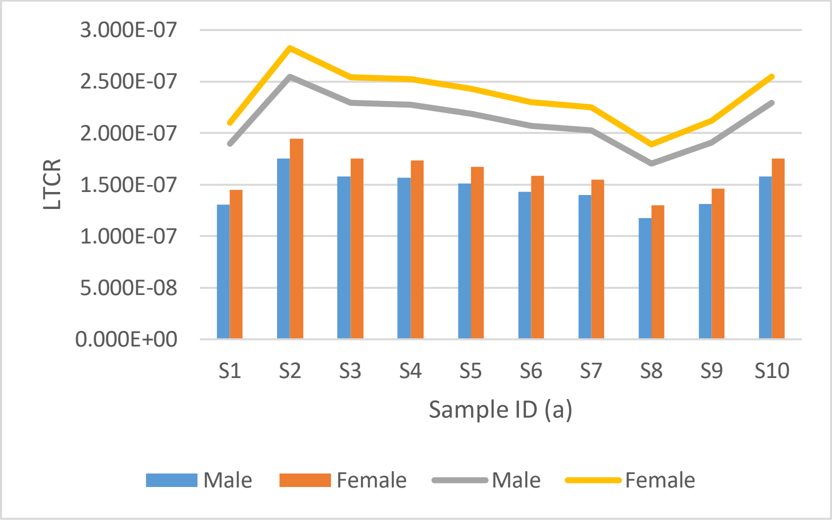

Figure 4-13: Estimated lifetime cancer risk (LTCR) mortality and morbidity for tritium in groundwater samples collected from Dibate village.

Fig.4-13 shows the LTCR results for the data collected from Dibate, the mortality rate for males varied from 1.17 x 10^{-7} to 1.75 x 10^{-7}, with a mean average of 1.46 x 10^{-7}, and the mortality rate for female varied from 1.30 x 10^{-7} to 1.94 x 10^{-7} with an average of 1.62 x 10^{-7}. The morbidity rate for males ranged from 1.71 x 10^{-7} to 2.55 x 10^{-7}, with a mean average of 2.12 x 10^{-7}, while the morbidity rate for females ranged from 1.89 x 10^{-7} to 2.82 x 10^{-7} with a mean average of 2.35 x 10^{-7}. It can be observed that S8 had the lowest LTCR in both mortality and morbidity for male and female while S2 had the highest LTCR. The slight difference in the LTCR results from different activity concentrations and different sampling locations, some locations have a high tritium activity concentration while some have a low concentration.

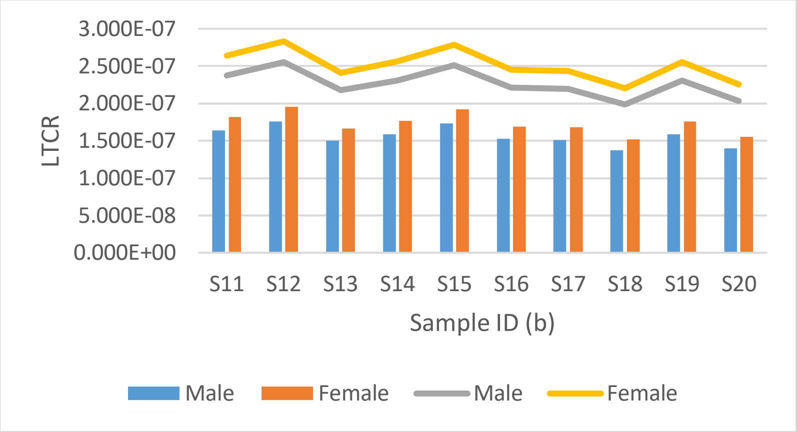

Figure 4-14: Estimated lifetime cancer risk (LTCR) morbidity and mortality for tritium in groundwater samples from Lokaleng.

Figure.4-14 show the LTCR from Lokaleng, the mortality rate for males varied from 1.36836 x 10^{-7} to 1.76 x 10^{-7}, with a mean average of 1.56 x 10^{-7}, and the mortality rate for female varied from 1.30 x 10^{-7} to 1.94 x 10^{-7} with an average of 1.73 x 10^{-7}. The morbidity rate for men ranged from 1.71 x 10^{-7} to 2.55 x 10^{-7}, with a mean average of 2.26 x 10^{-7}, while the morbidity rate for women ranged from 1.89038 x 10^{-7} to 2.82 x 10^{-7} with a mean average of 2.51 x 10^{-7}. S18 had the lowest LTCR in both mortality and morbidity for male and female while S15 had the highest LTCR.

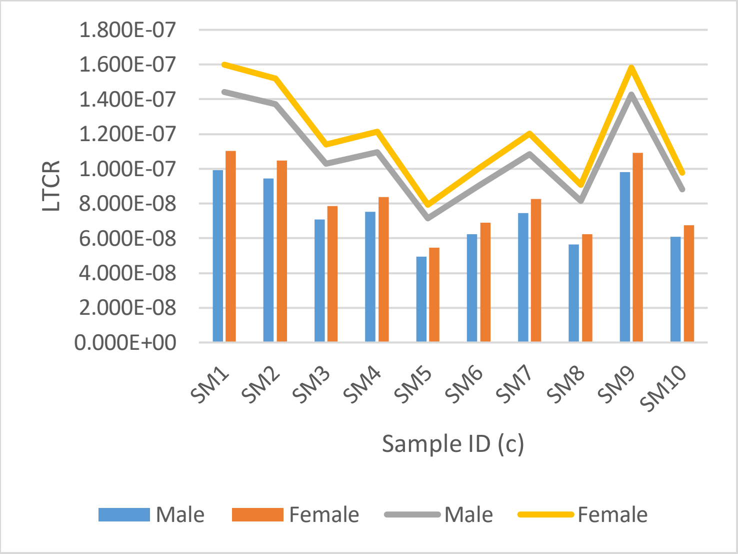

Figure 4-15: Estimated lifetime cancer risk (LTCR) mortality and morbidity for tritium in groundwater samples from Moletsamongwe,Lekung, Airport view and Seweding.

Samples from Moletsamongwe, Lekung, Airport view and Seweding are shown in Figure.4-15. The mortality rate for male's ranged from 4.49 x 10^{-8} to 9.91 x 10^{-8}, with a mean average of 7.41 x 10^{-8}, and the mortality rate for female varied from 5.46 x 10^{-8} to 1.10 x 10^{-7} with an average of 8.23 x 10^{-8}. The morbidity rate for men ranged from 7.14 x 10^{-8} to 1.44 x 10^{-7}, with a mean average of 1.07 x 10^{-7}, while the morbidity rate for women ranged from 7.92 x 10^{-8} to 1.59 x 10^{-7} with a mean average of 1.19 x 10^{-7}. SM15 had the lowest LTCR in both mortality and morbidity for male and female while SM1 had the highest LTCR.

Table 4-6: Estimated lifetime cancer risk (LTCR) for radiocarbon in groundwater samples.

Sample ID	**Activity (Bq/L)**	**Mortality**		**Morbidity**	
		Male	**Female**	**Male**	**Female**
SM1	1.86	2.31E-06	2.36E-06	3.35E-06	3.43E-06
SM2	1.72	2.13E-06	2.18E-06	3.09E-06	3.16E-06
SM3	1.39	1.72E-06	1.76E-06	2.50E-06	2.56E-06
SM4	1.61	1.99E-06	2.04E-06	2.89E-06	2.96E-06
SM5	0.90	1.11E-06	1.14E-06	1.62E-06	1.65E-06

SM6	1.13	1.39E-06	1.43E-06	2.03E-06	2.08E-06
SM7	1.30	1.61E-06	1.65E-06	2.34E-06	2.40E-06
SM8	1.25	1.55E-06	1.59E-06	2.25E-06	2.31E-06
SM9	1.18	1.46E-06	1.49E-06	2.12E-06	2.17E-06
SM10	1.42	1.75E-06	1.80E-06	2.55E-06	2.61E-06
S1	0.57	7.02E-07	7.18E-07	1.02E-06	1.04E-06
S2	0.73	8.98E-07	9.19E-07	1.30E-06	1.34E-06
S3	0.51	6.26E-07	6.41E-07	9.10E-07	9.32E-07
S4	0.63	7.78E-07	7.96E-07	1.13E-06	1.16E-06
S5	0.72	8.91E-07	9.12E-07	1.29E-06	1.33E-06
S6	0.44	5.41E-07	5.54E-07	7.86E-07	8.04E-07
S8	0.49	6.01E-07	6.15E-07	8.73E-07	8.94E-07
S10	0.68	8.38E-07	8.58E-07	1.22E-06	1.25E-06
S11	0.84	1.04E-06	1.06E-06	1.51E-06	1.55E-06
S12	1.08	1.34E-06	1.37E-06	1.95E-06	2.00E-06
S13	0.92	1.14E-06	1.16E-06	1.65E-06	1.69E-06
S14	0.34	4.18E-07	4.28E-07	6.08E-07	6.22E-07
S15	1.30	1.61E-06	1.65E-06	2.34E-06	2.39E-06
S16	1.11	1.37E-06	1.40E-06	1.99E-06	2.04E-06
S17	0.64	7.97E-07	8.16E-07	1.16E-06	1.19E-06
S18	0.52	6.48E-07	6.64E-07	9.42E-07	9.64E-07
S19	0.97	1.20E-06	1.23E-06	1.74E-06	1.79E-06
S20	0.91	1.13E-06	1.15E-06	1.64E-06	1.68E-06

Figures (4-16 to 4-18) show the estimated mortality and morbidity LTCR results for groundwater results analysed for radiocarbon.

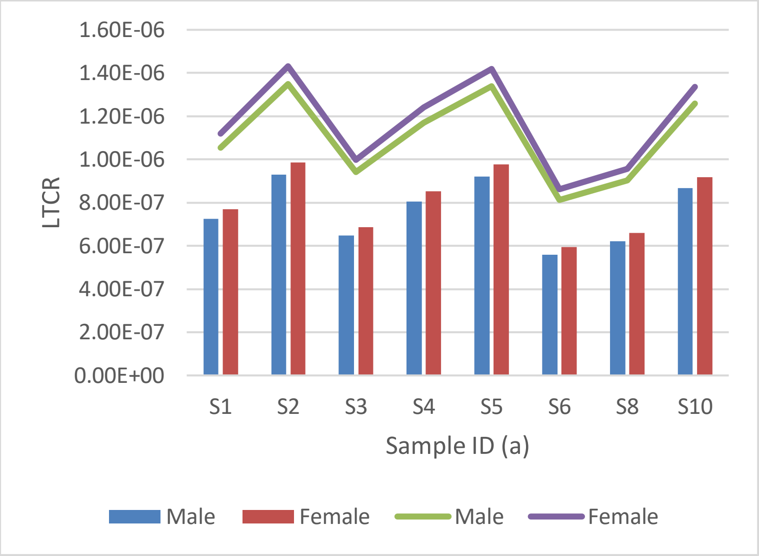

Figure 4-16: Lifetime cancer risk (LTCR) mortality vs morbidity between men and women for radiocarbon in groundwater samples from Dibate.

Fig 4-16 represent the data from Dibate, with an average result of 7.59 x 10^{-7} for male mortality rate and 1.10 x 10^{-6} morbidity, females had an average mortality rate of 8.05 x 10^{-7} and 1.17 x 10^{-6} for morbidity. S6 had the lowest LTCR in both mortality and morbidity for male and female while S2 had the highest LTCR.

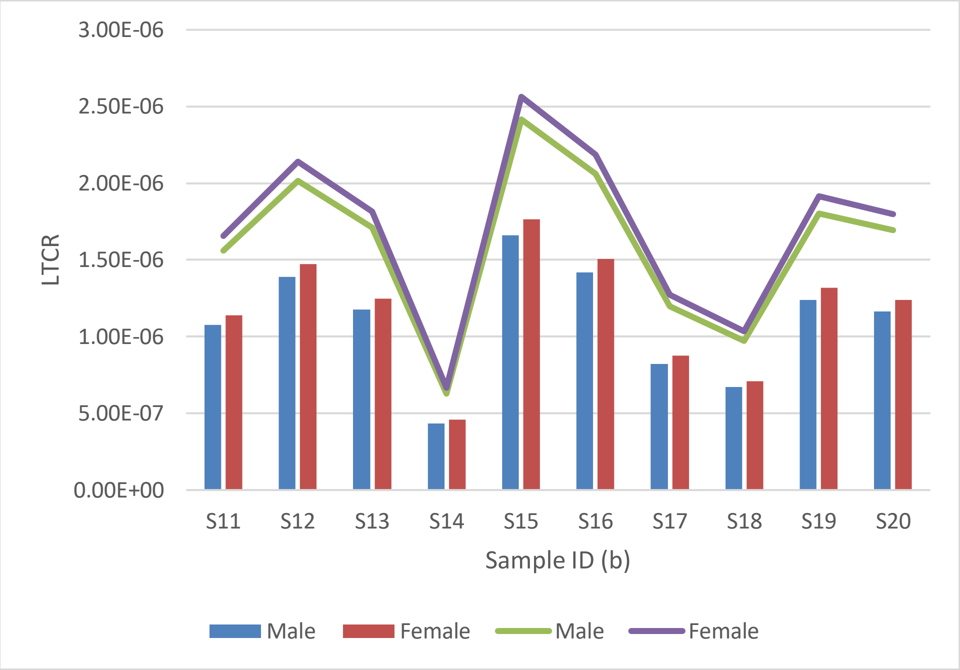

Figure 4-17: Lifetime cancer risk (LTCR) mortality vs morbidity between men and women for radiocarbon in groundwater samples from Lokaleng.

The samples from Lokaleng are shown in Fig.4-17, where the mean average for male mortality was 7.59 x 10^{-6} and 1.60 x 10^{-6} for morbidity, with a female mortality of 1.17 x 10^{-6} and 1.17 x 10^{-6} for morbidity. S14 had the lowest LTCR in both mortality and morbidity for male and female while S15 had the highest LTCR.

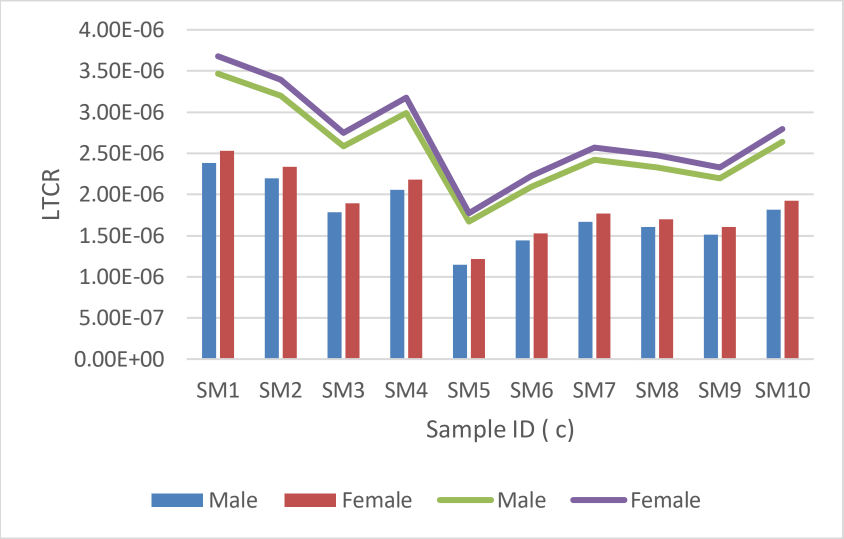

Figure 4-18: Lifetime cancer risk (LTCR) mortality vs morbidity between men and women for radiocarbon in groundwater samples from Moletsamongwe, Lekung, Airport view and Seweding.

Figure 4-18 show the results from the data collected from Moletsamongwe, Lekung, Aiport -view, the average male mortality rate was found to be 1.76 x 10^{-6} and 2.56 x 10^{-6} for morbidity, the average for female mortality was found to be 1.87 x 10^{-6} and 2.71 x 10^{-6} for morbidity. SM5 had the lowest LTCR in both mortality and morbidity for male and female while SM1 had the highest LTCR.

4.2 Discussions

Activity concentrations

The activity concentrations of ^{3}H and ^{14}C were determined from the groundwater (borehole) samples collected from the villages in Mafikeng. The results are presented in Figures 4-1 to 4-6. The data in counts per second (cps) was converted into activity (Bq/L). The activity was calculated using equation (1).

The activities of tritium in the villages were below the limits set by the U.S. Environmental Protection Agency (USEPA); of 740 Bq/L (Kocher and Hoffman, 2011); and WHO -10 000 Bq/L (WHO, 2011). The low activity levels of the tritium concentration were due to radioactive decay, high concentrations decrease over time. Furthermore, the intermediate storage of tritium in groundwater and absorption by plants lowers the tritium amount in the part of the water cycle that was more active (Juhlke et al., 2020). Therefore, it can be concluded from the obtained results that in these villages' borehole water was safe for drinking and members of the public were not under any cancer risk associated with the ingestion of tritium.

The activities of radiocarbon in these villages was below the limit set by WHO –l00Bq/L (WHO, 2011). It can be concluded that in these villages borehole water was safe for drinking due and members of the public were not under any cancer risks associated with ingestion of radiocarbon.

Although both tritium and radiocarbon are below the limits by the World Health Organization, tritium had high activity concentrations compared to radiocarbon, this is because with the direct counting method used in this study ,it is easier to detect tritium at low levels using the liquid scintillation counting technique than it is to detect radiocarbon. The activity concentration of tritium is detectable at low levels in water due to its short half-life.

There are no similar studies that were previously done for the analysis of tritium and radiocarbon in borehole waters in these specific villages.

Annual effective dose rate (AED)

The tritium annual effective dose rate (AED) difference in Figures 4-7, 4-8 and 4-9 results from the difference in activity concentrations because the dose rate was directly affected by the activity concentration; when the activity was high, so was the AED and when the activity was low, the AED was also low.However, the activity concentrations of the borehole waters collected differs depending on the physicochemical and geochemical conditions and the geological formation of the soil and bedrock of each area (Almasoud et al., 2020). The activity concentrations and annual effective dose rates from the studied villages vary for the samples analysed for both tritium and radiocarbon and that might be due to the geological variations in the studied areas.The estimated dose values from each of the studied villages, were found to be below the recommended annual dose value of 100 μSv as per guidelines for drinking-water quality set by the Word Health Organization (WHO, 2011).

Lifetime cancer risk (LTCR)

The mortality and morbidity rates for the lifetime cancer risk (LTCR) as result of consuming the studied groundwater (borehole water) were calculated for adults; males and females with an average lifetime expectancy of 58.6 years for males and 65.0 years for females respectively. The comparisons for LTCR mortality and morbidity for between men and women are depicted graphically in Figure 4-13 to Figure 4-18.

It can be observed from Figures 4-14 to 4-18 that women have a high lifetime cancer risk mortality and morbidity in all the samples analysed for both tritium and radiocarbon. Women have a long lifetime expectancy than men, which explains why women have a lifetime cancer risk slightly higher than men do. When comparing the sets of results for groundwater samples analysed for radiocarbon and tritium, it was evident that the samples analysed for radiocarbon had a lifetime cancer risk (morbidity and mortality) higher than the ones analysed for tritium. Although the samples analysed for radiocarbon had a lower activity concentration than the samples with tritium, radiocarbon has a greater cancer risk coefficient compared to tritium, which results in an overall high lifetime cancer risk. However, the lifetime cancer risk values for this study were lower than the radiological cancer risk limit of 1.63×10^{-3} set by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR 2008 report) (Radiation, 2011). Therefore it can be concluded that the borehole water from these villages is safe to drink.

These are the first results done for tritium and radiocarbon analysis in these villages and thus provide valuable baseline information, which can be used to monitor underground water aquifer discharges, recharges and pollution.

Limitations of the study

Tritium is commonly used as ideal environmental tracer because it can be rapidly transported through environmental pathways and taken up by organisms, and its activity in water samples can be measured at low level. Knowing the accurate levels of past ^{14}C makes it possible for new discoveries and provides connections across broad research areas. As a result of its production in the atmosphere and subsequent dispersal through the carbon cycle, radiocarbon (^{14}C) is a key tracer for studying the Earth system. For the purpose of this study, tritium and radiocarbon were chosen because unlike other radionuclides such as radon, uranium and deuterium there is insufficient data for tritium and radiocarbon in groundwater within the studied areas. Hence this is focused on tritium and radiocarbon, this data would be useful in assessing the radiological impact of these radioisotopes in the studied areas which would be useful to local water professionals in the management of water resources within the studied villages in Mahikeng.

CHAPTER 5 CONCLUSIONS AND RECOMENDATIONS

In this study, tritium and radiocarbon activity concentrations in 30 groundwater (borehole) samples from different villages in Mahkeng were determined by the Perkin Elmer ultra-low liquid scintillation counter 2000. The average activity concentration for groundwater samples with tritium for samples from Dibate village was 3.61 ± 0.01 Bq/L. Samples collected from Lokaleng village in Mahikeng had the average activity concentration of 3.86 ± 0.01 Bq/L while samples from Moletsamongwe, Lekung, Airport view and Seweding villages had a lower activity concentration for tritium, with an average of 1.83 ± 0.02 Bq/L.

The average activity concentration for radiocarbon in groundwater samples collected from Dibate village was 0.59 ± 0.01 Bq/L. Samples collected from Lokaleng village had an average activity concentration of 0.86 ± 0.01 Bq/L. Samples collected from Moletsamongwe, Lekung, Airport view and Seweding villages had an average activity concentration of 1.37 ± 0.01 Bq/L. The activity concentrations for all the collected samples were lower than the international recommended limits for radionuclides in water intended for human consumption.

The total annual effective dose (AED) for ingestion ranges from for ^{3}H groundwater samples from Dibate village had a mean average of 0.05 μSv/y, groundwater samples collected from Lokaleng village, had an average AED of 0.05 μSv/y while the AED for ground water samples from Moletsamongwe, Lekung, Airport view and Seweding had an average of 0.02 μSv/y.

The AED for ^{14}C groundwater samples from Dibate village was an average of 0.25 μSv/y, groundwater samples collected from Lokaleng village, had an average AED of 0.36 μSv/y and the AED for ground water samples from Moletsamongwe,Lekung, Airport view and Seweding, had an average of 0.58 μSv/y.

The annual effective dose rate values for ^{14}C are higher than those ^{3}H because ^{14}C has a higher dose coefficient. The estimated dose values from the studied villages, were found to be below the recommended annual dose value of 0.1mSv/100 μSv.

The lifetime cancer risk was estimated to have an average result of 7.59 x 10^{-7} for male mortality rate and 1.10 x 10^{-6} morbidity, females had an average mortality rate of 8.05 x 10^{-7} and 1.17 x 10^{-6} for morbidity, in samples from Dibate, while samples from Lokaleng had an average male mortality of 7.59 x 10^{-6} and 1.60 x 10^{-6} for morbidity, with a female mortality of 1.17 x 10^{-6} and 1.17 x 10^{-6} for morbidity and samples from Moletsamongwe, Lekung, Aiport –view had the average male mortality rate of 1.76 x 10^{-6} and 2.55 x 10^{-6} for morbidity, the average for female mortality was found to be 1.87 x 10^{-6} and 2.71 x 10^{-6} for morbidity.

The radiological hazards data in this study show that the potential radioactive risks caused by tritium and radiocarbon were within acceptable limits in the study area. There were no health risk is posed to the public by the ingestion of the water from these sources, which could help put the public at ease regarding any concerns they might have about the effects radioactivity in groundwater.

Although the radiological doses in this study are well within the limits, according to ALARA, no dose should be acceptable if it can be avoided. Therefore, radiological studies are important from time to time to monitor the quality of the villages' aquifers which are being abstracted for consumption by mankind.

5.1 Recommendations

This is the first study of tritium and radiocarbon in groundwater consumed in the studied villages in Mahikeng. The reported data in this study will help to establish a valuable baseline data for tritium and radiocarbon activity concentrations in borehole water consumed in Mahikeng, which will be useful for future researchers. This study will contribute scientific knowledge for the radiological assessment of tritium and radiocarbon in drinking water since the annual effective dose rates and lifetime cancer risks were assessed in this study. This will also help develop guidelines for the radiological protection for the people in the areas or the province even.

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APPENDIX A: SAMPLE GPS COORDINATES

Sample number	**latitude**	**longitude**
S1	-25.8429676	25.6097997
S2	-25.8429676	25.6097997
S3	-25.8441266	25.611218
S4	-25.8441266	25.611218

S5	-25.8415218	25.6067778
S6	-25.8442014	25.6091702
S7	-25.8442014	25.6091702
S8	-25.8453056	25.6067778
S9	-25.8453056	25.6067778
S10	-25.8415218	25.6067778
S11	-25.8370903	25.5864261
S12	-25.8370903	25.5864261
S13	-25.8353096	25.5673012
S14	-25.8353096	25.5673012
S15	-25.8493044	25.56718832
S16	-25.8351831	25.5699057
S17	-25.8331338	25.5617832
S18	-25.8453842	25.566073
S19	-25.8493044	25.56718322
S20	-25.8331338	25.5671832
SM1	-25.833158	25.568738
SM2	-25.826389	25.570833
SM3	-25.846111	25.564694
SM4	-25.84	25.564833
SM5	-25.855472	25.579889
SM6	-25.851778	25.56175
SM7	-25.839167	25.535528
SM8	-25.838444	25.536639
SM9	-25.841528	25.511833
SM10	-25.827444	25.516083