APPLICATION OF BIOLOGICAL SAMPLE OXIDISER AND LOW-LEVEL LIQUID SCINTILLATION COUNTER FOR THE DETERMINATION OF ^{14}C AND ^{3}H CONTENT IN WATER FROM THE HARTBEESPOORT DAM IN NORTH-WEST PROVINCE

by

LAMLILE HLAKANIPHILE NTANDO KHUMALO

submitted in accordance with the requirements

for the degree of

MASTER OF SCIENCE

in the subject

ENVIRONMENTAL SCIENCE

at the

UNIVERSITY OF SOUTH AFRICA

SUPERVISOR: DR M S SONOPO

CO-SUPERVISOR: PROF S J MOJA

February 2016

Dedication

To my kids, my daughter Nosipho and my son Thembelani, who have always been understanding and supportive.

Declaration

Name: Lamlile Hlakaniphile Ntando Khumalo

Student number: 45665583

Degree: Master of Science in Environmental Science

The title of the dissertation as appearing on the copies submitted for examination:

APPLICATION OF BIOLOGICAL SAMPLE OXIDISER AND LOW-LEVEL LIQUID SCINTILLATION COUNTER FOR THE DETERMINATION OF ^{14}C AND ^{3}H CONTENT IN WATER FROM THE HARTBEESPOORT DAM IN NORTH-WEST PROVINCE

I declare that the above dissertation/thesis is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.

SIGNATURE DATE 2016/05/27

Acknowledgements

I would like to express my deepest gratitude to the following individuals, whose patience, support and guidance have contributed towards the success of this research study.

First and foremost, I am most thankful to my research Supervisor at Necsa, Dr. Molahlehi Sonopo, for encouraging my research and encouraging me to grow in the research field, without his guidance and his continuous support; I would not have finished this research. To my research Co-Supervisor, Professor Shadung Moja, I would like to express my special appreciation for his guidance, motivation and immense knowledge.

To my Manager at RadioAnalysis at Necsa, Mr. Sello Mokhobo, I am forever grateful for the opportunity to conduct this research, for the time he`s given me, for the financial support granted and for his continuous support. To the RadioAnalysis laboratory expert, Mr. Deon Kotze, I would like to express my gratitude for his brilliant comments, suggestions and his immense knowledge. I am forever grateful to Ms Immanda Louw for her patience, guidance and encouragement; I could not have imagined a better mentor. To my laboratory Supervisor, Ms. Monika Buys, for her continuous support and for her encouragement.

I would also like to express my deepest appreciation to my colleagues at RadioAnalysis for being supportive, for always willing to help and for allowing me to use the instruments whenever there was a chance. Lastly, I would like to express my deepest gratitude to The South African Nuclear Energy Corporation SOC Limited – Necsa for financial support and the time that the company has provided for me to be able to complete this research in time.

Abstract

The aim of the research study was to evaluate the levels of ^{14}C and ^{3}H radionuclides in Hartbeespoort Dam water and to determine if these radionuclides are within regulatory concerns. Water samples from Hartbeespoort Dam were prepared using the Sample Oxidiser Method and measurements of selected radionuclides were done using Liquid Scintillation Counter Quantulus 1220.

The results evaluated suggest that water from Hartbeespoort Dam contains levels of ^{14}C and ^{3}H radionuclides that are within regulatory limits. The highest average concentration for ^{14}C measured was 3.77E+01 (+/-2.47E-01) Bq/L, whereas the highest average concentration measured for ^{3}H was 2.74E+01 (+/- 2.30E-01) Bq/L. The observations made regarding the impacts of climate on the ^{14}C radionuclide were that, the concentration levels were higher during winter season when there was a rain than during rainy seasons. Tritium results showed that the climate conditions did not have any significant impacts on the concentration levels. When the concentrations of these radionuclides are above regulatory levels (^{14}C is 100 Bq/L and ^{3}H is10000 Bq/L), their impacts may cause harm to public`s health and the environment. Therefore, Necsa as a nuclear facility owner and National Nuclear Regulator (NNR) as a regulator are responsible for ensuring the public protection from radioactive effluents that contain not just $^{3}H$ and $^{14}C$, but any radionuclide which may cause harm to public`s health.

Key terms: *Tritium, carbon-14, liquid scintillation counter, sample oxidiser, environment, nuclear facilities, radionuclides, liquid effluent, quench curves and water.*

Table of Contents

Tables and Figures

Tables

Figures

Chapter 1: The Introduction

Water is the most precious natural resource that exists on the planet and it plays a vital role in both environment and human life (Orebiyi & Awomeso, 2008). Almost all organisms contain it; some live in it and most drink it (McCracken, 2004). Although humans recognize the fact that water is the most critical natural resource, some of their activities degrade water quality by polluting rivers, lakes, dams and oceans. Water quality is one of the present and future critical environmental issues worldwide, including South Africa. It is affected by a wide range of natural and human influences (Meybeck *et al*., 1996). Human activities interfere significantly on water quality. More obvious effects are polluting activities, such as the discharge of domestic, industrial, urban and other wastewaters (including water from nuclear facilities) into the watercourse (whether intentional or accidental). Although water may be available in adequate quantities, the uses that may be made of it can be limited due to its unsuitable quality.

Degraded water quality makes streams, lakes and coastal waters unpleasant and unsafe (McCracken, 2004). If severe, it can kill large numbers of fish, birds, and other animals and in some cases, killing all members of species in a contaminated area. Fish and shellfish harvested from radioactive contaminated waters may be unsafe to eat. Humans who ingest contaminated water can become ill, and, with prolonged exposure, may develop cancers or bare children with hereditary defects. Kachel (2008), states that the threat to humans and the environment very much depend on the radioactivity, the bio-distribution and the half-life of the isotope. However, lethal damage is very difficult to detect in short term tests, as actual damage does not usually occur immediately after exposure.

Water quality does not have an impact only on human health, animals and aquatic species, but also on the economy. When water quality is the factor in the production of market goods, then it affects the costs of goods being produced. The improvement of water quality reduces the industrial production costs while, the market price of goods will also be reduced United. The economists in USA have conducted

numerous studies on the value of water quality over the years. The results of these studies indicate that the annual benefits of USA from improving water quality could total tens of billions of dollars per annum (United States Department of Agriculture (USDA), 2006). The socio-economic impacts of the release of radioactive contaminants and wastes into the aquatic environment from human activities results with the following impacts:

- avoidance of amenities and products due to perceptions of effects of contamination,
- costs of public reassurance,
- risks to human health, and
- maintenance of monitoring and radiological protection activities for public reassurance purposes.

Therefore, enhanced capacity for scientific assessment, monitoring and early warning is therefore critical and necessary (Calmet, 2014) to eliminate and/or minimize the impacts of radionuclide waste on the environment.

Over the last decades, several organizations including the World Health Organization (WHO) have shown keen research interest in monitoring the water quality due to increasing rates of deterioration due to radioactive material, with the aim of creating control methods and proposing water protection strategies. For instance WHO published international guidelines from 1958 (WHO, 1958) and the International Standardization Organization (ISO), cooperating with WHO has been publishing standards on radioactivity test methods since 1978. These standards focused on monitoring radionuclides in water from the beginning and the guidelines are based on the assumption that monitoring the environment, food quality and the protection of human health are inseparable. These guidelines are in line with the system of radiological protection, with the increasing use of nuclear energy and public concern with the potential radioactivity effect on health (Calmet, 2014).

Environmental monitoring of radioactive carbon-14 (^{14}C), tritium (^{3}H) and stable isotopes (^{2}H, ^{13}C, ^{18}O) levels in the atmosphere and biosphere started about four decades ago. The measurements of atmospheric ^{14}C and ^{3}H have been performed since 1976 and 1978, respectively (Krajcar-Bronic *et al*., 1998).These radioactive isotopes were artificially introduced into the environment during past nuclear testing and are still legally discharged in liquid and gaseous effluents by the nuclear industry (Eyrolle-Boyer *et al*., 2015). According to Calmet (2014), radionuclides are commonly measured in the course of controlled radioactive gaseous and liquid releases and radiological, environmental and food monitoring.

Carbon-14 and tritium isotopes are produced by nuclear reactions that occur naturally in the environment, in nuclear weapon testing and in nuclear reactors. The waste generated by nuclear industry contains different amounts of ^{14}C and ^{3}H isotopes which vary depending on the reactor type, plant operation, method of fuel reprocessing and the radioisotope production process. These isotopes are considered to be problematic and they enter freely into water, plants, animals and humans. These elements are essential, biologically-regulated and are highly mobile in the environment and human body (IAEA, 2007).

1.1. Background

Carbon-14 and tritium are naturally occurring radioisotopes that are produced continuously in the atmosphere by cosmic ray neutron interaction with nitrogen and hydrogen, respectively, and are also produced as a by-product or special product in nuclear reactor systems (IAEA, 2004). According to IAEA (2004) radioactive waste that contains ^{14}C and ^{3}H is continuously generated by the nuclear industry, for example, in nuclear reactor operations, spent fuel reprocessing, radioisotope production, and in medical research. Nuclear Industry Association of South Africa (NIASA), (2012) recommends nuclear facilities to routinely discharge small but carefully monitored and controlled quantities of radioactive material into the air and water. Some of these materials consist of ^{14}C which is created by neutron

bombardment of nitrogen dissolved in water and others consist of ^{3}H which is created through irradiation of boron dissolved in the coolant water.

South Africa has two nuclear facilities which are Koeberg Nuclear Power Station and Necsa's Pelindaba site respectively, Figure 1.1(a) and (b). Koeberg Nuclear Power Station is located 28 km north of Cape Town, Western Cape Province where the liquid effluent is mixed with the fast moving cooling-water outfall that discharges into Atlantic Ocean. On the other hand, Necsa's Pelindaba site is located 40 km west of Pretoria in the North West Province and it includes the SAFARI-1 research and isotope production reactor where the liquid effluent is released into the Crocodile River upstream of the Hartbeespoort Dam. Both sites discharge gaseous effluent through the ventilation stacks (NIASA, 2012). Discharge facilities are typically municipal or industrial operations that release effluent water into the aquatic environment (Johnson *et al*., 2008).

Figure 1.1 (a) Koeberg Nuclear Power Station (b) Pelindaba, SAFARI-1 (**NIASA, 2012)**

Releasing liquid effluent into the Crocodile River upstream of the Hartbeespoort Dam might have a negative impact on the quality of dam water. According to UNEP (2006), the effects of human activities on water quality are both widespread and varied in the degree to which they affect the ecosystem and/or restrict water use. The importance attached to water quality depends on its actual and planned uses, for an example, water that is to be used for drinking should not contain any chemicals or substances that could be hazardous to health (UNEP, 2006). The Hartbeespoort Dam was built in

1923 for irrigation purposes. It soon became a water source for primary consumption, industrial and also an attractive recreational destination for many water-sports enthusiasts and local and international tourists (Department of Water and Sanitation, 2015). Therefore if the quality of the Hartbeespoort Dam water is degraded, then water from the dam will no longer be of any importance use.

The liquid effluent that is released from SAFARI-1 reactor into Crocodile River is being routinely monitored by sampling water, sediment and fish from the Crocodile River and Hartbeespoort Dam. Milk from the surrounding farms, plants material from the surrounding area and air filters on the Pelindaba site are also routinely monitored for gross alpha/beta and gamma radiation as per the requirements for South Africa`s National Nuclear Regulator (NNR) (Nuclear Industry Association of South Africa (NIASA), 2012). NIASA (2012) further state that typically, the radioisotopes responsible for off-site exposure due to liquid effluent comprise a mixture of beta/gamma emitting fission and activation products. ^{14}C and ^{3}H radioisotopes are part of the beta mixture in the liquid effluent that is being released from Safari-1. ISO/FDIS 13168, 2014 states that the natural activity concentrations of ^{14}C and ^{3}H can vary according to local geological and climatic characteristics, at a level below 0.1 Bq/l and below 5 Bq/l respectively. These radioactivity levels can be locally enhanced by nuclear facilities authorised discharges of low level radioactive effluent into the environment.

1.2. Problem Statement

The research study was conducted to evaluate the levels of ^{14}C and ^{3}H radionuclides in Hartbeespoort Dam water and to determine if these radionuclides are within regulatory concerns. Since water from Hartbeespoort Dam is used for, inter-alia, mainly for irrigation purposes and for domestic consumption (Department of Water and Sanitation, 2015), as part of environmental protection, it is important to ensure that the ^{14}C and ^{3}H levels are within acceptable limits by monitoring the environment. Roughly 80% of water is used for irrigation and domestic consumption and compensation flows uses lesser water. Recently irrigation canals are supplied with

110 – 150 million m^3 of water per annum depending on weather conditions. Madibeng Local Municipality is totally dependent on the water from the dam. Inhabitants around the dam and large settlements downstream, including the town of Brits, use purified dam water for drinking purposes (Department of Water and Sanitation, 2015). According to IAEA, environmental protection includes the protection of living organisms other than humans and the protection of natural resources, including land, forests, water and raw materials, together with a consideration of non-radiological environmental impacts (IAEA, 2004).

Since South Africa intends to increase the nuclear reactors from two to eight, there is an urgent need to refine current methods that can monitor or measure the levels of radioactivity in the natural environment. Through this study, a method that is capable of detecting ^{14}C and ^{3}H in river and dam water systems was developed. This method will enable nuclear facilities such as Necsa to be able to screen out ^{14}C and ^{3}H radionuclides from Hartbeespoort Dam and its feeding stream, Crocodile River.

The research questions of the study are:

- Does water from Hartbeespoort Dam contain ^{14}C and ^{3}H radionuclides?
- Is it possible to prepare and measure the concentration of each radionuclide using catalytic sample oxidiser and LSC for the purpose of environmental monitoring?
- Who is responsible for ensuring that the water retains its regulatory limit when it comes to radionuclides in question?
- Does the climate have any impact on the ^{14}C and ^{3}H radionuclides regarding the environment?

1.3. Aims and Objectives

The aim of the research study was to evaluate the levels of ^{14}C and ^{3}H radionuclides in Hartbeespoort Dam water and to determine if these radionuclides are within regulatory concerns.

The objectives of the study are:

- To develop a method for the determination of ^{14}C and ^{3}H in water from Hartbeespoort Dam.
- To determine the presence of ^{14}C and ^{3}H in water from Hartbeespoort Dam.
- To prepare and measure the concentration of each radionuclide using catalytic sample oxidiser and LSC for the purpose of environmental monitoring.
- To evaluate if the content of ^{14}C and ^{3}H in water is within the regulatory concerns.
- To determine if the climate have any impact on the ^{14}C and ^{3}H radionuclides regarding the environment.

1.4. Chapter breakdown

Chapter 1: **Background** – This chapter gives an overview of how the nuclear facilities contribute to the distribution of ^{3}H and ^{14}C isotopes to the environment. In this chapter, the importance of monitoring the environment for radionuclides and evaluating the impacts of ^{3}H and ^{14}C is expressed in detail.

Chapter 2: **Literature review** – This chapter gives an overview of the impacts caused by ^{14}C and ^{3}H on the environment which are released from the nuclear installations either through ventilation stacks into the air or as liquid effluent (contaminated water) into the water. The evaluation of different methods that can be utilized for the determination of the isotopes in question is also discussed in this chapter.

Chapter 3: **Research methodology** – This chapter gives clarity on methodologies used to measure the contents of ^{3}H and ^{14}C in water samples. In this chapter, the location of the study area where samples that are used in this study were collected is detailed. Research methodology involves methods used to optimise the equipments used for sample preparation and sample measurements and also involves the methods used to collect and analyse data.

Chapter 4: **Results and Discussion** – This chapter aims to present and interpret the results and also to discuss the findings. The establishment of confident results is essential, taking into account that important decisions are based on the analytical results. The results are presented in the form of Tables and Figures.

Chapter 5: **Conclusion and Recommendations** – in this chapter the conclusions are drawn based on the observations made from the result findings and recommendations are made to provide solutions.

Chapter 6: **References and Appendices**

6.1: References – Here is the breakdown of sources of information consulted.

6.2: Appendices – Raw data.

Chapter 2: The Literature Review

In South Africa, the National Nuclear Regulator (NNR) has determined that no member of the general public, including people living around nuclear installations, may be exposed to more than the internationally accepted limit of one millisievert per year (1 mSv/y). This regulation is for all sources of radiation, therefore nuclear installations must ensure that no one receives more than 0,25 mSv/y (in addition to the natural background level) as a results of effluent discharged (NIASA, 2012).

Discharge limits are usually attached to or incorporated into the facility license and become the legal limits with which operator or licensee should comply (IAEA, 2004). The discharge limits should satisfy the requirements for the optimization of protection of the environment and the condition that doses to the individual members of the population who can be expected to receive the highest dose due to their lifestyle habits and location (Sellafield Ltd, 2012) (critical group) should not exceed the appropriate dose constraints (IAEA, 2000). Part of the requirements for the protection of the environment with regards to liquid effluents being discharged into the environment is to determine the impacts of each radioisotope in the mixture of effluents being discharged. The mixture of effluents may contain ^{3}H and ^{14}C radioisotopes that are artificially introduced into the environment by nuclear industries (Eyrolle-Boyer *et al.*, 2015). Since both ^{3}H and ^{14}C are mobile in the environment (IAEA, 2004), it is important to determine the impacts they might have on the environment. The literature indicates that there are quite a number of impacts associated with ^{3}H and ^{14}C radioisotopes on the environment.

2.1. The impacts of ^{14}C on an environment

Carbon-14 (^{14}C) is a pure beta emitter with energy of 156.5 keV and half-life of 5700 ± 30 years. It is considered as a radionuclide of interest in nuclear power production (Yim & Caron, 2006); (Huang *et al*., 2015). Therefore, it can be a radionuclide of major concern after mixing with stable ^{12}C, ^{13}C followed by the biological incorporation into biota, due to its long half-life and high mobility in the environment,

as carbon is the fabric of life. The environment contains ^{14}C that is of natural origin and man made. Relatively large amounts of ^{14}C have been released into the environment as a result of atmospheric nuclear weapon testing, emissions from nuclear engineering installations and the application and processing of isotopes (ISO 13162, 2011). During these processes different carbon isotopes such as stable nuclides carbon-12 (^{12}C) and carbon-13 (^{13}C) as well as the radioactive ^{14}C are incorporated into the organic material in the exact same proportions in which they occur in nature (Edler & Kaihola, 2007). According to Lemon (1997) the ^{14}C concentration in the atmosphere has been both increased and decreased due to human activities. When humans began large scale burning of fossil fuels, the amount of carbon in the atmosphere was increased. Living organisms take up carbon from their food or via breathing or photo synthesis. Carbon-14 is a low beta emitter, with a low penetrating power which causes radiation stress mainly due to internal irradiation, if it is incorporated. From the radiobiological standpoint, ^{14}C is integrated in cellular components (proteins, nucleic acids), particularly cellular DNA (Le Dizes-Maurel *et al.*, 2009).

Carbon-14 is released to the environment through gaseous and liquid discharges and is also released through the disposal of solid radioactive waste (Blowers *et al*., 2011). This radioactive isotope is easily transferred during biological processes and soil-plant interactions involving carbon compounds. Carbon dioxide ($^{14}CO_2$) rapidly equilibrates with the air in the lungs when inhaled and it also enters many components of the body tissue. It has been found that ^{14}C can be easily concentrated in food chain. Therefore, accumulation of ^{14}C in the human body via ingestion of contaminated food results in significant impacts compared with that from respiration which is insignificant (IAEA, 2004). The guidance level for ^{14}C is 100 Bq/L. The values can be modified by a national legislation of countries with nuclear facilities, usually lowered (WHO, 2011).There is a demand for ^{14}C analysis for both waste characterisation and environmental purposes due to the activity levels of ^{14}C in the environment (Blowers *et al*., 2011). It is reported as the radionuclide that is contributing the second highest internal effective dose to the human body,

approximately 3500 Bq (ISO/TC 147, 2011).Thus, it is necessary to assess the radiological impacts of ^{14}C on the public and the environment regularly (Limer *et al*., 2015).

There have been a large number of scientific investigations in the past regarding ^{14}C waste management and the concerns of the public health over the release of ^{14}C from nuclear power plants. Most of these investigations were performed in the 80`s and 90`s (Yim & Caron, 2006). This investigations included, characterizing ^{14}C inventory in plant systems and in plant waste streams, characterizing the amount and chemical forms of ^{14}C release to the environment, understanding the fate and transport of ^{14}C in the environment, applying necessary processing and treatment of ^{14}C waste, finding appropriate waste forms for ^{14}C immobilization and isolation. Garnier-Laplace & Roussel-Debet (2001) have found that ^{14}C in liquid effluents that is released as carbonates, is incorporated in the organic carbon. **Figure 2.1** shows the *carbon cycle in freshwater hydrosystems* where the main forms are organic carbon, particulate carbon and inorganic carbon.

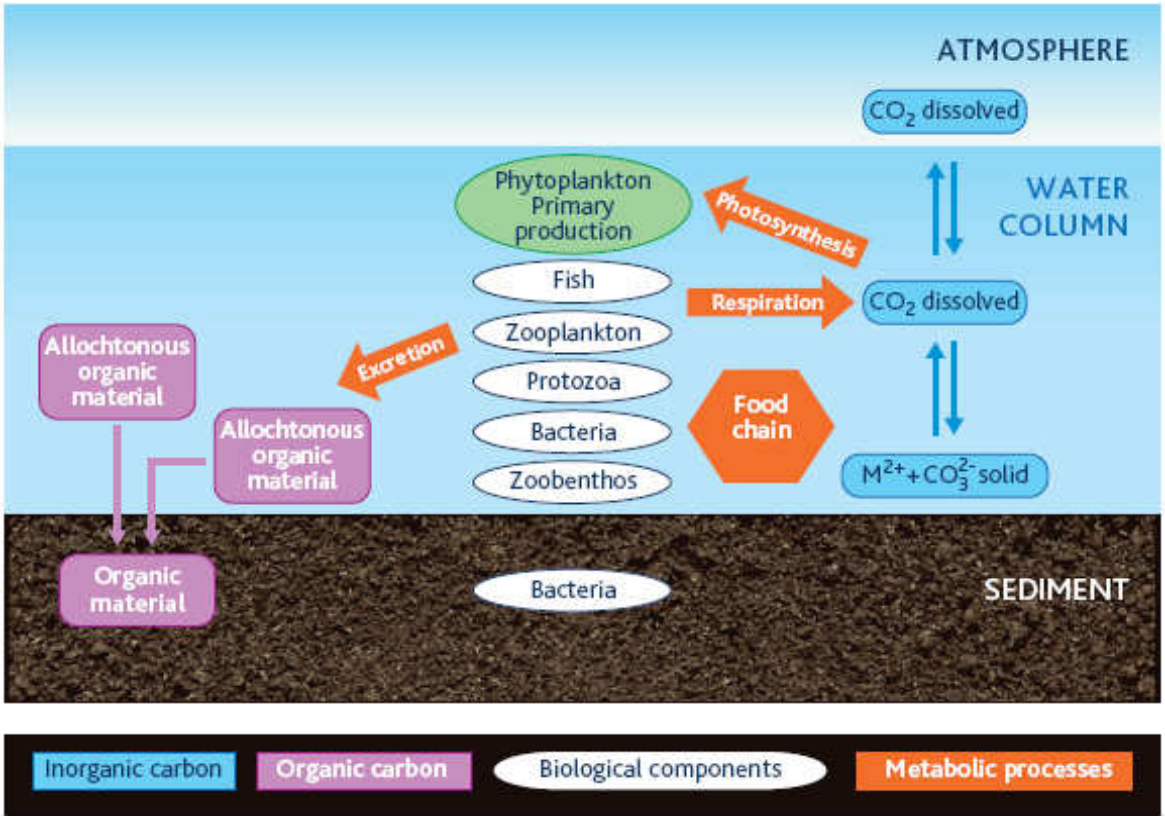


***Figure 2.1**: Carbon cycle in freshwater hydrosystems* (Garnier-Laplace & Roussel-Debet, 2001).

Roussel-Debet *et al.* (2006) conducted a study on the distribution of ^{14}C in the terrestrial environment close to French nuclear power plants. Their findings were that the ^{14}C activity measurements carried out highlight, on one hand, a small but significant increase in ^{14}C in the immediate environment of each site. On the other hand, the measurements showed the decline in specific radioactivity in carbon terrestrial environment over time. Whereas Yim & Caron (2006) studied the life cycle and management of ^{14}C from nuclear power generation. Their aim was to provide the basic/up-to-date understanding of lifecycle of ^{14}C. The research started from the production of ^{14}C in reactors, to eventually its transport and its potential incorporation in natural cycles, emissions potential from nuclear power plants, types of wastes and waste forms, the potential of this radionuclide for migration in the environment, and other environmental aspects.

They found out that although ^{14}C in the environment is not at a level to pose threat to public health; it may be a concern if appropriate measures are not enforced.

In 2005, Aquilonius & Hallberg performed a study on the process-oriented dose assessment model for the ^{14}C due to releases during normal operation of a nuclear power plant in Sweden. A process-oriented assessment model for uptake of carbon and dose releases of ^{14}C to air was developed in order to take local conditions including ambient conditions and photosynthesis into account. Due to releases of radionuclides during normal operations, it was the requirement for Swedish nuclear utility companies to assess doses. The ^{14}C isotope was of special interest for this dose assessment study due to the role of carbon in the metabolism of all life forms. Several exposure pathways were examined when conducting this study. These includes direct consumption of cereals which are locally grown, vegetables and their roots, as well as consumption of milk and meat from cows having eaten fodder cereals and green fodder from the area around the nuclear plant. The resulting average air concentration of ^{14}C and site specific crop yield were used together to calculate the concentration of ^{14}C in various crops. However, the public dose was assessed using different exposure pathways. Aquilonius & Hallberg (2005) concluded that the length of growing season, mean temperature during growing season and global radiation, do not generate any large differences in crop yield between the nuclear power plant sites in Sweden. The authors are of the opinion that this is probably due to the relatively small differences in climate change in Sweden, especially since the nuclear power plants are all on the coast (Aquilonius & Hallberg, 2005).

Limer *et al*. (2015) studied the impacts of ^{14}C discharges from a nuclear fuel reprocessing plant on surrounding vegetation in the vicinity of AREVA-NC La Hague nuclear fuel reprocessing plant in France. This study compared two different models to reproduce the observed variability in grass ^{14}C activity. The first model is TOCATTA-X model, which has been designed to model ^{14}C and ^{3}H in the terrestrial environment over short to medium timescales. The second model is SSPAM^{14}C, which has been intended to model the transfer of ^{14}C in the soil-plant-atmosphere

with consideration over both short and long timescales. The main aim of this study was to investigate the strengths and weaknesses of the two models and to investigate if modelling could be improved. The study showed that due to the different set of objectives, both TOCATTA-X and SSPAM^{14}C models adopt different approaches in terms of processes and times for representing the transfer of ^{14}C from the atmosphere to grass. The study`s implication is that models developed in the context of waste disposal, at the long timescales associated with post-closure safety can be considered. These models can also be modified to include more physical and physiological processes to improve the predictions of short to medium term dynamics in ^{14}C specific activity in agricultural ecosystems (Limer *et al*., 2015).

2.2. The impacts of ^{3}H on an environment

Tritium is a naturally occurring or manmade radionuclide whose monitored level can be used to estimate humans` exposure around nuclear fuel reprocessing plants and fission facilities (Fukutani *et al*., 2008). Thus, it is important to evaluate the environmental impacts of ^{3}H in environmental samples, in particular those that are for human consumption (Palomo *et al*., 2007). It is necessary to monitor ^{3}H concentrations regularly in order to establish background levels so that exposures to workers or the general public near nuclear facilities can be assessed in everyday situations or accidents (Fukutani *et al*, 2008).

^{3}H is a radioactive isotope of hydrogen with a half-life of 12.3 years (IAEA, 2004). ^{3}H exist in three different forms or components: (HTO), gaseous tritium (HT) and organically bound tritium (OBT) (Calmon & Garnier-Laplace, 2010). According to Lemon (1997), since the beginning of atmospheric nuclear testing, large quantities of ^{3}H have been introduced into the atmosphere. Other sources of ^{3}H are weapons production industries nuclear industries and digital watch manufacturers. These industries release ^{3}H into the lower atmosphere and directly into the hydrologic cycle. Tarancon *et al*. (2010) are of the opinion that the secondary contribution of ^{3}H comes from rersearch activities in which ^{3}H is used mainly as a tracer in biological or environmental studies. ^{3}H most commonly enters the environment in a gaseous form

(T_2) or as a replacement for one of the hydrogen atoms HTO instead of ordinary, non-radioactive water (Nikolov *et al*., 2013). According to IAEA (2004), HTO is transferred to humans via inhalation, diffusion through skin and ingestion. Inhalation is the only meaningful pathway of the gas containing both hydrogen and HT to humans. Osborne (2002) is of the opinion that the impacts of ^{3}H to human health depend on the different ages, relative to adults, when living in environments with different amounts of ^{3}H in air, water or food. Therefore determining the levels of ^{3}H contamination in the environment gives an indication of how the human health will be impacted upon.

World Health Organization (WHO) proposed the international approach to assess the safety of drinking water with respect to its radionuclide screening levels and guidance levels (Calmet *et al*., 2013). The limit that is commonly used as a guideline is the one for (WHO, 2011) which is 10000 Bq/L for a man of 70 kg who drinks 2 litre of water per day. Due to its low energy beta emission and corresponding short range in air, ^{3}H poses a risk only when ingested, inhaled or absorbed through the skin (Dingwall *et al*., 2011). The upper limit for ^{3}H activity in water is 10000 Bq/L (European Commission, 1998; Dingwall *et al*., 2011), therefore, values exceeding the limit could indicate that there is a leakage or release that occurred on a power plant and further analysis are then realized to check if other radionuclides are present in water (Nikolov *et al*., 2013).

In 1979, Brown studied the environmental ^{3}H in trees by monitoring the distribution of tritium in the free water and organically bound hydrogen of trees growing in the vicinity of the Chalk River Nuclear Laboratories (CRNL). The study was performed to monitor the behaviour of ^{3}H in the environment. The CRNL Liquid Waste Disposal Area provided a useful site for studying ^{3}H dispersal in the natural environment. While studying HTO in the free water of trees, three factors were considered: 1) the pickup of atmospheric HTO by a tree, 2) regional pattern of leaf HTO around an industrial source and 3) the HTO content of a sequence of tree rings. Whereas studying organically bound ^{3}H in tree rings compared two factors, trees in the disposal area and trees that are off site.

The findings were that analysis of the ^{3}H content of tree leaf moisture was found to provide a convenient means of observing regional atmospheric dispersal of tritiated water from an industrial source and the relevance to population exposure considerations were due to the concentrations established in such vegetation by a given release since they combine contributions from atmospheric moisture, precipitation and soil water averaged over a few weeks.

In 2011, the research study on ^{3}H in the environment of Gulf of Finland basin was conducted to evaluate the impacts of ^{3}H radionuclide on the environment. This study was conducted due to the expanding construction of nuclear industrial plants and nuclear power stations on the shores of the Baltic Sea in Gulf of Finland (Kulkova & Davivochkina, 2011). This activity created a real possibility for the introduction of radioactive wastes into the vegetation and the water of Baltic Sea basin. It has been found that the countries located around Baltic Sea are under disaster of radionuclide pollution due to the industrial waste from nine countries which has nuclear power reactors on their coasts that discharge the liquid effluents into Baltic Sea. The Baltic Sea is shallow and is isolated from the Atlantic Ocean. This was the reason for Baltic Sea to have low capability for purification and the time it takes for the water exchanging process can go up to twenty seven years. To conduct this study, a Sample Oxidizer 307 was used for sample preparation and LSC Quantulus 1220 was used for the measurements of vegetation and water samples from the Baltic Sea region. The results of the study showed that the ^{3}H content in vegetation is much higher than in water. The results obtained during the study accurately testify that ^{3}H concentration in biological objects which has organic connections is 5.5 times higher than in water. Furthermore, they discovered that in biological compounds ^{3}H has more strong organic bonds than in water and the vegetation receives the ^{3}H from water, air and soil. Their study indicated that there was a significant difference on the distribution of ^{3}H concentration in different types of water, snow cover and vegetation of Finnish Bay basin. **Figure 2.2** indicates the *transfer of ^{3}H in terrestrial environments at the air-soil-plant interfaces and in animals, including transfer to foodstuffs.*

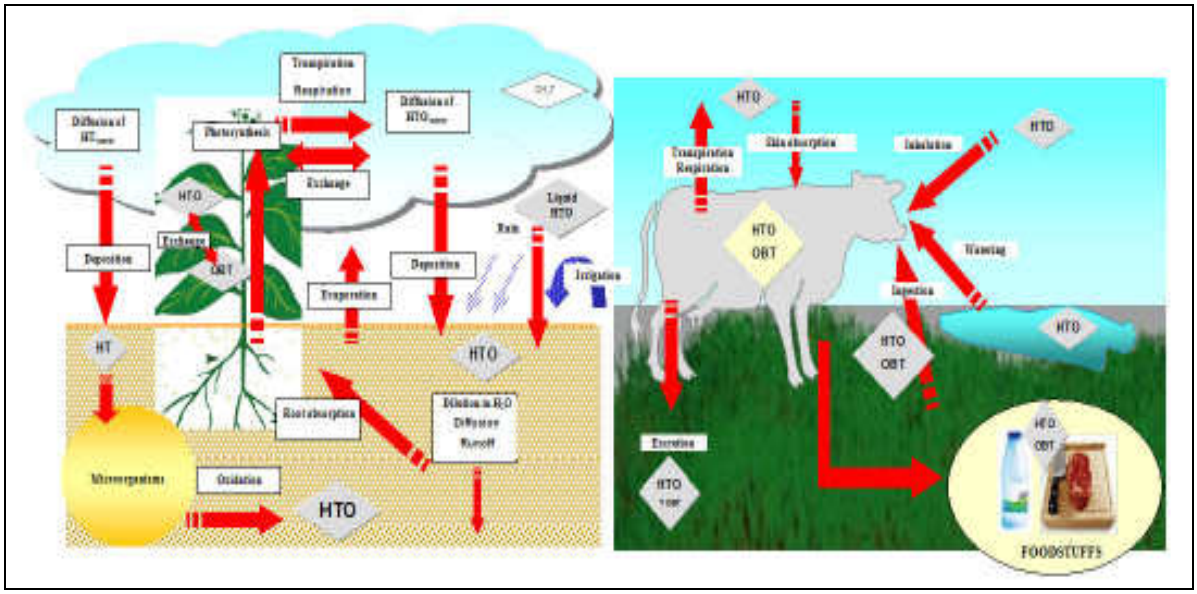


Figure 2.2: *Tritium transfer in terrestrial environments at the air-soil-plant interfaces and in animals, including transfer to foodstuffs* (Calmon & Garnier-Laplace, 2001).

The research study of potential impacts of ^{3}H exposures on health of the general public was conducted in Canada (Osborne, 2002). In this study three factors were looked into, firstly, ^{3}H in the Canadian environment, secondly, radiation doses to people living in environments contaminated with ^{3}H and lastly the health effects from exposure to ^{3}H. Osborne (2002) discovered that most of the ^{3}H with which humans come into contact with is in the form of water and emissions from the nuclear facilities and some from industrial facilities that use ^{3}H. Osborne (2002) further states that away from nuclear facilities in Canada, concentrations of tritium in air and in water are typically 0.1 Becquerel per cubic metre (Bq/m^3) and 5 Becquerel's per litre (Bq/L) respectively, whereas in the regions around nuclear facilities these values are typically $1Bq/m^3$ and 30 Bq/L. The conclusion was that there have not been any direct observations in humans of cancers or genetic disorders occurring as a result of radiation doses from ^{3}H and that the radiation doses to Canadians from ^{3}H in the environment; even close to the facilities are too low to have any observable health consequences (Osborne, 2002).

Cliffroy et al. (2006) conducted a study on a dynamic model for assessing radiological consequences of tritium routinely released by nuclear power plants in rivers. This study was done by applying a dynamic model for assessing the transfer of ^{3}H in food chain to the Loire River in France, where fourteen nuclear power plants situated on five different sites operate. Several potential exposure pathways in the aquatic and terrestrial ecosystems were considered by the model during this exercise: Transfer of ^{3}H through the aquatic food chain (especially fish), Use of river water for agricultural purposes (irrigation), transfer of radionuclides through the terrestrial food chain (vegetables, meat and milk) and subsequent internal exposure of humans due to the ingestion of contaminated foodstuffs. This study demonstrated that ^{3}H released that is being routinely released by nuclear power plants is intermittent. Therefore, it was necessary for the researchers to develop a dynamic model accounting for transfer of both HTO and OBT in environmental compartments. The Loire River case study had three conclusions:

- There was no significant increase of the total dose observed along the Loire River,
- Water ingestion represents the most important dose pathway; however, the ingestion of contaminated foodstuffs, especially milk, fruits, vegetables and root vegetables represent about one-third of the total dose, and
- For all the compartments investigated, HTO doses are predominant, even if for some exposure pathways HTO and OBT doses are comparable.

2.3. The impacts of both ^{14}C and ^{3}H on an environment

It is possible to use environmental monitoring data, resulting from tests on levels of radioactive material sampled in the environment and activity concentration levels in foodstuffs including water as input values for the dose model parameter. Governments, industry and the public need access to adequate and reliable information on radioactivity concentration in food and the environment in order to make optimal informed decisions on minimizing risks and protecting public health and the environment (Calmet, 2014).

Monitoring of environmental levels of radioactive (^{14}C, ^{3}H) and stable isotopes (^{2}H, ^{13}C, ^{18}O) in the atmosphere and biosphere started about four decades ago, approximately at the same time as the significant anthropogenic disturbance of natural distributions of ^{14}C and ^{3}H occurred (Krajcar-Bronic et al*.,* 1998). To test the performance of the models for the environmental transfer, the international Atomic Energy Agency's Environmental Modelling for Radiation Safety (EMRAS) model evaluation programme included a ^{3}H and ^{14}C Working Group (TCWG) (Yankovich et al., 2008). Tritium and carbon-14 integrate into water and closely follows the water cycle and as a result, these two elements persist in both terrestrial and aquatic environments (Eyrolle-Boyer *et a*l., 2015).

Popoaca *et al.* (2014) conducted an exercise for environment routine monitoring program at the Cernavoda Nuclear Power Plant (Cernavoda NPP) in Romania. This study included determination of ^{3}H and ^{14}C in organic sample after separation through combustion method. The objectives of this study were to measure the radionuclide concentrations in environmental media, to assess the increased radiation levels in specified pathways and to contribute to the public reassurance through the results of the routine monitoring program which may have demonstrated negligible public impact of the Cernavoda NPP operations. This program was based on the site-specific derived emission limit (DELs) document for the Cernavoda NPP, which identifies probable radionuclides that may be released from station and the probabilities of environmental pathways of these radionuclides. The study showed that there were no significant differences between the actual and the background levels. Since the actual levels are so low, the public`s heath safety could be assured.

Eyrolle-Boyer *et al*. (2015) conducted a study on ^{3}H and ^{14}C background levels in pristine aquatic systems and their potential sources of variability. Tritiated water, OBT and ^{14}C analysis were performed on surface sediments collected over the past decades from rivers in mainland France at points located far from the influence of the nuclear industry as part of a radiological survey and environmental monitoring. For ^{3}H analysis, some samples were combusted, while some were distilled and then measured by LSC, while accelerator mass spectrometry was utilized for ^{14}C analysis.

The results showed that the mean OBT concentration of the sediments in French rivers were not significantly different from the mean HTO content on record for rainwater for the same period. The data acquired within the continental aquatic system which were beyond the reach of industrial sources indicate that the ^{14}C levels within the matrices studied, were significantly lower than the baseline values that were established for the terrestrial and atmospheric compartment. It was observed that OBT and ^{14}C levels were within the suspended particles or sediments downstream of liquid discharges of nuclear facilities were strongly affected by inputs from pristine tributaries, hydrology, the origin of the floods and event chronologies. Therefore, it was recommended that these parameters should be taken into consideration to explain the variability of ^{14}C and OBT in the environment.

2.4. Sample preparation methods for the determination of ^{14}C and ^{3}H in water

There are quite a number of techniques that can be used for sample preparation determination of ^{3}H and ^{14}C in environmental water. Just to mention the few; electrolytic enrichment method, direct method, distillation method, filtration and multiple ionic extraction chromatography, benzene synthesis method and sample combustion method by biological sample oxidiser. A number of studies have been conducted to test or compare these methods for sample preparation of ^{3}H and ^{14}C (Singleton *et al*., 2002). Below are some of the methods that can be used for the determination of ^{3}H and ^{14}C on environmental samples.

2.4.1. Benzene Synthesis method

One method that has been widely used for low-level ^{14}C measurements is the benzene synthesis method. This method involves the conversion of sample carbon to benzene. It is a highly sensitive and precise technique that has found a wide application for carbon dating, but also been applied for environmental samples (Begg *et al*., 1992; Cook *et al*., 1998; DeFilippis, 1991; Otlet *et al.*, 1997).

The disadvantages of benzene synthesis method are: it requires a larger amount of starting material compared to the combustion furnace, and requires the additional

step of preparing the sample in a readily combustible form. The analysis using benzene synthesis takes longer to be completed, and the analyst is required to be at the rig for the entire working day. The method is demanding in terms of both time and concentration and therefore, more time is needed to train an analyst to conduct benzene synthesis method. Furthermore, this method is costly and it produces benzene as a final product which is a known to be carcinogenic, and therefore requires extreme caution. However, the advantages are that this technique is highly sensitive and precise. Another advantage is that benzene is a clear solution with high carbon content (92.3%) and is fairly resistant to quenching (Singleton *et al*., 2002).

2.4.2. Combustion Method by sample oxidiser

The sample oxidizer is the sample preparation method that is user friendly and it can handle a diversity of samples with a high degree of precision and accuracy. The method has options for the analysis of organic and inorganic samples. There are two designs for this method, the first being the non-catalytic oxidiser which is designed around flame combustion principle and the second being the catalytic oxidiser normally called biological sample oxidiser Sample oxidiser could be an excellent choice, if the rapid method is required for analysis, (Nikolov *et al.*, 2013).

The advantage of using sample oxidiser is that the process is automated and in addition, it is specifically designed for the combustion of samples containing both ^{14}C and ^{3}H (Mat, 1995). Other advantages of using sample oxidiser are that the samples can be wet, dry or freeze-dried, and samples containing H and/or C can be combusted (Cook *et al.,* 2003). The method is ideally suitable for both single and dual label ^{3}H and ^{14}C. Radioactive recovery is excellent (>97%), and there is no chemiluminescence interference. Moreover, there is no colour quenching interference, and the sample processing time is rapid. The time that is actually spent on the ^{14}C measurements is far more cost effective. Time needed to train the analyst to operate the combustion furnace unsupervised is significantly less, and the main advantage is the considerable savings in labour are some of the advantages of a combustion method (Singleton *et al.,* 2002).

Even though combustion method is ideally suitable for both ^{3}H and ^{14}C, it also has some disadvantages. These disadvantages are initial capital investment, it is only suitable for ^{3}H and ^{14}C, need a gas supply (oxygen and nitrogen), and must be operated in a fume hood and reagents are corrosive and flammable (Cook *et al.,* 2003). Other disadvantages are that the maximum sample size for environmental sample is about 1 g, it is very challenging to create a representative environmental sample due to small sample size. Since the sample size is so small, the homogenization must be thorough and few replicate samples are needed to check the variation in the samples (Vartti, 2009).

2.4.3. Electrolytic enrichment method

The traditional electrolytic ^{3}H enrichment method relies on the principle that light hydrogen is electrolyzed more easily than tritium (Fukutani *et al*., 2008), Electrolytic enrichment is applied in order to increase the tritium concentration to an easily measurable level (Nikolov *et al*., 2013). Sample preparation using electrolytic enrichment method followed by measurement on LSC instrument has advantages of giving much lower limits of detection and it is the preferred method for mineral drinking water studies (Nikolov *et al*., 2013). Electrolytic enrichment has its disadvantages as well. It is time consuming and water sample preparation by electrolytic method can last for eight days (Baresic *et al*.,2010), while the same water sample could be prepared in a couple of hours (5-6) by direct method or even better using the automatic Sample Oxidizer, which could take for about 5-10 minutes (Nikolov *et al*., 2013).

2.4.4. Wet oxidation method

Wet oxidation method is utilised to separate and quantify ^{3}H and ^{14}C radionuclides in inorganic and organic radioactive waste generated at nuclear facilities (Ahn *et al*., 2013). Blowers *et al*. (2011) have demonstrated that wet oxidation technique consists of conversion of all carbon in the sample to carbon dioxide in the presence of sulphuric/chromic/ phosphoric acid.

The advantages of wet oxidation method are that it is capable of analysing a wide variety of sample matrices including soil, sediment, marine biota and vegetation with a typical sample size ranging from 0.9 to 8 g dependent upon the expected carbon content of the material, and is also capable of simultaneous determination of ^{14}C, total ^{3}H and natural carbon content (Blowers *et al*., 2011).

The disadvantages of wet oxidation method are that the reaction mixture should not be overloaded, the appearance of droplets of oil or fatty material in the water following the distillation process may indicate that the oxidation is incomplete. If this occurs, the analysis should be repeated using smaller quantities of sample or larger volumes of reagents (Environmental Agency, 2005).

2.5. Techniques for the analysis of ^{14}C and ^{3}H in water

2.5.1. Accelerator Mass Spectroscopy (AMS)

The AMS technique is widely employed in the earth and environmental sciences for purposes such as radiocarbon dating and also studying the circulation of the world`s oceans. High sensitivity of AMS measurements enables the use of low chemical and radioisotope doses and relatively small sample sizes, which enables studies to be performed safely in humans, using exposures that are environmentally or therapeutically relevant while generated little radioactive waste (Brown *et al.*, 2005). The AMS technique has a clear superiority over other radiometric methods for dating samples of sub milligram size. However, the AMS equipment is very expensive and bulky (Theodorsson, 1991).

AMS is the most sensitive method available for detecting and quantifying rare long-lived isotopes with high precision. Other advantages of AMS are that it takes relatively small sample size due to high sensitivity, and is generating little radioactive waste. AMS disadvantages are that numerous precautions need to be in place throughout the procedure to ensure the amount of isotope present is within the dynamic range of the spectrometer and to minimise the potential for contamination, and to ensure that the isotope detected in the sample is associated with the labelled

compound under investigation. AMS measurements do not provide any structural information, therefore any sample characterization or identification must be performed before sample preparation using chromatographic or electrophoresis separation techniques (Brown *et al*., 2005).

2.5.2. Gas Proportional Counter

Gas Proportional Counting (GPC) techniques have been used since 1978 for the measurement of non-enriched samples (Baresic *et al*., 2010). Gas Proportional Counters have generally been performing better because of lower background and greater stability until late 1980`s. The introduction of LSCs has overshadowed the ability of GPC to be the better performing instrument, due to LSC`s system that is designed specifically for determination of low-level radioisotopes (Theodorsson, 1991). The GPC technique is not acceptable for the low-level activity determination for ^{3}H because of its worse detection limit (Baresic *et al*., 2010). The GPC method for tritium measurement is more complex than the LSC technique, but the counting characteristics are better. However, chemical preparations for ^{14}C measurement using GPC technique are more complex but the method gives better precision. Therefore, the GPC technique is recommended for ^{14}C dating in archaeology and geochronology. The GPC technique also requires a larger amount of sample (Obelic *et al*., 2004).

2.5.3. Liquid Scintillation Counter

Scintillation counting is one of the most important developments in the application of radioisotopes needed by scientists, physicians, engineers and technicians from diverse discipline. Scintillation counting is useful for the detection and quantitative measurement of radioactivity (Benito *et al.,* 2012). Liquid scintillation counters are extremely versatile and sensitive tools which grew over the years, out of the need to detect and measure efficiently low energy beta radioactivity (Polach, 1987). The 1220 Quantulus liquid scintillation spectrometer is well suited for detecting extremely low levels of radioactivity (PerkinElmer Inc, 2011). Quantulus is an ultra-low level

spectrometer which provides stable measurement conditions, where no atmospheric pressure correction is needed, and low radioactivity sample counting. Samples containing ^{3}H and ^{14}C are most commonly placed in a sealed counting vial located between two photomultiplier tubes on a common axis (Polach, 1987). Because of it`s both passive and active shielding for background reduction, Quantulus far surpasses the performance of any other LSC (PerkinElmer Life and Analytical Sciences, 2005). Liquid Scintillation Counting technique has principles and applications which describe useful information in order to avoid some pitfalls while using LSC technique (Environmental Agency, 2005).

Liquid Scintillation Counter technique was used to conduct this study. Hence, detailed information on its principles and applications.

Principles of Liquid Scintillation Counting

Liquid Scintillation Counting is defined by the incorporation of the radio-labelled analyte into uniform distribution. This analytical technique uses a liquid chemical medium that is capable of converting the kinetic energy of nuclear emission into light energy (University of Wisconsin - Milwaukee, 1998). The basic principles of LSC are radioactive emissions, measurement of radiation and isotope quantitation, mechanism of liquid scintillation counting, liquid scintillation signal interpretation, the complete scintillation cocktail, chemiluminescence and static electricity and waste disposal issues (National Diagnostics, 2004).

Radioactive Emissions

Beta particle is emitted in a radioactive decay. The solution is a solvent for the sample material to assure efficient transfer of energy between the beta particle and the solution (University of Wisconsin - Milwaukee, 1998). Due to a change within the atom`s nucleus, radioactive decay occurs with the emission of particles or electromagnetic radiation from an atom. Forms of radioactive emission include alpha particles, beta particles and gamma rays (Benito *et al*., 2012).

Measurement of radiation and isotope quantitation

The quantitation of the isotope is required by most research applications of radioisotopes at some stage, which is done by measuring the intensity of radiation emitted (National Diagnostics, 2004). There are three forms in which the energy is absorbed by the medium: heat, ionization and excitation (University of Wisconsin - Milwaukee, 1998). The specific range of energy corresponds to each channel (channels are also known as counting windows), and counts with energies above or below set limits are excluded from a particular channel (Benito *et al.,* 2012).

Mechanism of Liquid Scintillation Counting

The key point of LSC is that the scintillation takes place in solution of a scintillator, rather than in a solid crystal. Liquid scintillation cocktails absorb the energy emitted by radioisotopes and re-emit it as flashes of light. Cocktail contains two basic components that contribute towards accomplishing two components, absorption and re-emission, the solvent and the phosphor (also known as scintillator). The solvent and the phosphor provide the scintillation of the mixture. The role of the solvent is to act as an efficient collector of energy, and it must conduct that energy to the phosphor molecules instead of dissipating the energy by some other mechanism (National Diagnostics, 2004).

The scintillators are broadly divided into two classes: primary and secondary scintillators. The role of primary scintillators is to provide the conversion of captured energy to the emission of light; these scintillators must be capable of being excited to a light emitting state by excited solvent molecules. Whereas, the role for the secondary scintillator is to capture the fluorescence energy of the excited primary scintillator, and re-emits it as a longer wave length signal (National Diagnostics, 2004).

Liquid Scintillation Signal Interpretation

In LSC there is a release of energy which is not due to the phenomenon of scintillation from the sample as photons. Even in the absence of the radioactive sample producing interferences (chemiluminescence, photoluminescence and quench) in the detection process, this energy unduly increases the count or gives light pulses (Benito *et al*., 2012). The intensity of each light pulse corresponds to the emission energy and the number of pulses per second corresponds to the number of radioactive emissions (National Diagnostics, 2004).

The Complete Scintillation Cocktail

Most scintillation cocktails which are designed for aqueous samples contain surfactants, which emulsify the sample into the organic solvent. Emulsion cocktails are less efficient than pure solvent cocktails because these surfactant and other additives are less effective at energy capture than the solvent (National Diagnostics, 2004).

Chemiluminescence and Static Electricity

Chemiluminescence is another commonly encountered artefact which is caused by any chemical reaction which generates an excited product molecule, which decays to emit light. Many scintillation counters use coincidence counting to eliminate counts due to chemiluminescence. Another source of counts that are not authentic is static electricity. The energy from static electric build-up can be released as a burst of light from the cocktail. If counts from an individual sample vary unpredictably from one measurement to the next, the cause is likely to be a static (National Diagnostics, 2004). Most of the systems offer an option which employs a static charge device and/or electrostatic controller (University of Wisconsin - Milwaukee, 1998).

Waste Disposal Issues

Waste disposal is an aspect of LSC which must be considered in experimental design because of LSC`s ability to add components to the sample increasing the volume of radioactive material by up to 1000 fold. These components of the LSC such as

cocktails may present a hazard or a disposal problem in addition to the radioactivity (National Diagnostics, 2004).

Applications of Liquid Scintillation Counting

Liquid Scintillation techniques are used for the detection of radio labelled isotopes in areas as diverse as biomedicine, ecology and industry. Liquid Scintillation Counting capabilities include detection of alpha, beta and gamma emitters. Detecting and counting alpha and beta emitting radionuclides are routine tasks in nuclear energy and environmental monitoring. However, LSCs are not very useful for the identification of alpha emitting radionuclides because of the energy resolution that is quiet poor. Liquid Scintillation Counting is the most important application in detection of beta emitters. It is often the technique of choice for weak beta emitters such as ^{3}H and ^{14}C (Benito *et al*., 2012).

In order for the performance results of LSC instrument to be meaningful, the instrument should be calibrated at least every six months or when the functions indicate problem (Environmental Safety: Administration & Finance, 1994). Liquid scintillation counting technique relies on the efficient transfer of energy for both electronic and light. The interference of this energy transfer process from any other factors which are not accounted for is likely to produce incorrect results (Environmental Agency, 2005). Quenching is one of the factors that interfere with the energy transfer process. There are two main types of quenching, chemical quenching which occurs during the transfer of energy from the solvent to the scintillator and colour quenching which is an attenuation of light (Thomson, 2012). When these quenching effects are ignored, the produced results may under-estimate the true value (Environmental Agency, 2005). When the number of produced photons is reduced due to the collective effect of quench, the detected counts per minute (CPM) will also be reduced and therefore, reduces the counting efficiency (Thomson, 2012). To determine the activity concentration of a sample in LSC, it is necessary to measure the level of quench of the sample first, and then make corrections for the measured reduction in counting efficiencies (Thomson, 2012). The high efficiency of

LSC technique makes it particularly suitable for the measurement of very low activity levels (Rauret *et al*., 1989). Increasing efficiency of detection, decreasing the background, increasing the collection time or the sample size, can improve the Minimum Detectable Activity (MDA) also referred to as Lower Limit of Detection (LLD) by (Canberra Industries, Inc., 2010). MDA is not a characteristic of the sample measured, but is a characteristic of the instrument`s limit for detecting radioactivity (University of Toronto).

Other factors affecting LSC measurements are the instrumental conditions which are width and position of the counting window, the sample mixture conditions, water content and total volume must be optimised. Optimising these conditions will result in good performance analysis of low-levels of beta-emitting radionuclides and mainly for those with low energies like ^{14}C and ^{3}H (Rauret *et al*., 1989).

Carbon-14 and tritium are low-level, Beta (β)-emitting radioactive isotopes of carbon and hydrogen, respectively, which are amongst the radioisotopes which forms part of liquid effluent that is being discharged in to the environment. In order to address the health concerns associated with radionuclides on the environment, ^{14}C and ^{3}H should be measured. The measurement of low activity levels of Beta (β)-emitting radionuclides in environmental samples are carried out either by GPCs or LSCs (Rauret *et al*. 1989). The high efficiency of these techniques makes it particularly suitable for the measurement of very low activity levels. Even though GPC is the common method for low-level counting, it is better to use LSC for analyzing natural water samples because in LSC the water sample is directly combined with an appropriate aqueous scintillation cocktail while the required pre-treatment is minimal and the counting efficiency is higher than that of GPC (Nikolov *et al.,* 2013).

Obelic *et al.* (2004) compared three different methods for low-level ^{14}C measurement and two methods for measurement of low- level ^{3}H activity in environmental samples that have been developed in the Zagreb Radiocarbon and Tritium Laboratory. Basic parameters for controlling both techniques for ^{3}H measurement were presented as Gas Proportional Counter and LSC and all three techniques for ^{14}C measurement

(GPC, LSC-A and LSC-B) methods, where LSC-A is absorption of the carbon dioxide (CO_2) and LSC-B is the benzene synthesis. Based on the measurements carried out, GPC technique for ^{3}H measurement was found to be more complex than the LSC one, but the counting characteristics were better and LSC-A method for radiocarbon measurement was found to be quick, cheap and simple and requires less carbon than the other two methods. Therefore LSC measurement techniques of ^{3}H in water and of ^{14}C in various samples by CO_2 absorption are suitable for quick and accurate determination of environmental contamination (they could be used for quick determination of increased environmental ^{14}C and ^{3}H contamination in case of a nuclear incident), although both are not recommendable for applications requiring higher precision (Obelic *et al.,* (2004).

Bronic *et al.* (2012) reported on an inter-comparison study of low-level ^{3}H and ^{14}C activity measurements in various environmental samples. This study was conducted by two laboratories, Ruder Boskovic Institute (RBI) based in Zagreb, Croatia and the Department of Physics of the University of Novi Sad (DP-UNS) based in Serbia. Both laboratories used the same type of instrument for sample measurements, ultra low-level LSC Quantulus 1220, but used different techniques for sample preparation. RBI used electrolytic enrichment method for sample preparation whereas; DP-UNS used 307 sample oxidiser method for sample preparation. At RBI laboratory, after electrolytic enrichment, the samples were distilled, then mixed with UltimaGold LLT scintillator and used direct measurement for the determination of ^{3}H activity. The direct absorption of carbon dioxide in a mixture of Carbo-Sorb E and Permafluor E was used for the determination of ^{14}C activity at RBI laboratory. The DP-UNS laboratory used two methods from the determination of ^{3}H activity and one method for the determination of ^{14}C activity. The first method used for ^{3}H activity determination was a rapid method where the sample is mixed with Optiphase HiSafe 3 scintillator and then measured my LSC. The second method was a combustion method where environmental samples were combusted completely in an oxygen atmosphere to carbon dioxide and water. After the combustion, two separate samples (a sample of ^{3}H [water] and ^{14}C [carbon dioxide]) were trapped at ambient temperature, thus

reducing the cross contamination. It was observed that water samples prepared by the electrolytic enrichment at RBI laboratory resulted in lower MDA and better precision. However, the simpler direct sample preparation method used at DP-UNS gave comparable results. The comparison of the methods used by both RBI and DP-UNS laboratories for the ^{14}C measurements was not possible because of the unknown proportion of carbon in the DUNS sample preparation method (Krajcar Bronic *et al*., 2012).

The study of Tritium activity levels in environmental water samples from different origins of Catalonia in Spain was conducted to determine if the nuclear station of Asco affects the tritium levels (Palomo *et al*., 2007). In this study a distillation procedure was utilised as a pre-treatment step to prevent quenching before using liquid LSC for sample measurements. The study examined different types of water samples namely, tap water directly from the public supply, the mineral bottled water samples purchased from local supermarkets, water samples from wells and other sources, rainwater and river water samples. The study confirmed that water samples analysed have low tritium content, most of the samples presented activities lower than the minimum detectable activity (MDA). It was found that the nuclear station of Asco does not significantly affect the ^{3}H levels in the river, so the water is appropriate for human consumption after treatment.

A comparative study of pre-treatment procedures for ^{3}H monitoring in water samples from environmental protection programs was conducted to compare three different sample pre-treatment techniques (Tarancon *et al.,* 2010). These different sample pre-treatment techniques used for comparison were distillation, filtration and multiple ionic extraction chromatography and further measurements by Quantulus LSC. In this study, different types of water samples (rain water, drinking water, surface water, underground water and sea water from two different locations) from the proximities of Spanish nuclear power plants were used for comparison. Their objective was to evaluate an alternative pre-treatment technique that is suitable for the determination of ^{3}H activity procedures. This study revealed that distillation technique is simple but time consuming pre-treatment technique, especially in routine analysis. Whereas in

case of filtration and multiple selective ion exchange column pre-treatment techniques, the results show that both can be applied as a preliminary tool to discriminate between ^{3}H active and non-active waters in environmental monitoring programs. Both filtration and multiple selective ion exchange column methods are less time consuming than distillation method and in the case of filtration, it is extremely cheap. Distillation technique was recommended as the procedure for use in the determination of tritium activity in waters with complex matrices, especially sea water due to the interference from high salt content contained (Tarancon *et al.,* 2010).

The exercise of applying direct liquid scintillation counting to low level ^{3}H measurement was conducted by Varlam *et al*. (2009) to evaluate different types of procedures that could be applied to measure environmental ^{3}H level. Usually these procedures are all based on measuring ^{3}H concentration in extracted water samples by LSC technique. There are two standard methods that are published for ^{3}H measurement in aqueous samples. These methods were used in this exercise to measure ^{3}H level in the environment. These methods have same principle with small differences between the chemical treatments of water samples. The first method treats water sample by adding sodium thiosulphate to convert iodine to iodide and sodium carbonate to make the sample alkaline. The second method, the water sample is mixed with sodium hydroxide and potassium permanganate. For both standard methods, distillation and liquid scintillation methods are common. The findings for this exercise were that both standard methods give the same results if they are used according to the recommendations.

Comparison of two techniques for low level ^{3}H measurement utilising GPC and LSC exercise was conducted by Baresic *et al*. (2010). During this exercise low-level ^{3}H activities in natural/non-polluted waters were measured, e.g. in precipitation and groundwater. This measurement required special techniques for water treatment and detection of low-level radioactivity. Non-enriched samples were used for GPC technique and a method of electrolytic enrichment of water samples was utilized followed by measurement using LSC Quantulus. The study showed that LSC results were acceptable while two of the GPC results were in the waning level, which was not

acceptable. The study also pointed out that LSC results have smaller errors than GPC results. The authors (2010) concluded that for low ^{3}H activity, the GPC system is not suitable because of higher/worse detection limit. LSC system with low detection limit and with better precision is more suitable for most natural water samples including precipitation and groundwater samples.

In 2009, Vartti optimized the counting conditions for ^{14}C measurements for sample oxidizer and the Quantulus liquid scintillation counter methods. Finland has four nuclear power stations at two sites. It has been stated that ^{14}C is one of the major contributors to the airborne radioactive releases in Finland. In recent years, ^{14}C measurements in the environment have become a part of the monitoring program in the vicinities of Finnish nuclear power plants. As part of the monitoring program, Vartti (2009) conducted this study by measuring samples that were collected from the vicinities of the Finnish nuclear power plants in Finland. Sample preparation was done using 307 Sample Oxidiser method and further measured by low-level LSC Quantulus 1220. The study was successful but a small sample size (approximately 1 g) per sample was found to be very challenging where the radioactivity concentrations are very low and it was very difficult to obtain a representative sample from the environment. It was recommended that the sample combustion method must be further developed, but the first results shows that it can be used for monitoring purposes at environmental levels (Vartti, 2009).

Blowers *et al.*, (2011) conducted an inter-comparison exercise to determine the ^{14}C activity concentrations in a range of solid, environmental level materials amongst ten participating radiochemistry laboratories in the United Kingdom. This study was conducted using three IAEA reference materials and an in-house laboratory quality assurance material that were dispatched in 2006. The exercise incorporated four different techniques, three different combustion furnace types and six models of LSC. During this study, it was necessary to further consider a number of factors that might have contributed to the determination of activity concentrations in the samples. Out of ten laboratories, six of them used combustion method, one laboratory used direct counting method, another one used wet oxidation method and the last one used

combustion and benzene conversion together. All the techniques produced results which demonstrate that they are capable of determining ^{14}C in environmental materials below activity concentrations of 400 Bq/kg. However each of these analytical methods has practical and scientific advantages and disadvantages. The conclusion of this exercise showed that all techniques used in this exercise are capable of successfully analysing ^{14}C in environmental level materials; however, there is a shortage of certified environmental reference.

Chapter 3: Research Methodology

This chapter gives clarity on methodologies used to measure the contents of ^{3}H and ^{14}C in water samples. The location of the study area where samples were collected is detailed. Research methodology involves methods used to optimise the equipments used for sample preparation and sample measurements and it also involves the methods used to collect and analyse data.

3.1. Study area

This study took place at Hartbeespoort Dam which is situated at about 20 km west of Pretoria along the Crocodile River in North West Province, South Africa. Hartbeespoort Dam falls within the Crocodile (West) Marico River catchment area. The upper portion of the catchment, south east of the dam, is located in the Gauteng Province, the north and north east corners lie in the Limpopo Province whereas the central or western sections fall within the North West Province (Department of Water and Sanitation, 2015). **Table 3.1** indicates the facts about Hartbeespoort Dam were given by the Department of Water and Sanitation (2015) and **Figure 3.1** indicates *Hartbeespoort Dam.*

Table 3.1: Hartbeespoort Dam facts

Year of completion	1923, raised in 1970
Purpose	Irrigation, industrial and domestic
River	Crocodile River
Type	Variable radius arch wall of mass concrete
Gross storage capacity	205 million m^2
Wall height above the lowest foundation	59,3 m
Crest length	100,6 m
Material content of dam wall	68000 m^3 concrete
Type of spillway	Controlled, crest gates
Capacity of spillway	2322 m^3/s
Full surface area	2062 ha

3.2. Sampling

A total of twenty samples were collected from Hartbeespoort Dam. The samples were collected in different seasons to find out if change in seasons would have any effects on the results of ^{14}C and ^{3}H and how this change impacts the environment. The literature has indicated that the levels of ^{3}H and ^{14}C vary with change of seasons. Five composite samples for each season were collected, starting on the third quarter: June-August (04 Jul 2014), September-November (06 October 2014), December-February (03 February 2015) and March-May (08 April 2015). The samples were

collected using three litre (3 L) plastic bottles at five different locations (for representative sampling) around Harbeespoort dam. Sampling point one was located at 25°45'44.0"S 27°53'16.4"E, which was at the entr ance of Crocodile River. Sampling point two was located at 25°46'15.8"S 27°5 1'56.2"E which was approximately 5 km away from point one. Sampling point three was located at 25°45'46.4"S 27°50'26.5"E which is about 5 km away from point two. Point four was located at 25°44'23.1"S 27°51'13.7"E, which is appr oximately 10 km away from point three and point five was located at 25°45'08.4"S 27 °53'04.1"E, which is approximately 7 km away from point 4. Water samples were returned to the laboratory to be analyzed. **Figure 3.1** shows the sampling areas from **P1** to **P5**, where **P** stands for sampling point

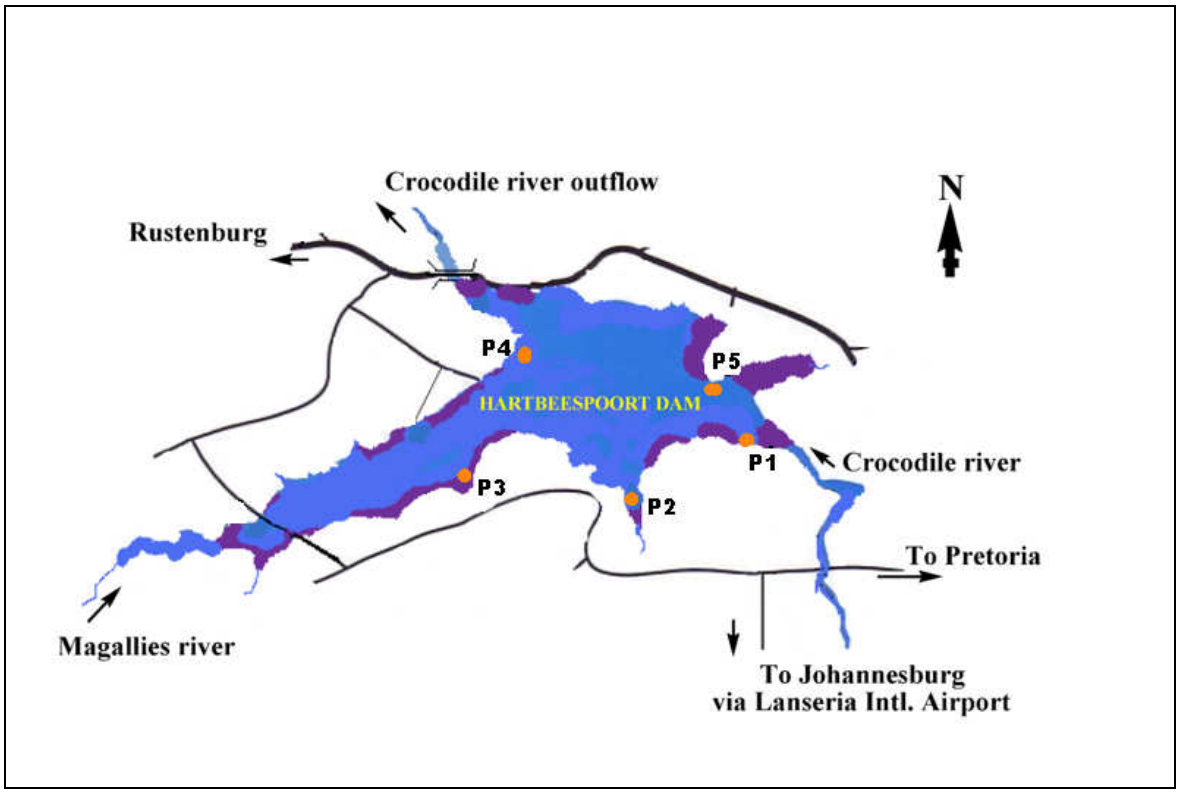


Figure 3.1: *Hartbeespoort Dam map* (Mbukwa *et al*., 2012).

3.3. Materials and Apparatus

Materials: Oxysove-C-400 (Zinsser Analytic), Oxysolve-T-400 (Zinsser Analytic), Methanol, Nitrogen gas, Oxygen gas, ^{14}C standard, ^{3}H standard, nitro-methane and distilled water.

Apparatus: Catalytic Sample Oxidiser – OX501 (Zinsser Analytic), Ultra Low Level Liquid Scintillation Spectrometer – Quantulus 1220 (PerkinElmer), Liquid Scintillation plastic vials (Zinsser Analytic), 3 L plastic bottles, glass ladle, porcelain boats, splitting spout tips (Zinsser Analytic), pipette and 1 L glass beakers.

3.4. Optimization of Instruments

Generally, it is important to ensure that the working conditions in the measurement being undertaken are of the good quality. In order to achieve performance that is satisfactory in the measurement of low activity levels in aqueous solution, instrumental conditions such as the width and position of counting window for each solution should be optimised (Rauret *et al*., 1989).

3.4.1. Optimizing OX-501 Biological Material Oxidiser

To achieve the accurate results and reproducible analysis that is acceptable, the sample oxidiser instrument for sample preparation, required optimisation. As part of optimisation, the recovery factors for both ^{3}H and ^{14}C were checked to determine if they achieve values that are 96 percent (%) or more and the memory effect for the sample oxidiser instrument that is less than 50 CPM.

The recovery for the sample preparation method using sample oxidiser was checked by preparing eight samples {2 x total of known activity (approximately 15000 DPM for ^{3}H and 10000 DPM for ^{14}C) , 2 x blank post total activity, 2 x combusted of known activity and 2 x blank post combusted activity} for each isotope. Standards were included for all the sample runs to ensure that the sample oxidiser is operating efficiently with no leakage. Total activity (transferred direct to the vial while combusting a blank piece of tissue) was used as a benchmark to monitor whether

some activity was lost during the combustion of activity, while running blanks after activity determined whether there was some activity left in the combustion tube. **Table 3.2** indicates the order used for recovery check:

Table 3.2: Recovery factor indication

Vials	**CPM for ^{3}H**	**CPM for ^{14}C**
Blank before 1	15.125	9.037
Blank before 2	6.714	5.422
Total activity 1	5961.764	10668.406
Total activity 2	5942.474	10578.185
Blank post total activity 1	10.429	3.717
Blank post total activity 2	7.9575	3.052
Combusted activity 1	5955.770	9852.571
Combusted activity 2	5008.783	8669.855
Blank post combusted activity 1	8.589	107.251
Blank post combusted activity 2	9.202	135.854

For each set of samples (e.g. for each quarter), the recovery factor was checked using the formula (R. J. Harvey Instrument Corporation, 2009):

$$Recovery\ Factor = \frac{Average\ Combusted\ activity}{Average\ Total\ activity}$$

The memory for the instrument was checked for both ^{14}C and ^{3}H. The formula used for memory check was:

Memory Effect =

$$Average\ blank\ post\ combustion\ (CPM) - Average\ blank\ before\ combustion\ (CPM)$$

The results for the Recovery Factor and Memory Effect for ^{3}H and ^{14}C for each quarter are indicated in **Table 3.3** below:

Table 3.3: Recovery Factor and Memory Effect values from Quarter 1 to Quarter 4

Quarter	Recovery Factor (%)		Memory Effect (CPM)	
	^{3}H	^{14}C	^{3}H	^{14}C
One	98	96	>50	<50
Two	96	97	<50	<50
Three	97	91	<50	<50
Four	89	105	<50	<50

The results for the recovery factor calculations indicated that the percentage for ^{14}C on the third quarter was 91% and for ^{3}H on the fourth quarter was 89% which was less than the 96% which is the specification. This might be due to the cracking of spout tips that were used to collect both ^{3}H and ^{14}C into the vial. The reason for these tips to crack might be the pressure when bubbling oxygen through the spout tips into the vials to trap ^{3}H and ^{14}C in a LSC cocktail.

3.4.2. Calibration for Ultra Low Liquid Scintillation Spectrometer – Quantulus 1220

Quench calibration curves for ^{3}H and ^{14}C were performed to determine efficiency of each sample measurement. Quench curves were obtained by preparing six calibration standards with different amount of quenching solution. For the ^{14}C quench curve, the stock solution which contained 0.5 mL of nitromethane and 19.5 mL of Oxysolve-C in a 20 mL plastic vial was prepared. From the stock solution, five quench

standards were prepared with different volumes of stock solution added to them. The quench standards were prepared in the following order: vial 1 (0 mL of stock solution), vial 2 (0.5 mL of stock solution), vial 3 (1.0 mL of stock solution), vial 4 (1.5 mL of stock solution) and vial 5 (2.0 mL of stock solution. Each vial of quench standard for ^{14}C contained different volumes of stock solution, approximately 0.2 ml of certified ^{14}C standard solution (containing activity of 731.653 Bq/g on the reference date: 15 December 2014) and different volumes of Oxysolve-C cocktail. For ^{3}H, distilled water was used as a quench solution. Each vial of ^{3}H contained different volumes of water, approximately 0.5 g of ^{3}H certified standard solution (which contained activity of 994.85 Bq/g on the reference date: 01 November 2002) and different volumes of Oxysolve-T cocktail. **Table 3.4** shows the preparation for the quench standards.

Table 3.4: Quench standards for ^{14}C and ^{3}H

Quench Standard	^{14}C			^{3}H		
	Volume of a Stock solution (mL)	Mass of ^{14}C certified standard (g)	Volume of Oxysolve-C (mL)	Volume of water (mL)	Mass of ^{3}H certified standard (g)	Volume of Oxysolve T (mL)
1	0	0.2211	19.0	0	0.5062	19.0
2	0.5	0.2271	18.5	0.5	0.5125	18.5
3	1.0	0.2220	18.0	1.0	0.5176	18.0
4	1.5	0.2169	17.5	1.5	0.4980	17.5
5	2.0	0.2121	17.0	2.0	0.5066	17.0
6	2.5	0.2059	16.5	2.5	0.5153	16.5

The prepared quench standards were measured on the LSC Quantulus 1220 using WinQ program to set up of all parameters. The standards were measured for 30 minutes each to determine the CPM for each. These quench standards had known activities (DPM) which enabled the determination of the region of interest for both ^{3}H and ^{14}C. For ^{3}H the area of interest ranged from channel 20 to 300 and for ^{14}C the region of interest ranged from channel 100 to 400. The same regions of interests were used to determine the activities of the unknown for each radioisotope.

CPM values for the quench standards were obtained from the Easy View program, which were then used to calculate the efficiencies and eventually plot a quench curve. A quench standard curve is a series of standards in which the radioactivity (DPM) per vial is constant and the amount of quench increase from vial to vial. In this study, the calculations were all done manually. The counting efficiency was calculated using the following formula (Thomson, 2014):

$$Counting\ efficiency = \frac{CPM}{DPM}$$

The quench curves were plotted using the QIP measured from the standards and the calculated counting efficiencies for standards. The equations obtained from the quench curves were then used to calculate the efficiencies for the samples and then the activities for each sample. A quench curve used the relationship between counting efficiency and QIP to correct the measured CPM to DPM. When a quench curve was plotted, the value of DPM in each standard was determined (Thomson, 2014). **Figures 3.2** and **3.3** indicate the quench curves for the determination of ^{3}H and ^{14}C efficiencies, respectively, in the LSC measurements. These quench curves were prepared using Oxysolve-T for ^{3}H and Oxysolve-C for ^{14}C.

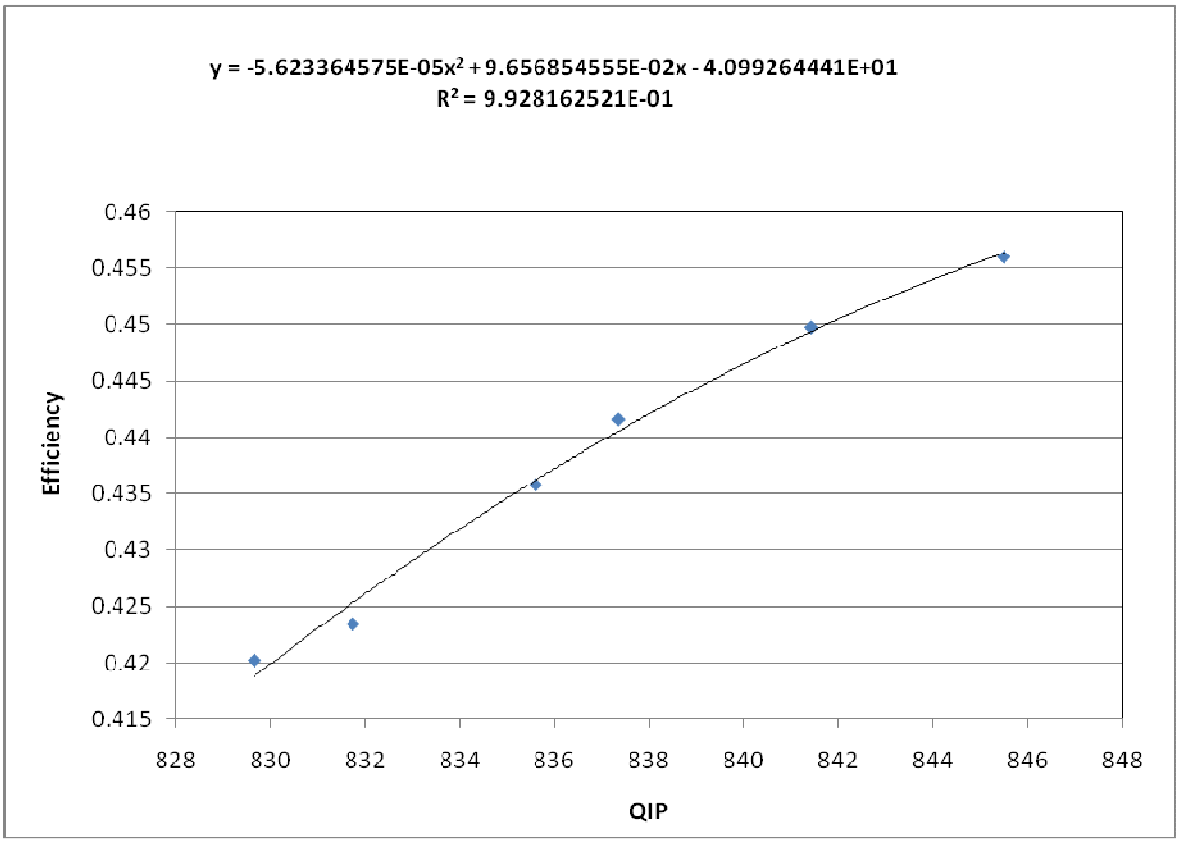


Figure 3.2: *Quench calibration curve for the determination of efficiency of ^{3}H in the LSC measurements*.

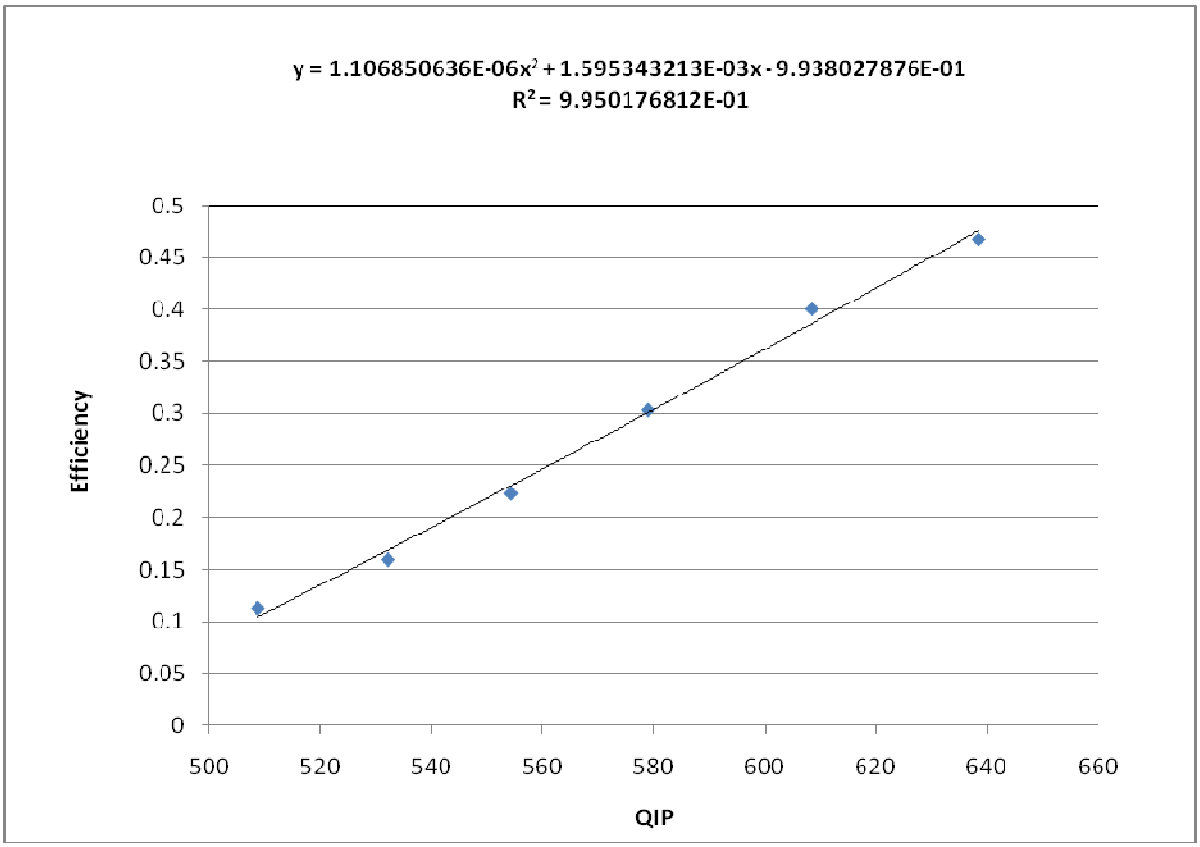


Figure 3.3: *Quench calibration curve for the determination of efficiency of ^{14}C in the LSC measurements*.

To compare the quench curves, the quench standards purchased from PerkinElmer with known activities were also counted to evaluate if the results correlates to each other. The results for the PerkinElmer quench standards were not significantly different from the results of the quench standards that were prepared in the laboratory. **Figures 3.4** and **3.5** indicate the quench curves for ^{3}H and ^{14}C respectively, plotted using PerkinElmer quench standards.

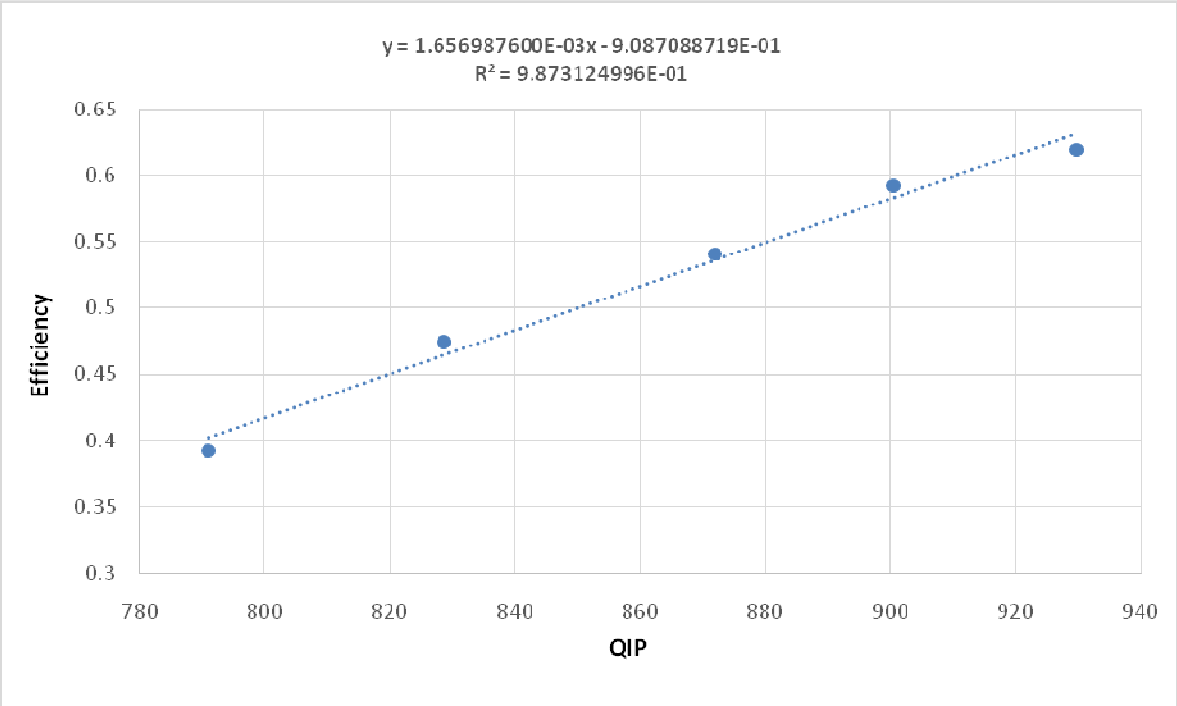


Figure 3.4: *Quench calibration curve using PerkinElmer standards for the determination of ^{3}H efficiency in the LSC measurements.*

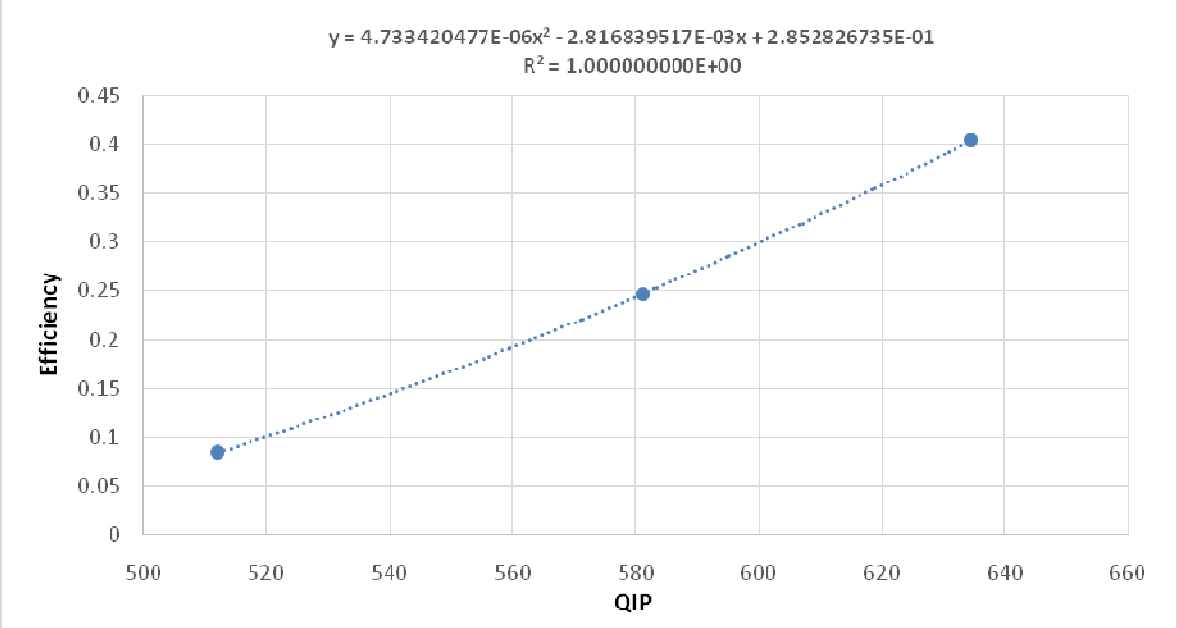


Figure 3.5: *Quench calibration curve using PerkinElmer standards for the determination of ^{14}C efficiency in the LSC measurements*.

3.5. Sample preparation

Biological Material Sample Oxidiser instrument was used for sample preparation. According to Thomson (2012), sample oxidation is the complete combustion of a sample using a combustion technique. This technique is principally used for ^{3}H and ^{14}C, it is the only technique that can physically separate ^{3}H and ^{14}C prior to counting, thereby elimination many of the errors associated with the counting of dual labelled samples. The sample oxidiser instrument – OX-501 Biological Material Oxidiser was set at following conditions (Table 3.5):

Table 3.5: Sample oxidiser conditions

Combustion zone	900 ^{0}C
Catalyst zone	680 ^{0}C
Flow rate of oxygen and nitrogen	350 cc/min
Combustion time	4 min

1000 mL of each sample was transferred into a 1 L beaker and kept on the fume hood for a week to evaporate the samples to a more concentrated 50 mL sample. 1 mL of each evaporated sample was pipetted onto a small piece of tissue into a porcelain boat and loaded on a ladle of which was inserted into a sample oxidiser for combustion. The combustion of each sample was done in triplicate. The combustion side initiates the oxidation of organic materials and converts the sample to a gaseous state. The sample and the ladle absorb heat energy from the system when the sample is first introduced and a transient temperature drop of as much as 50 ^{0}C which may be seen in the first minute and the temperature will rise back to 900 ^{0}C by the end of the assay. It then passes the combusted products through a series of catalysts at 680 ^{0}C and then traps the ^{14}C dioxide and tritiated water directly in the scintillation vials, which contain trapping solution. The cocktail was then dispensed into the capture vial into both vials for ^{14}C and ^{3}H. The vials were all placed in the

liquid scintillation counter for the measurement of ^{14}C and ^{3}H concentrations. **Figure 3.6** shows *OX-501 Biological Sample Oxidiser (on the left) and the schematic diagram of Sample Oxidiser (on the right).*

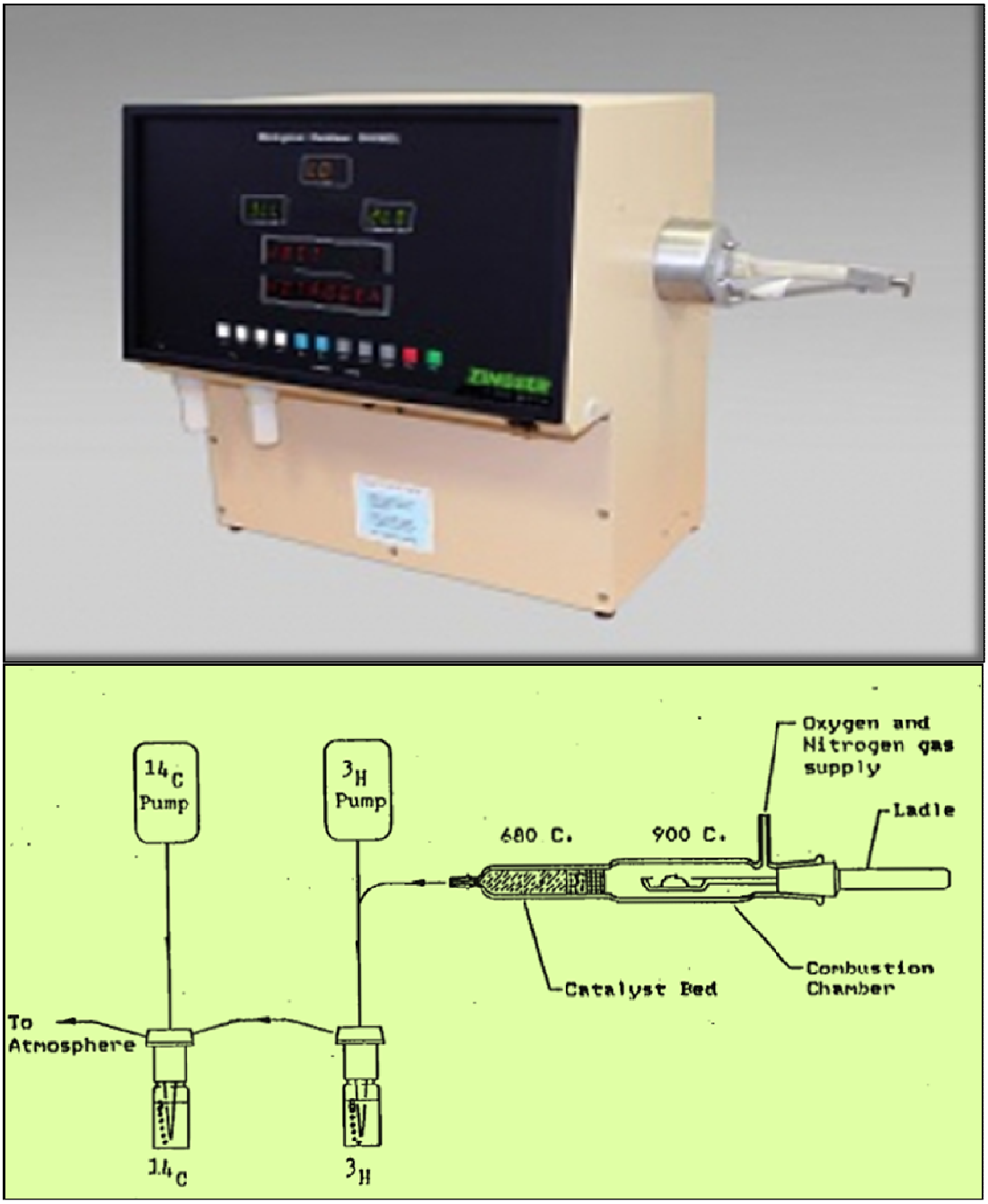


Figure 3.6: *OX-501 Biological Sample Oxidiser (top)* (Zinsser Analytic, 2015) *and the schematic diagram of Sample Oxidiser (bottom)* (Mat, 1995).

3.6. Data collection and data analysis

After the sample preparation stage was completed, the samples were measured for 30 minutes using low-level LSC to obtain the activities of ^{3}H and ^{14}C. The optimal counting window used was determined to be between channels 20 to 300 for ^{3}H and between channels 100 to 400 for ^{14}C. **Figure 3.7** shows the picture of LSC Quantulus 1220.

Figure 3.7: *Ultra-low-level LSC Quantulus 1220 (PerkinElmer Life and Analytical Sciences, 2005)*.

The counting efficiencies of the samples were calculated using the equation obtained from quench curves where the QIPs were plotted against the efficiencies of the standards. The counting efficiencies were then used to calculate the activities of each sample using the equation below:

$$A = \frac{Ra - Rb}{\varepsilon \times c \times V \times e^{-\lambda t}}$$

Where (Nikolov *et al.*, 2013):

A = is the activity concentration (Bq/L)

Ra = is the count rate of the sample (cps)

Rb = is the count rate of the background (cps)

ε = is the efficiency of the sample measurement

c = is the trapping efficiency of sample oxidiser

V = is the volume of the sample analysed (L)

$\lambda = (\frac{\ln 2}{T1/2})$ is the decay constant

t = is the elapsed time between sampling and counting (days)

$T_{1/2}$ = is the half-life (days)

$e^{-\lambda t}$ was used as 1 for both ^{14}C and ^{3}H, because the difference in days from the time the sampling was done to the time of counting is less than 365 days, so taking a worst case scenario and use 500 days as the time between sampling and counting, with ^{3}H Half-life = 4500 days, then $e^{-\lambda t} = 0.9259$, and ^{14}C half-life = 2091450 days then $e^{-\lambda t}$= 0.9998.

The uncertainty of measurement was calculated using the formula (University of Toronto):

$$Uncertainty\ (Bq) = \frac{\sqrt{\frac{Sample\ count\ rate\ (cpm)}{Counting\ time\ (min)} + \frac{Backgroundcount\ rate\ (CPM)}{Counting\ time\ (min)}}}{Detector\ efficiency \times time(sec) \times volume\ (L) \times trapping\ efficiency}$$

The Detection Limit (L_d) was calculated using the formula:

$$Ld\ (counts) = 2.71 + 4.65\sqrt{Rb \times tb}$$

A factor of 4.65 is derived from the statistics and it accounts for a 5% probability and for radioactivity calculation, whereas the factor 2.71 is often added to the L_d term to account for the zero blank case which corresponds to a 5% probability of a false negative (Cook *et al.*, 2003).

And the Minimum Detectable Activity (MDA) was calculated using the formula with an addition of the trapping efficiency factor C (Nikolov *et al.*, 2013):

$$MDA\ (Bq/L) = \frac{2.71 + 4.65\sqrt{Rb \times tb}}{\varepsilon \times tb \times V \times c}$$

The results for the blank, control sample and water samples from LSC were calculated using Microsoft Excel spreadsheet and the sample activity was determined. The sample activities were compared to the regulatory requirements for WHO (Minister of Public Works and Government Services Canada, 2008) which is less than 10000 $Bq.L^{-1}$ for ^{3}H and 100 $Bq.L^{-1}$for ^{14}C.

Chapter 4: Results and Discussion

This chapter aims to present, explain and interpret the results of ^{3}H and ^{14}C radionuclides and also to discuss the findings. The results are presented in the form of tables and figures.

4.1. Results

4.1.1. ^{14}C results

After preparing samples using sample oxidiser, the samples were then measured on LSC for 30 minutes each to obtain the SQP values and CPM values. The SQP results were then used to calculate the detection efficiencies for ^{14}C using the formula from the quench curves and the CPM values were used to calculate the activity in Bq/L. The CPM values were also used to calculate the uncertainties. The uncertainty was calculated to determine the range of which the true activity value lies. The uncertainty depends on the parameters used to calculate the activity. **Table 4.1** represents the ^{14}C results for the first quarter, where **Q** represents quarter and **P** represents point.

Table 4.1: Quarter one - ^{14}C results

First quarter by Sample Oxidiser method: sampling period June – August		
Sample	*Activity (+/- Uncertainty)(Bq/L*	*MDA (Bq/L)*
Q1P1	3.52E+01 (+/- 2.70E-01)	3.86E+00
Q1P2	5.45E+01 (+/- 3.00E-01)	3.34E+00
Q1P3	3.70E+01 (+/- 2.15E-01)	2.38E+00
Q1P4	3.85E+01 (+/- 2.75E-01)	3.94E+00
Q1P5	2.35E+01 (+/- 1.75E-01)	2.39E+00
Average	3.77E+01 (+/- 2.47E-01)	3.18E+00

The above results indicate that during June to August 2014 period, which is the winter period in South Africa, the activity concentration value of ^{14}C at Hartbeespoort Dam was observed to range between 2.35E+01 (+/- 1.75E-01) Bq/L and 5.45E+01 (+/-

3.00E-01) Bq/L with the average activity of 3.77E+01 (+/- 2.47E-01) Bq/L. The second point was observed to have the highest ^{14}C activity concentration and the fifth point had the lowest activity concentration. The difference in concentrations of ^{14}C might be caused by different reasons, which might be rainy season, fires around a particular area causes the ^{14}C to be more concentrated in atmosphere, if a dam has plants at a sampling area, those plants might absorb some of the ^{14}C radionuclide, which will result in less concentrated ^{14}C radionuclide in water being sampled in that area. All values were above the MDA by the average of twelve fold, and therefore could be reported. **Figure 4.1** indicates the sample points against the activity concentration in Bq/L.

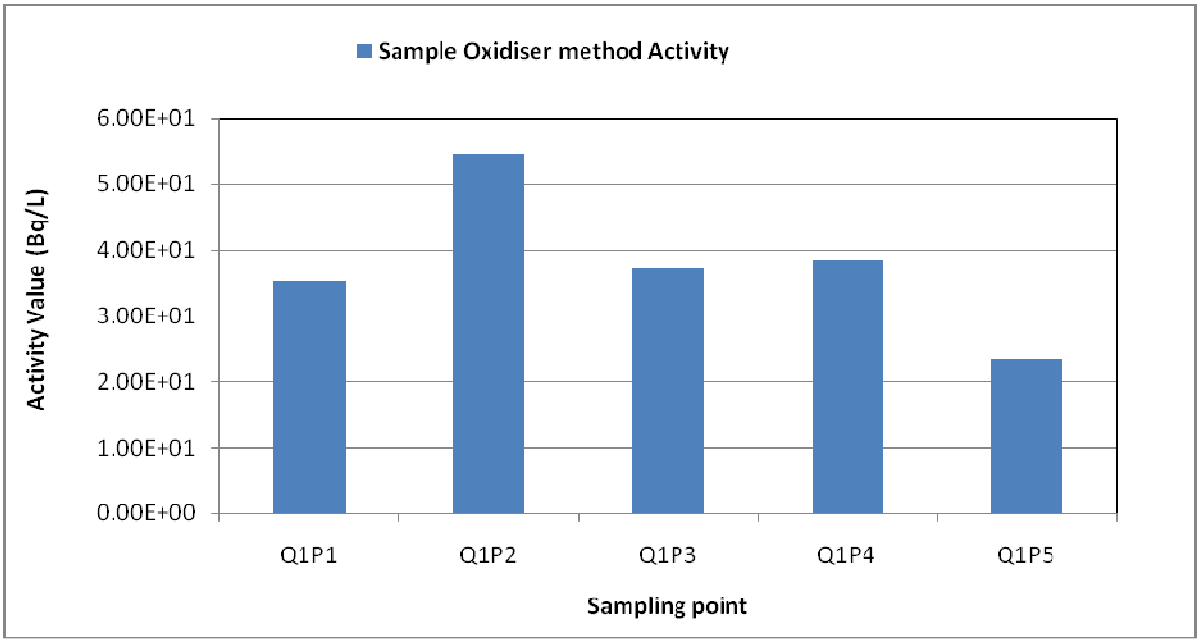


Figure 4.1: *^{14}C measurements - Quarter one*

Sampling for quarter two was done during the spring season which is from September to November. **Table 4.2** indicates the activity concentrations and the MDA values for ^{14}C during spring season.

Table 4.2: Quarter two - ^{14}C results

Second quarter by Sample Oxidiser method: sampling period September – November		
Sample	*Activity (+/- Uncertainty (Bq/L)*	*MDA (Bq/L)*
Q2P1	1.99E+01 (+/- 1.45E-01)	1.70E+00
Q2P2	1.30E+01 (+/- 1.46E-01)	2.62E+00
Q2P3	9.11E+00 (+/- 1.13E-01)	2.21E+00
Q2P4	2.81E+00 (+/- 5.77E-02)	1.88E+00
Q2P5	3.19E+00 (+/- 5.60E-02)	1.67E+00
Average	9.62E+00 (+/- 1.03E-01)	2.02E+00

The activity concentrations for ^{14}C in water samples that were collected from September to November were low but above the MDA values. The average concentration was 9.62E+00 (+/- 1.03E-01) Bq/L with the average MDA of 2.02E+00 Bq/L. **Figure 4.2** indicate the graph of ^{14}C sampling points against activity concentration. First point was observed to have the highest concentration.

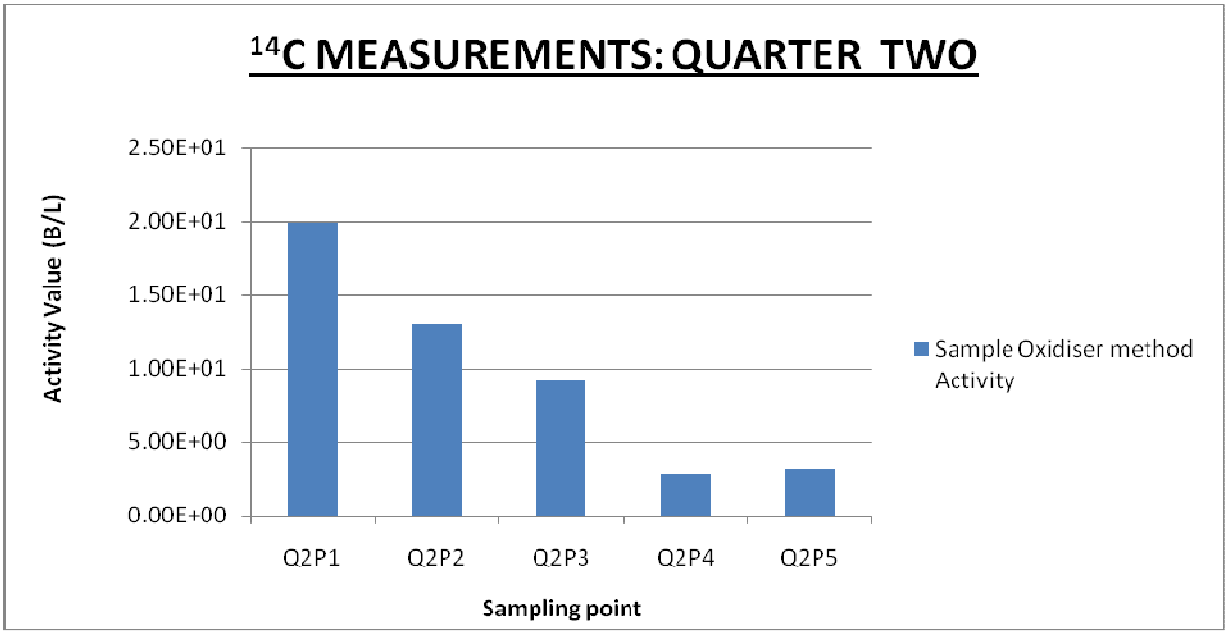


Figure 4.2: *^{14}C measurements - Quarter two*

The samples for the third quarter were sampled during the summer season which is December to February. During this season of the year, the weather is very hot. **Table 4.3** indicates the activity concentrations obtained for ^{14}C during summer season.

Table 4.3: Quarter three - ^{14}C results

Third quarter by Sample Oxidiser method: sampling period December-February		
sample	*Activity (+/- Uncertainty) Bq//L*	*MDA (Bq/L)*
Q3P1	7.98E+00 (+/- 9.78E-02)	7.90E-02
Q3P2	6.65E+00 (+/- 9.96E-02)	1.29E-01
Q3P3	6.41E+00 (+/- 1.09E-01)	1.84E-01
Q3P4	4.82E+00 (+/- 8.46E-02)	1.18E-01
Q3P5	3.84E+00 (+/- 7.28E-02)	1.00E-01
Average	5.94E+00 (+/- 9.28E-02)	1.22E-01

The ^{14}C activity concentrations obtained were low. The low MDA values enabled the LSC to measure these low activity concentrations without any problems. The average activity concentration was 5.94E+00 (+/- 9.28E-02) Bq/L with the average MDA value of 1.22E-01 Bq/L. **Figure 4.3** indicates that first point activity concentration was just above the concentrations for other four points.

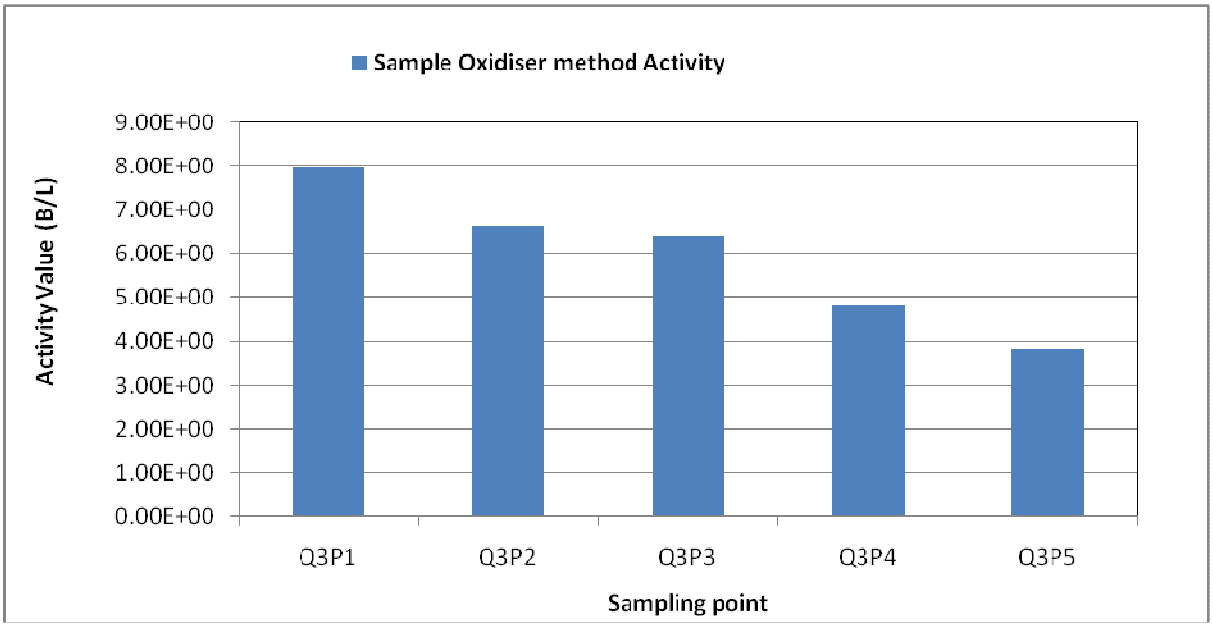


Figure 4.3: *^{14}C measurements - Quarter three*

The samples for the fourth quarter were collected during the autumn season, which is from March to May. The activity concentration values for ^{14}C during autumn season are indicated on **Table 4.4**.

Table 4.4: Quarter four - ^{14}C results

Fourth quarter by Sample Oxidiser method: sampling period March - May		
Sample	*Activity (+/- Uncertainty) Bq/L*	*MDA(Bq/L)*
Q4P1	3.29E+00 (+/- 7.51E-02)	2.05E+00
Q4P2	1.11E+00 (+/- 2.63E-02)	7.76E-01
Q4P3	1.68E+00 (+/- 4.98E-02) (<MDA)	1. 73E+00
Q4P4	3.38E-01 (+/- 2.65E-02) (< MDA)	1.98E+00
Q4P5	4.02E+00 (+/- 8.74E-02)	2.56E+00
Average	2.09E+00 (+/- 5.30E-02)	1.82E+00

The activity concentration values for ^{14}C during the period of March to were observed to be very low. Two of these values were below the MDA values, third point and fourth point. The average concentration was 2.09E+00 (+/- 5.30E-02) Bq/L with the MDA value of 1.82E+00 Bq/L. The average concentration was just above the average MDA value by 0.27 Bq/L. **Figure 4.4** indicates the sampling points where fourth point is has the lowest concentration of all the points.

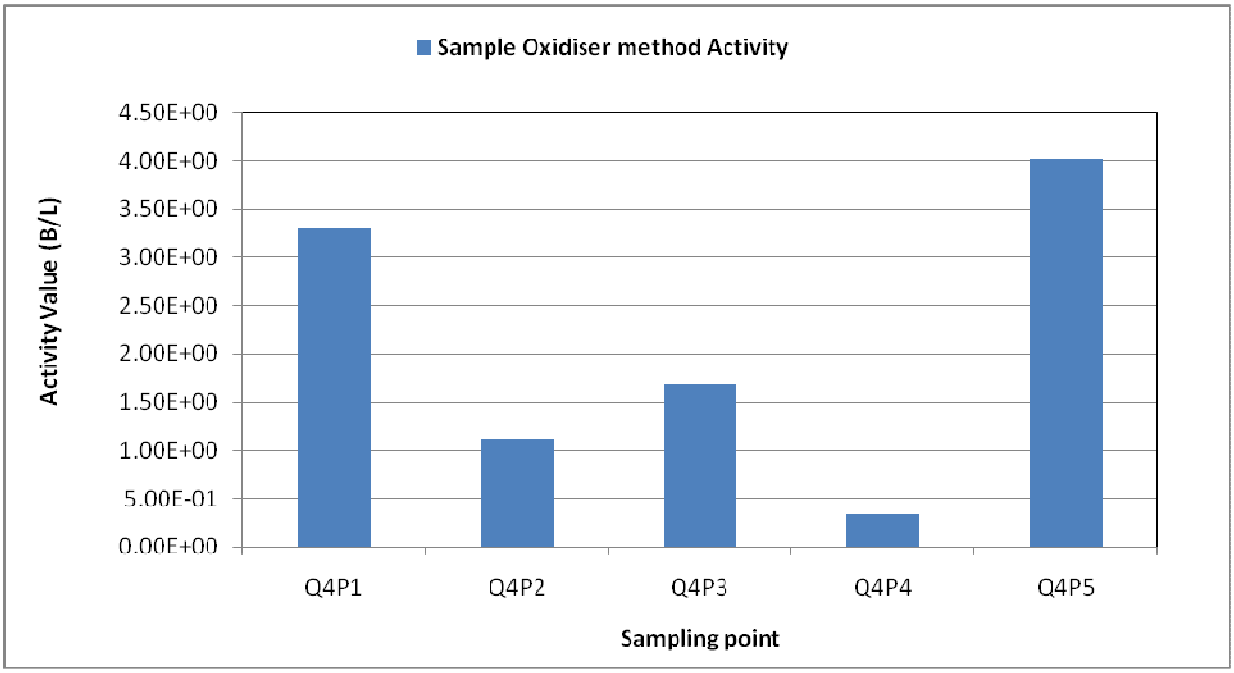


Figure 4.4: *^{14}C measurements - Quarter four*

4.1.2. ^{3}H results

The Tables below represent the results for ^{3}H water samples which were collected in different seasons. These samples were prepared using both sample oxidiser method and direct measurement method. The direct method was used to determine if both methods correlate with each other since direct method is currently being used as a routine method in RadioAnalysis and Sample Oxidiser method have never been used before in the RadioAnalysis laboratory before this study. **Table 4.5** indicates the activity concentrations for ^{3}H for water samples that were collected during winter season.

Table 4.5: Quarter one - ^{3}H results

First quarter: sampling period June – August				
	Sample Oxidiser method		***Direct Measurement method***	
Sample	*Activity(+/- Uncertainty) Bq/L*	*MDA (Bq/L)*	*Activity (+/- Uncertainty) Bq/L*	*MDA (Bq/L)*
Q1P1	2.24E+01 (+/- 2.21E-01)	2.92E+00	1.88E+01 (+/- 2.95E-01)	1.36E+01
Q1P2	2.04E+01 (+/- 1.99E-01)	2.59E+00	1.78E+01 (+/- 2.81E-01)	1.40E+01
Q1P3	1.55E+01 (+/- 1.47E-01)	1.87E+00	2.57E+01 (+/- 3.83E-01)	1.35E+01
Q1P4	2.01E+01 (+/- 2.11E-01)	2.95E+00	1.96E+01 (+/- 3.07E-01)	1.40E+01
Q1P5	1.41E+01 (+/- 1.40E-01)	1.87E+00	2.46E+01 (+/- 3.75E-01)	1.37E+01
Average	1.85E+01 (+/- 1.84E-01)	2.44E+00	2.13E+01 (+/- 3.28E-01)	1.38E+01

The activity concentration values for ^{3}H for samples collected over the period of June – August were observed to be low for both Sample Oxidiser preparation method and direct method. The results for both sample preparation were observed to correlate to each other. The MDA values for direct method were high with an average of 1.38E+01 Bq/L and for Sample Oxidiser method, the average MDA value were very low with the value of 2.44E+00 Bq/L. The average activity concentration for Sample Oxidiser method was 1.85E+01 (+/- 1.84E-01) Bq/L and the average concentration for direct method was 2.13E+01 (+/- 3.28E-01) Bq/L. **Figure 4.5** below, indicates the sampling points against activity concentrations of ^{3}H.

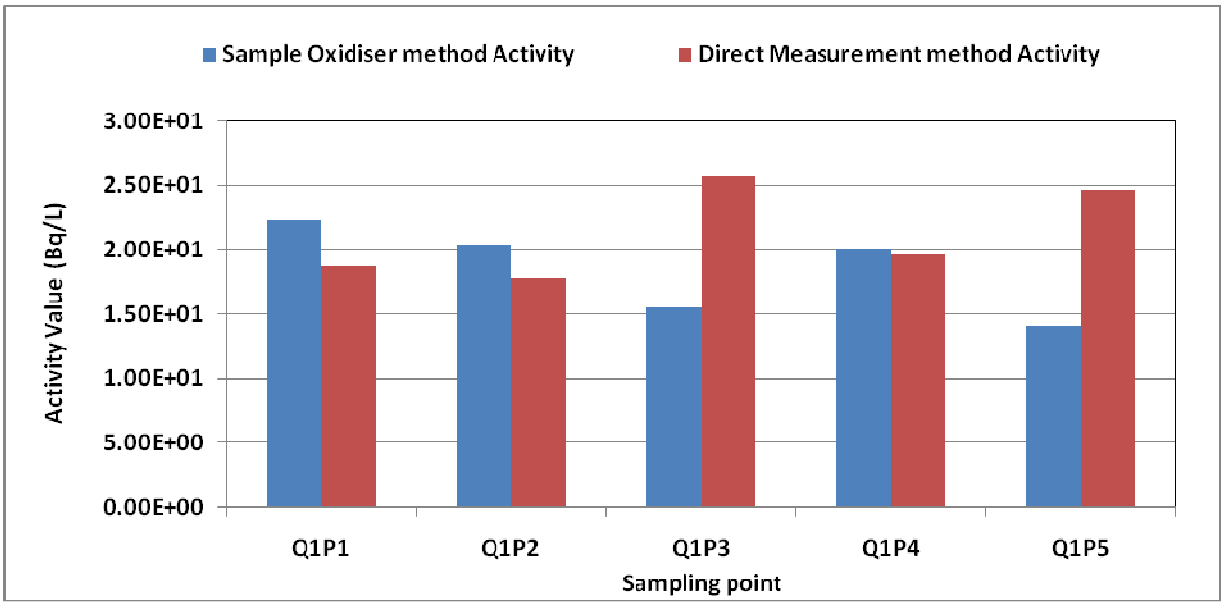


Figure 4.5: *^{3}H measurements - Quarter one*

The results for ^{3}H activity concentrations for the samples prepared using both methods are presented in **Table 4.6**. These samples were collected during the spring season.

Table 4.6: Quarter two - ^{3}H results

Second quarter: sampling period September - November				
	Sample Oxidiser method		***Direct Measurement method***	
Sample	*Activity (+/- Uncertainty) Bq/L*	*MDA (Bq/L)*	*Activity (+/- Uncertainty) Bq/L*	*MDA (Bq/L)*
Q2P1	2.22E+01 (+/- 1.65E-01)	2.03E+00	3.55E+01 (+/- 5.23E-01)	9.42E+00
Q2P2	2.94E+01 (+/- 2.38E-01)	3.20E+00	1.98E+01 (+/- 3.66E-01)	9.31E+00
Q2P3	2.00E+00 (+/- 5.86E-02)	2.62E+00	1.98E+01 (+/- 3.70E-01)	9.28E+00
Q2P4	3.56E+00 (+/-6.99E-02)	2.22E+00	1.91E+01 (+/ - 3.58E-01)	9.58E+00
Q2P5	1.86E+01 (+/- 1.50E-01)	2.00E+00	1.45E+01 (+/- 3.03E-01)	9.77E+00
Average	1.51E+01 (+/- 1.36E-01)	2.41E+00	2.18E+01 (+/-3.84E-01)	9.47E+00

The observation made for the samples prepared using Sample Oxidiser method, is that activity concentrations for ^{3}H at sampling points three and four were very low compared to other sampling points. Low activity concentration might be due to the spout tips that were observed to have cracks after combustion. When these two activity concentrations were compared to the results for the samples prepared using direct method, they did not correlate with each other. The average activity concentrations for Sample Oxidiser method was observed to be 1.51E+01 (+/- 1.36E-01) Bq/L with the average MDA value of 2.41E+00 Bq/L and the average activity concentration for direct samples were 2.18E+01 (+/-3.84E-01) Bq/L with the average MDA value of 9.47E+00 Bq/L. The results of ^{3}H are shown in **Figure 4.6**.

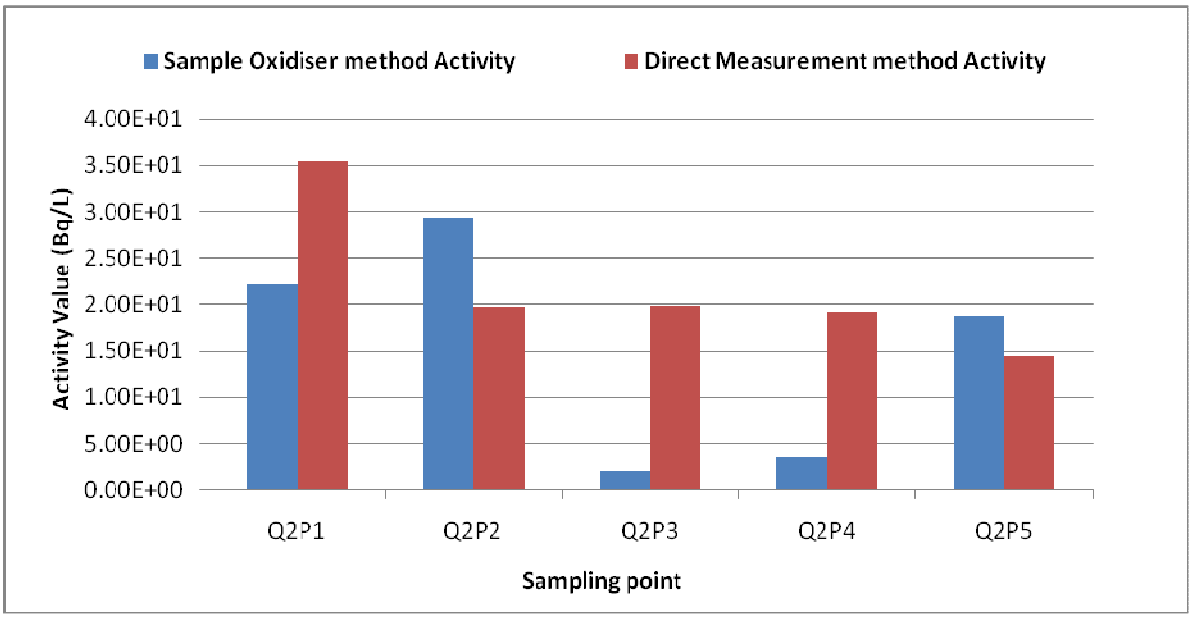


Figure 4.6: *^{3}H measurements - Quarter two*

The sampling for the third quarter was conducted during the summer season. The results for ^{3}H prepared by both methods are represented in **Table 4.7**.

Table 4.7: Quarter three - ^{3}H results

Third quarter: sampling period December - February				
	Sample Oxidiser method		***Direct Measurement method***	
Sample	*Activity (+/- Uncertainty) Bq/L*	*MDA (Bq/L)*	*Activity (+/- Uncertainty) Bq/L*	*MDA (Bq/L)*
Q3P1	1.90E+01 (+/- 1.58E-01)	2.19E+00	1.86E+01 (+/- 4.01E-01)	1.03E+01
Q3P2	5.56E+00 (+/- 9.61E-02)	2.81E+00	1.54E+01 (+/- 3.65E-01)	1.05E+01
Q3P3	2.84E+01 (+/- 2.38E-01)	3.32E+00	1.34E+01 (+/- 3.42E-01)	1.05E+01
Q3P4	2.39E+01 (+/- 1.94E-01)	2.63E+00	1.52E+01 (+/- 3.62E-01)	1.06E+01
Q3P5	2.45E+01 (+/- 1.91E-01)	2.48E+00	1.45E+01 (+/- 3.57E-01)	1.05E+01
Average	2.03E+01 (+/- 1.75E-01)	2.68E+00	1.54E+01 (+/- 3.65E-01)	1.05E+01

The activity concentrations for both Sample Oxidiser method and direct method were observed to be correlating to each other. The activity concentration for the sample collected at point two was observed to be lower than others. The MDA values for direct method were observed to be higher than that of the Sample Oxidiser method, which makes the concentrations to be too close to the MDA values. The results for the ^{3}H measurements are shown in **Figure 4.7**.

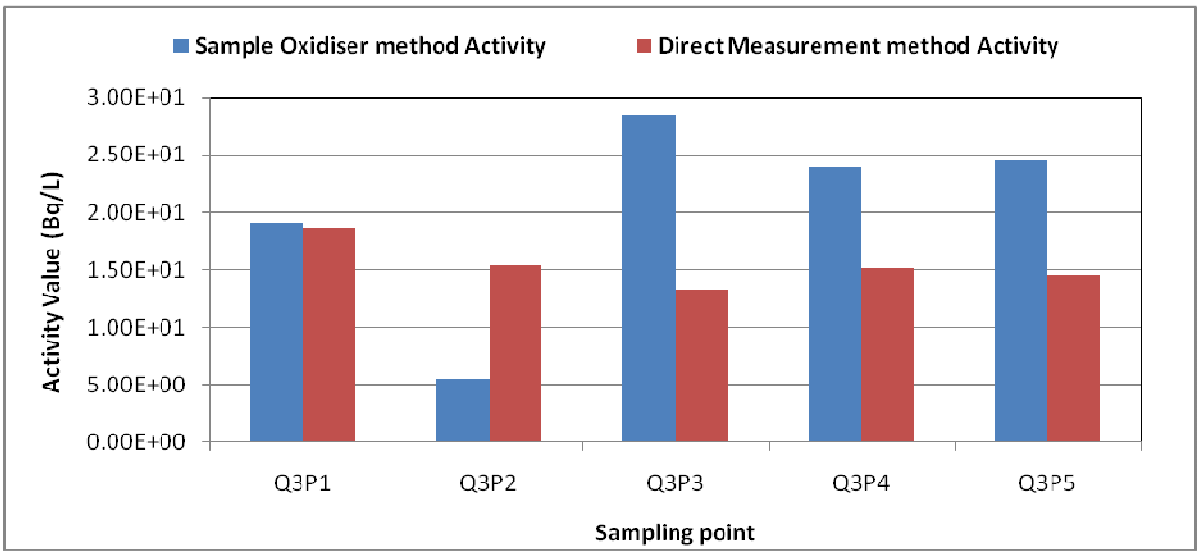


Figure 4.7: *^{3}H measurements - Quarter three*

The results for the fourth quarter measurements of ^{3}H by both preparation methods are indicated in **Table 4.8**: these results are for the samples which were collected during autumn season.

Table 4.8: Quarter four - ^{3}H results

Fourth quarter: sampling period March - May				
	Sample Oxidiser method		***Direct Measurement method***	
Sample	*Activity (+/- Uncertainty) Bq/L*	*MDA (Bq/L)*	*Activity (+/- Uncertainty) Bq/L*	*MDA (Bq/L)*
Q4P1	3.14E+01 (+/- 2.62E-01)	3.06E+00	1.70E+01 (+/- 2.58E-01)	1.32E+01
Q4P2	1.27E+01 (+/- 1.02E-01)	1.15E+00	2.69E+01 (+/- 3.94E-01)	1.33E+01
Q4P3	2.97E+01 (+/- 2.35E-01)	2.61E+00	3.85E+01 (+/- 4.91E-01)	1.35E+01
Q4P4	2.74E+01 (+/- 2.37E-01)	2.87E+00	2.32E+01 (+/- 3.49E-01)	1.34E+01
Q4P5	3.58E+01 (+/- 3.12E-01)	3.80E+00	2.52E+01 (+/- 3.74E-01)	1.35E+01
Average	1.85E+01 (+/- 1.84E-01)	2.44E+00	2.13E+01 (+/- 3.28E-01)	1.38E+01

The results for ^{3}H activity concentration for both sample preparation methods were observed to be correlating to each other. **Figure 4.9** indicates the results of ^{3}H activity concentrations for the samples collected during autumn season.

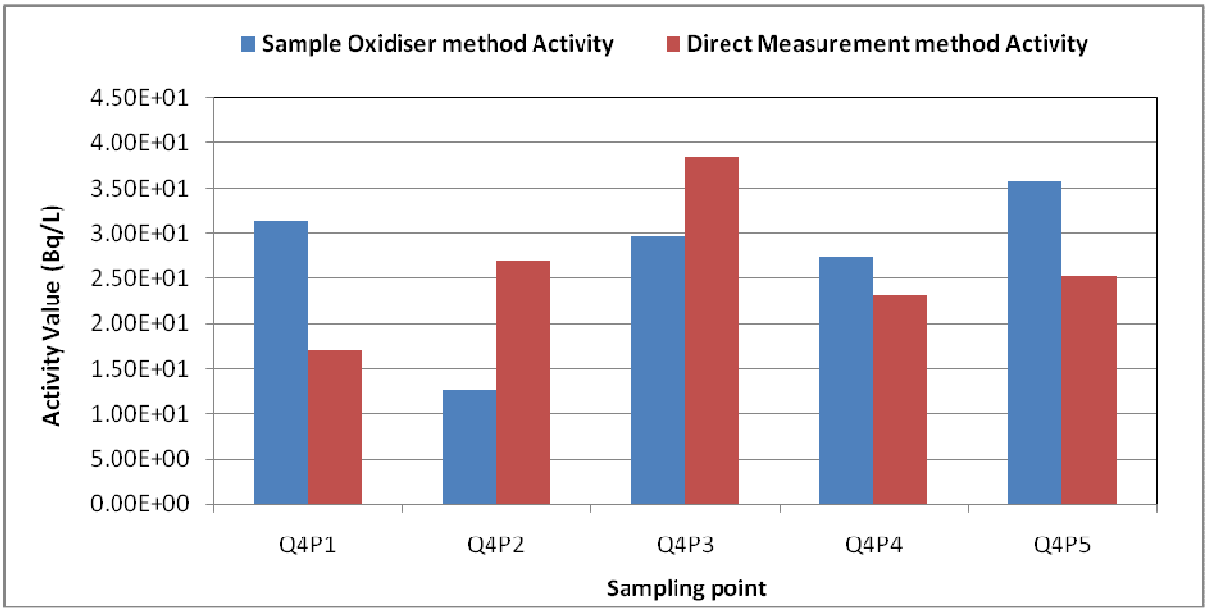


Figure 4.8: *^{3}H measurements - Quarter four*

The results for the average activity concentrations for both ^{3}H and ^{14}C radioisotopes for all four season are indicated in **Table 4.9**, where the first quarter is the winter season, quarter two is the spring season, quarter three is the summer season and quarter four is the autumn season.

Table 4.9: Average activity concentrations for both ^{3}H and ^{14}C

Seasonal Sampling	Sample Oxidiser: ^{3}H average activity (+/- uncertainty) (Bq/L)	Direct method: ^{3}H average activity (+/- uncertainty) (Bq/L)	Sample Oxidiser: ^{14}C average activity (+/- uncertainty) (Bq/L)
Q1	1.85E+01 (+/- 1.84E-01)	2.13E+01 (+/- 3.28E-01)	3.77E+01 (+/-2.47E-01)
Q2	1.51E+01 (+/- 1.36E-01)	2.18E+01 (+/- 3.84E-01)	9.62E+00 (+/-1.03E-01)
Q3	2.03E+01 (+/- 1.75E-01)	1.54E+01 (+/- 3.65E-01)	5.94E+00 (+/- 9.28E-02)
Q4	2.74E+01 (+/- 2.30E-01)	2.62E+01 (+/- 3.73E-01)	2.09E+00 (+/- 5.30E-02)

The overall results for ^{3}H activity concentrations were observed to be varying throughout the year for both sample preparation methods. There is no significant difference between the results for direct method and the results for Sample Oxidiser method; this confirms that the Sample Oxidiser method is working well. The ^{14}C activity concentration results were observed to be generally lower than the results for the ^{3}H activity concentrations, except for the activity concentrations for the first quarter. The results for ^{3}H and ^{14}C are indicated in **Figure 4.9**.

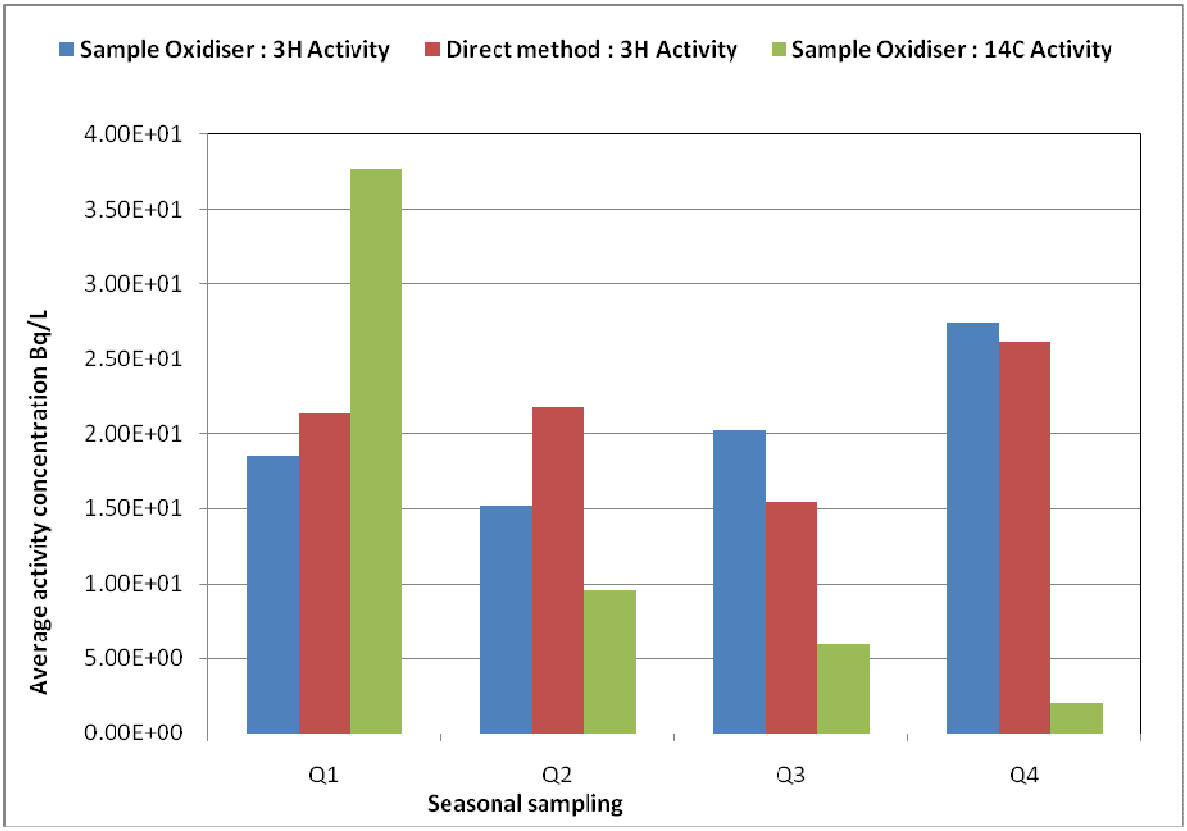


Figure 4.9: *Seasonal average activity concentrations for both ^{3}H and ^{14}C*

4.2. Discussion

4.2.1. Method and instrumentation optimization

The study of the determination of ^{14}C and ^{3}H content in water from the Hartbeespoort Dam indicated that sample preparation using Sample Oxidiser to combust samples is quick and easy to use since the products of sample combustion are water and carbon dioxide; therefore problems such as chemiluminescence, self-absorption and colour quenching are eliminated (Thomson, 2012). Thomas (2012) further states that, it has been observed that sample preparation is considered an inconvenient step on the way to obtaining results. Correct sample preparation in liquid scintillation analysis is essential for both accurate and reproducible analysis, and there is no amount of instrumental sophistication can ever compensate for the problems attendant to badly prepared samples. One of the problems which results from badly prepared samples is the carryover of sample into blanks which is called the memory effect. The memory effect should not be more than 50 CPM over background in a sample containing 100,000 DPM. The memory effect results in this study indicated that almost all the values were within specification of less than fifty (< 50 CPM), but for ^{3}H results on the first quarter was greater than fifty (> 50 CPM). There could be a number of reasons for the memory effect to be > 50 CPM, but the main one is that if the combustion time is shot, the sample combustion would not be completed which leaves some of the activity in a combustion chamber and then come out with the following sample to be combusted. When started utilizing the Sample Oxidiser instrument the combustion time was set to two (2) minutes, after counting the samples on LSC and observed that the memory effect was > 50, the combustion time was changed to Four (4) minutes. The change in combustion time made a difference, the results were improved, and the memory effect values were all < 50.

Another problem arising from the samples that are not prepared well on the Sample Oxidiser is the burn efficiency (also known as recovery factor). The recovery measurement of oxidiser should be greater or equal to 96%. The results for the recovery factor calculations indicated that the percentage for ^{14}C on the third quarter

was 91% and for ^{3}H on the fourth quarter was 89% which is less than the 96% which is the specification. This might be due to the spout tips that were used to collect both ^{3}H and ^{14}C into the vial. When changing the spout tips after combustion process, it was observed that some of the spout tips had some cracks after combustion. The reason for these tips to crack might be the pressure when bubbling oxygen through the spout tips into the vials to trap ^{3}H and ^{14}C in a LSC cocktail. Another reason the recovery factor to drop below 95% might be the indication that the catalyst inside the combustion tube requires to be changed. The major disadvantage about Sample Oxidiser instrument is that, only a maximum of 1.5 g per sample that can be combusted (Nikolov et al., 2013), which can be a problem for samples containing extremely low activities. Measuring the samples containing low activities such as ^{3}H and ^{14}C with combusted smaller mass might result in concentration activities that are below MDA and therefore could not be reported.

Since the measurements of low activity levels of beta-emitting radionuclides in environmental samples can either be measured using GPC or LSC, sample measurements using LSC has proven to be suitable and very efficient. There are quite a number of parameters that can affect the suitability of any measuring technique. According to Rauret et al. (1989), the high efficiency of the LSC technique makes it particularly suitable for the measurement of very low activity levels. **Appendix 1A - 9** indicate that the average efficiency for LSC during this study was 50% for ^{14}C and 46% for ^{3}H. Another parameter is the counting or measurement time. When counting environmental samples, the counting time should be longer so that the MDA and uncertainty can be as low as possible. The uncertainty values for ^{14}C were very low, ranging from 5.3E-02 Bq/L to 2.5E-01Bq/L. The MDA values for ^{14}C were ranging between 1.22E-01Bq/L and 3.18E+00 Bq/L. The results obtained for ^{14}C activity determination make counting time used for measurements acceptable, even though it can always be improved to get even better results. The uncertainty values for ^{3}H were higher than ^{14}C uncertainty values. The uncertainty range for ^{3}H samples prepared by Sample oxidiser method was between 1.36E-01 Bq/L and 2.30E-01Bq/L, whereas the range for MDA values was between 2.41E+00 Bq/L and

2.70E+00 Bq/L. For direct method, the uncertainty range was from 3.28E-01Bq/L to 3.84E-01Bq/L, which is slightly higher than the uncertainty prepared by Sample Oxidiser method and the MDA values ranged between 9.47E+00 Bq/L and 13.8E+00 Bq/L. The MDA results for ^{3}H activity concentration determination using direct method are very high. Tritium high MDA values indicate that measurement time used for the determination of ^{3}H was not adequate, especially for samples prepared by direct method. Lower uncertainty values give the best estimate of how far the results obtained might be from the true value. The larger uncertainty makes it impossible to say whether the difference between the two numbers is real or just due to incorrect measurements.

4.2.2. Carbon-14 results discussion

The results for ^{14}C activity concentrations for the second quarter and the third quarter samples collected at the entrance of the Crocodile River were observed to be much higher than the samples collected from other points. It was observed that during the autumn season, the activity concentration for sampling point four which is the Crocodile River outflow was much higher than the rest of sampling points. This might be because after the rainy season, some of the activity might have been transported by rain to the outflow of the Crocodile River. The trend for ^{14}C activity concentrations was observed to be decreasing from winter of year 2014 to autumn of year 2015. The decrease in activity concentrations of ^{14}C indicates that the seasonal change affects the mobility of the radionuclide in question. Other reasons for ^{14}C activity concentrations to fluctuate from one sampling point to another might be fires around a particular area which might cause the ^{14}C radionuclide to be more concentrated in atmosphere. The highly concentrated ^{14}C in the atmosphere is then absorbed by water at that particular area. Another reason might be that, if a dam has plants at a sampling area, those plants might absorb some of the ^{14}C radionuclide, which will result in less concentrated ^{14}C radionuclide in water being sampled in that area.

The results for ^{14}C recoveries for quarter one indicate that during winter season the activity concentration with the value of 3.77E+01 (+/-2.47E-01) Bq/L was higher than

the activity concentrations for other three seasons. The overall results for ^{14}C were very low for all seasons; they were very close to the MDA values. Since the WHO guidance level for radionuclides in drinking water is 100 Bq/L for ^{14}C (WHO, 2011), it gives assurance that the water from Hartbeespoort Dam contains small concentrations of ^{14}C that is within the regulatory limits. During winter season there is no rain expected to dilute the concentrations of the radionuclides. Whereas the results for quarter four indicate that during the autumn season the activity concentrations for ^{14}C were the lowest with the value of 2.02E+00 (+/-5.13E-02) Bq/L. There was a 0–25 % chance of rain during the month of July 2014 when the sampling was conducted, refer to **Appendix 10**. However when Krajcar-Bronic et al. (1998), conducted a study they discovered that ^{14}C values in the city of Zagreb in Croatia are much lower than in other cities during the colder time of the year. These might be due to different climate conditions in both countries. In South Africa, the winter season is cold and dry while the summer season is very hot with rain and sometimes floods expected but in Croatia, the winter season is very cold with snowfall and the summer seasons is hot with no or little rainfall (World Weather Online, 2014). Eyrolle-Boyer et al. (2015) state that rain or floods can significantly affect the activity concentration levels of radionuclides. The effects of rain or floods on ^{14}C and ^{3}H radionuclides is that, the concentration levels are modified by significantly diluting them. When the study of ^{3}H and ^{14}C background levels in pristine aquatic systems and their potential sources of variability were conducted, the end results indicated that the radionuclides contain very much lower activities compared to the activities measured before floods occurred.

4.2.3. Tritium results discussion

The activity concentrations for ^{3}H varied for all four quarters, they were all very low. For the samples measured, it was observed that the change in seasons did not have any effect on the ^{3}H activity concentrations. During the winter season, the weather indicated that there was 0 – 25% rain expected (refer to **Appendix 10**), during spring season, there was an indication that there was 25 – 50% rain expected refer to (**Appendix 11**), summer season indicated that there was 25 – 50% rain expected

(refer to **Appendix 12)** and **Appendix 13** indicates that there was 50 – 100% of rain expected during this autumn season. During the study that was conducted by Krajcar-Bronic et al. (1998), where they were looking at two decades of environmental isotope record in Croatia. During this study they reconstructed the past and predicted future levels of environmental isotopes. In this study it was observed that there was no rain on the days when the samples were collected, the activity concentrations for ^{3}H measured during that time were about four times higher than normal. However, during the following days there was a daily rain and the activity concentrations measured after the rain decreased. This observation confirmed that change in climate conditions affect the concentrations of radionuclides.

The second quarter results for ^{3}H prepared by both Sample Oxidiser method and direct method were observed to be very different from each other. Most of the Sample Oxidiser method results were very low compared to the direct method results. This might be due to the spout tips which were used to collect both ^{3}H and ^{14}C into the vial. When changing the spout tips after combustion process, it was observed that some of the spout tips had some cracks after combustion, mostly the tips for ^{3}H. The reason for these tips to crack might be the pressure when bubbling oxygen through the spout tips into the vials to trap ^{3}H and ^{14}C in a LSC cocktail. Another reason the recovery factor to drop below 95% might be the indication that the catalyst inside the combustion tube requires to be changed.

The highest activity concentration measured during this study in terms of ^{3}H was for quarter four, which was 2.03E+01 (+/- 1.75E-01) Bq/L using Sample Oxidiser method. Overall data evaluation for ^{3}H indicated that Sample Oxidiser preparation method correlate with direct sample preparation method. It was observed that most results for The highest ^{3}H activity concentration measured using direct method was for quarter two which was 2.18E+01 (+/- 3.84E-01) Bq/L. Both these values were below the regulatory levels which was 10,000 Bq/l for ^{3}H (WHO, 2011). Hence, the results give assurance to the national stakeholders that water from Hartbeespoort Dam contains very low levels of ^{3}H concentrations that is within regulatory regulations.

4.2.4. Regulatory measures

The international regulatory limits for public exposure to radionuclides are placed by WHO, in South Africa, NNR is responsible for the assurance that no public member should be exposed to more than internationally accepted limit of 1 mSv/y from all sources. According to IAEA (2004) generally, the owners or operators of nuclear facilities are responsible for setting up and implementing the technical and organizational measures necessary for ensuring protection of public from radioactive sources. Therefore Necsa is responsible for ensuring the public protection from its radioactive effluents that contain not just ^{3}H and ^{14}C, but any radionuclide which may cause harm to public`s health.

This study confirms that the concentrations of both ^{3}H and ^{14}C for the samples collected between July 2014 and April 2015 are at the level which cannot pose any harm or any negative impact to public`s health. The impacts of ^{3}H can be a transfer of this radionuclide through the aquatic food chain (especially fish), use of river water for agricultural purposes (irrigation), transfer of radionuclides through the terrestrial food chain (vegetables, meat and milk) and subsequent internal exposure of humans due to ingestion of contaminated foodstuffs (Cliffroy et al., 2006). On the other hand, ^{14}C is a radioactive isotope that is easily transferred during biological processes and soil-plant interactions involving carbon compounds. McCracken (2004) is of the opinion that generally, degraded water quality makes streams, lakes and coastal waters unpleasant and unsafe to swim in, to smell and to drink. If severe, water pollution can kill large numbers of fish, birds, and other animals, in some cases killing all members of a species in an affected area. Fish and shellfish harvested from radioactive contaminated waters may be unsafe to eat. Humans who ingest contaminated water can become ill, and, with prolonged exposure, may develop cancers or bare children with birth defects.

Chapter 5: Conclusions, Limitations and Recommendations

In this chapter, the conclusions drawn based on the results obtained and then recommendations are made in order to improve the findings.

5.1. Conclusions

Conducting this research study evaluated that the levels of ^{14}C and ^{3}H radionuclides in Hartbeespoort Dam water are within regulatory concerns, at the level which does not pose any threat to human health and the environment.

The results obtained for ^{14}C showed that during winter season, the concentration levels are higher than the other three seasons, while the rainy season's results were observed to have the lowest ^{14}C activity. This means that rain plays a huge role in diluting or transferring ^{14}C radionuclide. The overall results determined that liquid effluent released from SAFARI-1 reactor during the sampling period of July 2014 to April 2015 contained ^{14}C concentration levels that are far below the 100 Bq/L which is the limit for drinking water.

The overall activity concentrations for ^{3}H measured in water from Hartbeespoort Dam were far lower than the 10,000 Bq/L limit. For ^{3}H results, it was observed that the climate did not have any impact on the concentration of this radionuclide Tritium results for samples prepared using both Sample Oxidiser method and direct method were not significantly different from each other, but the MDA values for direct method were higher than the MDA values for the Sample Oxidiser method. The higher MDA value revealed that direct method requires more measurement time to get lower and better MDA values and therefore can be concluded that Sample Oxidiser method was the best method for ^{3}H sample preparation.

It can be concluded that Hartbeespoort Dam water contains acceptable levels of ^{3}H and ^{14}C concentrations that are within acceptable regulatory limits in South Africa and internationally. Since Hartbeespoort Dam water is being used for, inter alia, irrigation and domestic purposes, the national stakeholders can be assured that using water for these purposes is safe with regards to ^{3}H and ^{14}C radionuclides.

It can also be concluded that Necsa as the operational company that has the permit to discharge the liquid effluents in Crocodile River, ensures that the liquid effluent discharged is within the discharge limit as indicated by NNR.

5.2. Limitations

The limitations of this study were the limited resources such as radio-analytical instrumentations which are also being used for routine analysis. The finances were not enough to conduct a laboratory study using many samples as it is costly to analyse each sample.

Due to limited time, the other methods which could have been used to compare and verify the results for ^{14}C could not be performed. There was also not sufficient time to do measurements on different environmental studies in order to broaden the research and hence, gather sufficient data for decision making purposes. Most of the apparatus and materials could only be purchased in Europe where the delivery time was up to eight months, depending on the material purchased, this delay resulted in sample preparation time and sample measurement time to be very limited.

5.3. Recommendations

It is recommended that the method be developed further. Samples should be taken on the monthly basis and measured on a yearly basis to keep a trend on the activities of these two radionuclides. Trend observation will give true reflection on how the climate can affect the activity concentrations. The literature study revealed that other researchers have measured, *inter alia*, soil, vegetation, water species, air and sediments to determine the levels of ^{14}C and ^{3}H on the environment. Hence this study can be further developed by measuring sediments and fish from Hartbeespoort Dam, soil from the area surrounding nuclear installation and vegetation that is being irrigated using water from Hartbeespoort Dam, so as to determine if activity found in water can be transferred to the surrounding areas.

The Sample Oxidiser method for sample preparation still needs to be developed further. The method is working well but further investigation is required on spout tips that can work well and withstand the pressure and heat, which will not crack easily.

In future, sample measurement on a LSC can be evaluated by looking at any parameter that can affect the results. In this study the counting time for each sample was only 30 minutes. The literature has proven that when measuring the samples for 300 to 500 minutes can reduce the MDA value. The counting time is the parameter that affects the MDA value and the uncertainty. Increasing the counting time will reduce these parameters. When analyzing environmental samples such as ^{3}H and ^{14}C with very low activity, the best option is to select long counting time so that MDA values and uncertainty values are as low as possible.

It is recommended that natural resources such as water will have to be managed better at the planetary scale to preserve environmental quality. The management of water can be done taking into account the potential conflicting situations resulting from common uses. To ensure that water can be utilised safely without any potential harm to environment and human health, it is important that it is monitored for chemicals and radioactive substances regularly.

Chapter 6: References and Appendices and annexure

6.1. References

South African Weather Services. (2016). *Climate*. Retrieved January 21, 2016, from Historical Rain Maps: http://www.weathersa.co.za

Adam, F., Fig, D., Gilbert, D., Kantey, M., Musana, F., Schulz, N., et al. (2011). *The True Cost of Nuclear Power in South Africa.* Johannesburg, South Africa: Grrenpeace Africa.

Aghoyeh, R. Z., & Khalafi, H. (2012). Evaluation of tritium and Carbon-14 radioactivity in primary loop of Tehran Research Reactor (TRR). *Progress in Nuclear Energy , 60*, 135-139.

Ahn, H. J., Song, B. C., Sohn, S. C., Lee, M. H., Song, K., & Jee, K. Y. (2013). Application of a wet oxidation method for the quantification of 3H and 14C in low-level radwastes. *Applied Radiation and Isotopes , 81*, 62-66.

ALS Environmental. (2014). *Background Level Meaning*. Retrieved January 07, 2016, from Cumbria Analytical Laboratory: http://www.caslab.com

Aquilonius, K., & Hallberg, B. (2005). Process-oriented dose assessment model for 14C due to releases during normal operation of a nuclear power plant. *Journal of Environmental Radioactivity , 82*, 267-283.

Baresic, J., Horvatincic, N., Krajcar-Bronic, I., & Obelic, B. (2010). Comparison of two techniques for low-level tritium measurement - gas proportional and liquid scintillation counting. *Proceedings of Third European IRPA Congress* (pp. 1-5). Helsinki, Finland: Radiation Protection Technologies.

Begg, G. H., Cook, G. T., Baxter, M. S., Scott, E. M., & McCartney, M. (1992). Anthropogenic radiocarbon in the Irish Sea and Scottish coastal waters. *Radiocarbon , 34*, 707-716.

Benito, C., Jimenez, A., Sanchez, C., & Navarro-Sabate, A. (2012). Liquid and solid scintillation: principles and applications. In S. Jose-Ramon, & L. X. Xavier, *Handbook of instrumental techniques for materials, chemical and biosciences research* (pp. 1-11). Barcelona: Centres Cientifics i Tecnologics. Universitat de Barcelona.

Blowers, P., Caborn, J., Dell, T., Gingell, T., Harms, A., Long, S., et al. (2011). Determination of Carbon-14 in environmental level, solid reference materials. *Applied Radiation and Isotopes , 69*, 1323-1329.

Brooks, A. L., Couch, L. A., & Chad, S. A. (2013). Commentary: What is the Health Risk of 740 Bq L−1 of Tritium? A Perspective. *Health Physics , 104* (1), 104-118.

Brown, K., Dingley, K. H., & Turteltaub, K. W. (2005). Accelerator Mass Spectrometry for Biomedical Research. *Methods in Enzymology , 402*, 423-443.

Brown, R. M. (1979). *Environmental Tritium in "Trees in Behaviour of tritium in the Environment".* Vienna: International Atomic Energy Agency .

Calmet, D. (2014). ISO Standandars on Test Methods for Radioactivity Monitoring of Food and the Environment. *Radiation Emergency Medicine , 3* (1), 7-20.

Calmet, D., Ameon, R., Bombard, A., Forte, M., Fournier, M., Herranz, M., et al. (2013). ISO standards on test methods for water radioactivity monitoring. *Applied Radiation and Isotopes , 81*, 21-25.

Calmon, P., & Garnier-Laplace, J. (2010, December 18). Tritium and the Environment. *Radionuclide Fact Sheet* , pp. 3-26.

Canberra Industries, Inc. (2010). *Spectrum Analysis.* Retrieved October 19, 2015, from Canberra: http://www.canberra.com

Cliffroy, P., Siclet, F., Damois, C., & Luck, M. (2006). A dynamic model for assessing radiological consequences of tritium routinely released in rivers. Application to the Loire River. *Journal of Environmental Radioactivity , 90*, 110-139.

Coats, E. (2015). *What is environmental water?* Victoria: Victorian Environmental Water Holder.

Cook, G. T., Passo, C. J., & Carter, B. (2003). Environmental Liquid Scintillation Analysis. In M. F. L'Annunziata, *Handbook of Radioactivity Analysis* (pp. 543-573). USA: Academic Press, Elsevier.

Cook, G., Mackenzie, A. B., Naysmith, P., & Anderson, R. (1998). Natural and anthropogenic 14C in the UK coastal marine environment. *Journal of Environmental Radioactivity , 40*, 89-111.

Cooper, R., & Schindler, P. (2006). *Busness Research Methods.* New York : NY:McGraw-Hill.

DeFilippis, S. (1991). 55Fe and 59Fe: A Qualitative Comparison of Four Methods to Liquid Scintillation. *Radioactivity Radiochemistry* , 14-21.

Department of Water and Sanitation. (2015, February 02). *Harties Metsi A Me - My Water*. Retrieved November 27, 2015, from Dwa: Hartbeespoort Dam Remediation Programme: http://www.harties.org.za

Dingwall, S., Mills, C. E., Phan, N., Taylor, K., & Boreham, D. R. (2011). Human Health and the Biological Effects of Tritium in Drinking Water: Prudent Policy Through Science - Addressing the Odwac New Recommendation. *Formerly Nonlinearity in Biology, Toxicology, and Medicine , 9* (1559-3258), 6-31.

Edler, R., & Kaihola, L. (2007). *Determination of the 14C content in fuels containing bioethanol and other biogenic materials with liquid scintillation counting.* Boston: PerkinElmer precisely.

Environmental Agency. (2005). *Guidance on the measurement of tritium in environmental samples: Methods for the Examination of Waters and Associated Materials.* Leicestershire: Environmental Agency (National Laboratory Service).

Environmental Safety: Administration & Finance. (1994). *Radiation Protection Training Manual and Study Guide.* Retrieved August 19, 2015, from University of Maryland: Department of Environmental Safety, Sustainability & Risk: http//www.des.umd.edu

European Commission. (1998). *European Drinking Water Directive 58/83/EC of 3 November 1998 on the Quality of Water Intended for Human Consumption.* European Commission.

Eyrolle-Boyer, F., Claval, D., Cossonnet, C., Zebracki, M., Gairoard, S., Radakovitch, O., et al. (2015). Tritium and 14C backgound levels in pristine aquatic systems and their potential sources of variability. *Journal of Environmental Radioactivity , 139*, 24-32.

Fukutani, S., Fukui, M., Koyama, A., & Nishimaki, K. (2008). A Method of Calibration for Measurement of Low Level Tritium in Environmental Water using a Liquid Scintillation Counter. *Journal of Nuclear Science and Technolgy* (6), 89-92.

Garnier-Laplace, J., & Roussel-Debet, S. (2001). *Carbon-14 and the environment.* 92260 Fontenay-aux-Roses: Institut de radioprotection et de Surete Nucleaire.

Horrocks, D. L. (1974). *Applications of Liquid Scintillation Conting.* New York: Academic Press.

Huang, Y., Guo, G., Wu, L., Zhang, B., Chen, C., Zhang, H., et al. (2015). An analytical method for 14C in environmental water based on a wet-oxidation process. *Journal of Environmental Radioactivity , 142*, 1-8.

Huskisson, N. S., & Ward, P. F. (1978). A reliable method for scintillation counting of 14CO2 trapped in sollutions of sodium hydroxide, using a scintillant suitable for general use. *Int. J. Appl. Radiat. Isot.* (29), 729-734.

IAEA. (2004). *Management of Waste Containing Tritium and Carbon-14.* Venna, Austria: IAEA.

IAEA. (2007). *Modelling the Environmental Transfer of Tritium and Carbon-14 to Biota and Man.* Vienna, Austria: IAEA.

International Atomic Energy Agency. (2000). *Regulatory Control of Radioactive Discharges to the environment.* Venna: IAEA.

ISO 13162. (2011). *Water Quality - Determination of Carbon 14 Activity - Liquid Scintillation Counting Method.* Geneva, Switzerland: International Standardization Organization.

ISO 9698. (2010). *Water Quality: Determination of Tritium Activity Concentration - Liquid Scintillation Counting Method.* Geneva, Switzerland: International Organization for Standardization.

ISO/FDIS 13168. (2014). *Water Quality - Simultaneous determination of tritium and carbon-14 activities - Test method using liquid scintillation counting.* Switzerland: Organization for International Standards.

ISO/TC 147. (2011). *Water Quality: Determination of Carbon-14 activity - Liquid Scintilation Counting Method.* Geneva: International Organization for Standardization.

Johnson, M. J., Boelke, C., Chiarella, L. A., Colosi, P. D., Greene, K., Lellis-Dibble, K., et al. (2008). *Impacts to Marine Fisheries Habitat from Northfishing Activities in the Northeastern United States.* Gloucester, Massachusetts: US Department of Commerce - National Oceanic and Atmospheric Administration.

Kachel, M. J. (2008). Chapter 2: Threats to the Marine Environment: Pollution and Physical Damage. In M. J. Kachel, *The IMO`s Role in Protecting Vulnerable Marine Areas* (pp. 23-36). Berlin: Springer.

Kanipe, L. G. (1977). *Handbook for analytical quality control in radioanalytical laboratories.* Washington, DC 20460: U.S. Environmental protection Agency.

Krajcar Bronic, J., Todorovic, N., Nkolov, J., & Baresic, J. (2012). Intercomarison of Low-Level Tritum and Radiocarbon Measurements in Environmental Samples. *The First International Conference on Radiation and Dosimetry in Various Fields of Research RAD 2012* (pp. 2-4). Serbia: Faculty of Electronical Engineering.

Krajcar-Bronic, I., Horvatincic, N., & Obelic, B. (1998). Two decades of environmental isotope records in Croatia: Reconstruction of the past ans prediction of future levels. *Radiocarbon* , 399-416.

Krajcar-Bronic, I., Horvatincic, N., Baresic, J., & Obelic, B. (2009). Measurement of 14C activity by liquid scintillation counting. *Applied Radiation and Isotopes , 67*, 800-804.

Kulkova, M. A., & Davivochkina, A. V. (2011). Tritium in the Environment of Gulf of Finland. *International Journal of Chemical Engeneering and Applications , 2* (1), 8-11.

Le Dizes-Maurel, S., Maro, D., Lebaron-Jacobs, L., & Masson, M. (2009). Carbone 14. *Toxicologie nucleaire environmentale et humaine* , 603-618.

Lemon, A. (1997). *Groundwater Dating with Tritium and Carbon-14.*

Limer, L. M., Le Dizes-Maurel, S., Klos, R., Maro, D., & Norden, M. (2015). Impacts of 14C discharges from a nuclear fuel reprocessing plant on surronding vegetation: Comparison between grass field measurements and TOCATTA-X and SSPAM14C model computations. *Journal of Environmental Radioactivity , 147*, 115-124.

Madruga, M. J., Sequeda, M. M., & Gomes, A. R. (2008). Determination of Tritium in Waters by Liquid Scintillation Counting, LSC. *Advances in Liquid ScintillationSpectrometry* , 353-359.

Mat, N. (1995). *Standard Operating Procedure for Combustion of 14C- Samples with OX-500 Biological Material Oxidizer.* Malaysia: Malaysian Institute for Nuclear Technology Research (MINT).

Mbukwa, E. A., Msagati, T. A., & Mamba, B. B. (2012). Quantitative Variations of Intracellular Microcystin-LR, -RR and -YR in Samples Collected from Four Locations in Hartbeespoort Dam in North West Province (South Africa) During the 2010/2011 Summer Season. *International Journal of Environmental Research and Public Health* , 3484-3505.

McCracken, B. (2004). *Coastal Thermal Pollution and Related Policy Issues in th eUnited States: An Overview.* Retrieved 01 06, 2016, from Coastal Policy Summer: http://www.public.iastate.edu

Meybeck, M., Kuusisto, E., Makela, A., & Malkki, E. (1996). *Water Quality Monitoring - A Practical Guide to Design and Implementation of Freshwater Quality Studies and Monitoring Programmes.* Switzerland: UNEP/WHO.

Milton, G. M., & Brown, R. M. (1994). *A Review of Analytical Techniques for the Determination of Carbon-14 in Environmental Samples.* Chalk River: Atomic Energy Agency of Canada Ltd.

Mingote, R. M., & Rocha, Z. (2007). Uncertainty evaluation in tritium activity assay in water by using direct Liquid Scintillation Spectrometry. *Intrernational Nuclear Atlantic Conference.* Brazil: Associacao Brasileira de Energia Nuclear - ABEN.

Minister of Public Works and Government Services Canada. (2008). *Standards and Guidelines for Tritium in Drinking Water.* BOttawa, Ontario K1P 5S9, CANADA: Canadian Nuclear Safety Commission (CNSC).

National Diagnostics. (2004). *Principles and Applications of Liquid Scintillation Counting.* Charlotte, NC 28209: National Diagnostics.

Net-Focus Interactive cc . (2013). *Sout Africa Accomodation Map*. Retrieved January 23, 2016, from South Africa Accomodation: http://http://www.sa-venues.com

Nikolov, J., Todorovic, N., Jankovic, M., Vostinar, M., Bikit, I., & Veskovic, M. (2013). Differentmethods for tritium determination in surface water by LSC. *Applied Radiation and Isotopes* , 51-56.

Nuclear Industry Association of South Africa. (2012, October 10). Radioactiove Effluents:. *Fact Sheet 7* , pp. 1-4.

Obelic, B., Krajcar Bronic, I., Horvatncic, N., & Baresic, J. (2004). Comparison of Different Methods of Environmenal Radioactivity Measurements at the Zagreb Radiocarbon and Tritium Laboratory. *Radiocarbon* , 1-7.

Oh, J., Warwick, P. E., Croudace, I. W., & Lee, S. (2014). Rapid determination of tritium and carbon-14 in urine samples using a combustion technique. *Jornal of Radioanalytical and Nuclear Chemistry , 299*, 187-191.

Orebiyi, O., & Awomeso, A. (2008). Water and Pollution Agents in the 21st Century. *Nature and Science , 6* (4), 16-24.

Osborne, R. V. (2002). *Tritium in the Canadian Environment: Levels and Health Effects.* Deep River, Ontario: Ranasara Consultants Inc.

Otlet, R. L., Walker, A. J., Fulker, M. J., & Collins, C. (1997). Background carbon-14 levels in UK foodstuffs based on 1992 survey. *Journal of Environmental Radioactity , 34*, 91.

Palomo, M., Penalver, A., Aguilar, C., & Borrull, F. (2007). Tritium aactivity levels in environmental water samples from different origins. *Applied Radiation and Isotopes , 65*, 1048-1056.

PerkinElmer Life and Analytical Sciences. (2005). *Specifications: Liquid Scintillation Analyzers.* Retrieved October 28, 2015, from PerkinElmer: http://www.perkinelmer.com

PerkinElmer, Inc. (2011). *Radiometric Detection for a Safer Environment.* Waltham, MA 02451 USA: PerkinElmer.

Polach, H. A. (1987). Evaluation and status of liquid scintillation counting for radiocarbon dating. *Radiocarbon , 29* (1), 1-11.

Popoaca, S., Bucur, C., & Simionov, V. (2014). Determination of 3H and 14C in Organic Sample after Separation through Combustion Method. *Journal of Energy and Power Enginnering , 8*, 1687-1694.

R. J. Harvey Instrument Corporation. (2009). *Biological Material Oxidizer - ox-501 Unit: Operating Manual.* Tappan, NY: R. J. Harvey Instrument Corporation.

Rauret, G., Mestres, J. S., Ribera, M., & Rajadel, P. (1989). Optimization of Liquid Scintillation Counting Conditions to Determine Low Levels of Tritium and Radiostrontium in Aqueous Solution. *The 8th SAC International Conference on Analytical Chemistry. 115*, pp. 1097-1101. Cambridge, UK: Analyst.

Roussel-Debet, S., Gontier, G., Siclet, F., & Fournier, M. (2006). Distribution of carbon-14 in the terrestrial environment close to French nuclear power plants. *Journal of Environmental Radioactivity , 87*, 246-259.

Sellafield Ltd. (2012). *Monitoring our Environment: Discharges and Monitoring in the United Kingdom - Annual Report 2011.* Cumbria CA20 1PG: Nuclear Decommissioning Authority.

Singleton, D. L., Sanchez, A. L., & Woods, C. (2002). A comparison of two techniques to determine carbon-14 in environmental samples. *Journal of Radioanalytical and Nuclear Chemistry , 251*, 353-357.

Tarancon, A., Bagan, H., Rauret, G., & Garcia, J. F. (2010). Comparative study of pre-treatment procedures for 3H monitoring in water samples from environmental protection programs. *Science of the Total Environment , 408*, 2233-2238.

The Hiroshima Syndrome. (2015, May 30). *The Hiroshima Syndrome*. Retrieved November 11, 2015, from The Hiroshima Syndrome: http://www.hiroshimasyndrome.com

Theodorsson, P. (1991). Gas Proportional versus Liquid Scintillation Counting, Radiometric versus AMS Dating. *Radiocarbon , 33* (1), 9-13.

Thomson, J. (2012). *Chapter 8: Sample Preparation Techniques for Liquid Scintillation Analysis.* Chesterfield, England: Elsevier Inc.

Thomson, J. (2014). *Use and Preparation of Quench Curves in Liquid Scintillation Counting.* Waltham, MA 02451 USA: PerkinElmer, Inc.

Ultra Quick Host. (2004). *Harbeespoort Dam History and Information on Hartbeespoort Dam*. Retrieved July 18, 2014, from Gauteng Happenings: http://www.gautenghappenings.co.za

UNEP. (2006). *Challenges to International Waters - Regional Assessment in a Global Perspective.* Nairobi, Kenya: United Nations Environment Programme.

United States Department of Energy. (1994). *Primer on Tritium Safe Handling Practices.* Washington, DC: USDOE.

University of Toronto. (n.d.). *Module 6: Radiation Detection and Measurents*. Retrieved August 19, 2015, from University of Toronto, Environmental Health and Safety: http://www.ehs.utoronto.ca

University of Toronto. (n.d.). *Modulle 6: Radiation Detection and Measurents*. Retrieved August 19, 2015, from University of Toronto, Environmental Health and Safety: http://www.ehs.utoronto.ca

University of Wisconsin - Milwaukee. (1998). *Liquid Scintillation Counting.* Environmental Health, Safety and Risk Management. USA: Radiation Safety Program.

USDA. (2006). *Agricultural Resources and Environmental Indicators, 2006 Edition .* Washington D.C.: Economic Research Service.

Varlam, C., Stefanescu, I., Duliu, O. G., Faurescu, I., & Popescu, I. (2009). Applying direct liquid scintillation counting to low level tritium measurement. *Applied Radiation and Isotopes , 67*, 812-816.

Varlam, C., Stefanescu, I., Varlam, M., Popescu, I., & Faurescu, I. (2007). Applying the Direct Absorption Method and LSC for 14C Concentartion Measurement in Aqueous Samples. *Radiocarbon , 49* (2), 281-289.

Vartti, V. (2009). Optimizing the Counting for Carbon-14 for the Sample Oxidizer-Liquid Scintillation Counter Method. *Advances in Liquid Scintillation Spectrometry* , 293-298.

Welman, C., Kruger, F., & Mitchell, B. (2005). *Research Methodology.* Cape Town: Oxford City Press.

WHO. (2011). *Guidelines for Drinking-Water Quality.* World Health Organization. Geneva, Switzerland: WHO.

WHO. (1958). *International Standards for Drinking-Water.* Geneva: WHO.

World Weather Online. (2014). *Zagreb Monthly Climate Average, Croatia*. Retrieved January 23, 2016, from World Weather Online: http://www.worldweatheronline.com

Yankovich, T. L., Koarashi, J., Kim, S. B., & Davis, P. A. (2008). International study on the validation of models for the environmental transfer of tritium of carbon-14. (IAEA, Ed.) *Applied Radiation and Isotopes* (66), 1726-1729.

Yim, M., & Caron, F. (2006). Life cycle and management of carbon-14 from nuclear power generation. *Progress in Nuclear Energy* , 2-36.

Zinsser Analytic. (2015). *Liquid Scintillation.* Frankfurt, Germany: Zinsser Analytic GMBH.

6.2. Appendices and annexure

6.2.1. Appendices

Appendix 1A: Quench standards for ^{14}C

Carbon-14 quench standards in Oxysolve-C						
Ampoule received		37000	Bq in	5	grams	
		7400	Bq/g			
Transferred		4.9446	grams to	50.0101	grams	
Activity concentration in RadioAnalysis stock solution =					731.6530061	Bq/g
Standards	Mass (g)	Activity (Bq/g)	Activity (DPM)	CPM	QIP	Efficiency
1	0.2211	161.7684796	9706.108776	4538.737	638.31	0.46761654
2	0.2271	166.1583977	9969.503862	3994.516	608.34	0.400673499
3	0.222	162.4269674	9745.618044	2952.863	578.9	0.302993919
4	0.2169	158.695537	9521.73222	2118.833	554.3	0.222526002
5	0.2121	155.1836026	9311.016156	1483.52	531.97	0.159329548
6	0.2059	150.647354	9038.84124	1014.989	508.73	0.112291938
			*60 to convert activity Bq/g to dpm			

Appendix 1B: Quench standards for ^{3}H

Tritium quench standards prepared in Oxysolve-T						
Activity concentration in RadioAnalysis stock solution					994.85	Bq/g
Reference date					01-Nov-02	
DPM: Activity on measurement date (22 May 2015)					482.657755	
* Tritium requires measurement date for decay correction due to its short half life						
Standards	Mass	Activity (Bq/g)	Activity (DPM)	CPM	QIP	Efficiency
1	0.5062	244.3213555	14659.28133	6683.859	845.5	0.4559472
2	0.5125	247.3620993	14841.72596	6674.524	841.42	0.4497135
3	0.5176	249.8236539	14989.41923	6618.663	837.35	0.4415557
4	0.498	240.3635619	14421.81371	6284.124	835.61	0.4357374
5	0.5066	244.5144186	14670.86512	6211.495	831.75	0.4233898
6	0.5153	248.7135411	14922.81247	6270.269	829.67	0.4201801

Appendix 2A

^{14}C: data - Sample Oxidiser Measurements												
Sample	*Counting time (sec)*	*SQP*	*CPM*	*Average*	volume combusted (mL)	Efficiency	Gross count rate (Sample - Ra)	Nett to count rate (Ra-Rb)	Activity Value (Bq/L)	DL (CPM)	MDA (Bq/L)	uncertainty (Bq/ sample)
Bl before A	1800	635.84	13.843			0.4680717	415.29	317.66684				
Bl before B	1800	642.42	7.603	10.723		0.4878787	228.09	130.46684				
Total A	1800	645.63	10907.952		0.5	0.4975762	327238.56	327140.94	760448.8	61.54307	143.0587	242.7422788
Total B	1800	643.36	10907.11	10907.5	0.5	0.4907161	327213.3	327115.68	771020.1	61.54307	145.0586	246.1262495
Bl after Total A	1800	636.27	3.785			0.4693631	113.55	15.926838		61.54307		
Bl after Total B	1800	617.38	2.319	3.052		0.4130153	69.57	-28.053162		61.54307		
Combusted Activity A	1800	639.06	10453.061		0.5	0.4777525	313591.83	313494.21	758964	61.54307	148.9947	247.4853567
Combusted Activity B	1800	636.04	3315.864		0.5	0.4686723	99475.92	99378.297	245254.5	61.54307	151.8814	142.0437624
Combusted Activity C	1800	638.38	10503.466	10478.3	0.5	0.4757062	315103.98	315006.36	765905.5	61.54307	149.6356	249.1486591
Bl post combusted A	1800	642.93	14.314			0.4894179	13215.6	13117.977		61.54307		
Bl post combusted B	1800	643.1	14.317	14.3155		0.4899311	429.48	331.85684		61.54307		
Q1 P1 A	1800	641.75	16.639		18.8679245	0.4858575	499.17	401.54684	25.3319	61.54307	3.882494	0.232330204
Q1 P1 B	1800	646.07	27.481	22.06	18.8679245	0.4989072	824.43	726.80684	44.65188	61.54307	3.780941	0.30349953
Q1 P2 A	1800	644.59	55.849		21.2765957	0.4944318	1675.47	1577.8468	86.7403	61.54307	3.383259	0.399356728
Q1 P2 B	1800	651.43	16.877	36.363	21.2765957	0.5151559	506.31	408.68684	21.56326	61.54307	3.247154	0.196008682
Q1 P3 A	1800	646.62	46.37		29.4117647	0.5005716	1391.1	1293.4768	50.80846	61.54307	2.417444	0.258458027
Q1 P3 B	1800	654.33	23.492	34.931	29.4117647	0.5239737	704.76	607.13684	22.78351	61.54307	2.309474	0.169557426
Q1 P4 A	1800	649.24	35.425		18.8679245	0.5085093	1062.75	965.12684	58.17361	61.54307	3.709546	0.342823377
Q1 P4 B	1800	632.49	12.343	23.884	18.8679245	0.4580244	370.29	272.66684	18.2467	61.54307	4.118424	0.203711676
Q1 P5 A	1800	651.58	25.776		29.4117647	0.5156116	773.28	675.65684	25.766	61.54307	2.346929	0.181690216
Q1 P5 B	1800	648.14	21.208	23.492	29.4117647	0.5051748	636.24	538.61684	20.96437	61.54307	2.395416	0.165737908
Bl post Q1 A	1800	638.58	7.637			0.4763079	229.11	131.48684				
Bl post Q1 B	1800	645.25	3.035	5.336		0.496427	91.05	-6.5731622				
Average blank			160.08	5.336								
			97.623162									
			12.652273									

Appendix 2B

^{3}H: data - Sample Oxidiser Measurements

Sample	Counting time (sec)	SQP	CPM	Average	volume combusted (mL)	Efficiency	Gross count rate (Sample - Ra)	Nett to count rate (Ra-Rb)	Activity Value (Bq/L)	DL (CPM)	MDA (Bq/L)	uncertainty (Bq/ sample)
Bl before A	1800	863.09	4.328			0.4648897	129.84	117.53634				
Bl before B	1800	857.17	3.169	3.7485		0.4658839	95.07	82.766342				
Total Activity A	1800	854.08	301925.66		0.5	0.4648373	9057769.8	9057757.5	22206045	44.89193	110.0573	1347.101486
Total Activity B	1800	846.56	294986.16	298456	0.5	0.4578034	8849584.7	8849572.4	22028999	44.89193	111.7483	1351.988713
Bl post total A	1800	854.81	3.305			0.4651814	99.15	86.846342		44.89193		
Bl post total B	1800	854.44	2.862	3.0835		0.4650145	85.86	73.556342		44.89193		
Combusted Activity A	1800	846.27	290995.49		0.5	0.4574048	15313374	15313361	38152353	44.89193	111.8457	1780.022422
Combusted Activity B	1800	847.87	295168.79	290995	0.5	0.4594862	8855063.7	8855051.4	21961911	44.89193	111.339	1347.454226
Combusted Activity C	1800	847.62	286822.12		0.5	0.4591799	8604663.5	8604651.1	21355112	44.89193	111.4133	1329.152035
Bl post combusted A	1800	862.14	174.717			0.4653147	5241.51	5229.2063		44.89193		
Bl post combusted B	1800	870.29	97.685	136.201		0.4583684	2930.55	2918.2463		44.89193		
Q1 P1 A	1800	854.47	11.041		18.8679245	0.4650286	331.23	318.92634	20.71133	44.89193	2.915319	0.212648296
Q1 P1 B	1800	850.83	12.676	11.8585	18.8679245	0.4625777	380.28	367.97634	24.02329	44.89193	2.930765	0.229495733
Q1 P2 A	1800	851.23	13.017		21.2765957	0.4629199	390.51	378.20634	21.87974	44.89193	2.597059	0.206151469
Q1 P2 B	1800	856.69	11.347	12.182	21.2765957	0.4657918	340.41	328.10634	18.86436	44.89193	2.581047	0.190933454
Q1 P3 A	1800	851.58	12.608		29.4117647	0.4632046	378.24	365.93634	15.30499	44.89193	1.877569	0.146619353
Q1 P3 B	1800	854.5	12.99	12.799	29.4117647	0.4650426	389.7	377.39634	15.72191	44.89193	1.870148	0.148292247
Q1 P4 A	1800	855.97	11.211		18.8679245	0.465605	336.33	324.02634	21.01648	44.89193	2.911709	0.214062084
Q1 P4 B	1800	843.84	10.053	10.632	18.8679245	0.4536929	301.59	289.28634	19.25588	44.89193	2.988159	0.207676783
Q1 P5 A	1800	855.92	11.859		29.4117647	0.4655898	355.77	343.46634	14.29161	44.89193	1.86795	0.141353203
Q1 P5 B	1800	854.34	11.518	11.6885	29.4117647	0.4649667	345.54	333.23634	13.88452	44.89193	1.870453	0.139435768
Bl post Q1	1800	865.57	3.033			0.4633017	90.99	78.686342				
Bl post Q1	1800	855.14	2.453	2.743		0.4653173	73.59	61.286342				
Average Blank			82.29	2.743								
			12.303658									
			9.0713836									

Appendix 3A

^{14}C: Data - Sample Oxidiser Measurements												
Sample	Counting time (sec)	SQP	CPM	Average	volume combusted (mL)	Efficiency	Gross count rate (Sample - Ra)	Nett to count rate (Ra-Rb)	Activity Value (Bq/L)	DL (CPM)	MDA (Bq/L)	uncertainty (Bq/ sample)
Bl before A	1800	645.03	8.081			0.4957618	242.43	198.3327144				
Bl before B	1800	640.38	4.535	6.308		0.4817277	136.05	91.95271437				
Total A	1800	659.47	11891.67		0.5	0.5396483	356750.1	356706.0027	757253.8	52.92354	112.351775	231.487736
Total B	1800	652.16	11166.01	11528.84	0.5	0.5173738	334980.27	334936.1727	741650.8	52.92354	117.188848	233.970071
Bl post Total A	1800	634.61	2.966			0.4643798	88.98	44.88271437				
Bl post Total B	1800	654.88	6.887	4.9265		0.5256482	206.61	162.5127144				
Combusted Activity A	1800	643.47	3249.681		0.5	0.4910482	97490.43	97446.33271	227343.8	52.92354	123.47146	132.968409
Combusted Activity B	1800	650.93	11506.58		0.5	0.5136375	345197.43	345153.3327	769834.2	52.92354	118.04131	239.23955
Combusted Activity C	1800	649.11	10856.48	11181.53	0.5	0.5081151	325694.37	325650.2727	734228.4	52.92354	119.324234	234.907804
Bl post combusted A	1800	649.85	38.87			0.5103596	1166.1	1122.002714				
Bl post combusted B	1800	650.76	13.195	26.0325		0.5131214	395.85	351.7527144				
Q2P1 A (tip broke)	1800	643.48	13.741		35.71429	0.4910784	412.23	368.1327144	12.02329	52.92354	1.72849414	0.11501153
Q2 P1 B	1800	646.89	25.027		35.71429	0.5013889	750.81	706.7127144	22.60675	52.92354	1.6929498	0.15568511
Q2 P1 C	1800	648.64	27.993	22.25367	35.71429	0.5066902	839.79	795.6927144	25.18679	52.92354	1.6752372	0.16341716
Bl post Q2 P1	1800	635.85	6.274			0.4681017	188.22	144.1227144				
Q2 P2 A (tip broke)	1800	647.12	6.512		22.72727	0.5020852	195.36	151.2627144	7.593097	52.92354	2.65665999	0.11415684
Q2 P2 B	1800	644.88	10.638		22.72727	0.4953084	319.14	275.0427144	13.99552	52.92354	2.69300881	0.15515852
Q2 P2 C	1800	656.18	13.741	10.297	22.72727	0.5296086	412.23	368.1327144	17.51918	52.92354	2.51859523	0.16758372
Bl post Q2 P2	1800	644.85	4.194			0.4952177	125.82	81.72271437				
Q2 P3 A	1800	652.82	10.229		28.02703	0.5193801	306.87	262.7727144	10.34022	52.92354	2.08256435	0.1173188
Q2 P3 B	1800	630.87	6.99		28.02703	0.4531746	209.7	165.6027144	7.468558	52.92354	2.38681186	0.10719643
Q2 P3 C	1800	647.1	9.274	8.831	28.02703	0.5020247	278.22	234.1227144	9.531326	52.92354	2.15456028	0.11466912
Bl post Q2 P3	1800	653.05	3.512			0.5200795	105.36	61.26271437				
Q2 P4 A	1800	641.13	2.796		32.25	0.483988	83.88	39.78271437	1.459963	52.92354	1.94221117	0.04427689
Q2 P4 B	1800	653.09	5.769		32.25	0.5202011	173.07	128.9727144	4.403609	52.92354	1.80700674	0.07185333
Q2 P4 C	1800	644.26	3.853	4.139333	32.25	0.4934346	115.59	71.49271437	2.573442	52.92354	1.90502841	0.05705835
Bl post Q2 P4	1800	655.02	2.83			0.5260745	84.9	40.80271437				
Q2 P5 A	1800	643.28	2.353		35.71429	0.4904745	70.59	26.49271437	0.866323	52.92354	1.73062243	0.03290672
Q2 P5 B	1800	652.82	5.285		35.71429	0.5193801	158.55	114.4527144	3.534359	52.92354	1.63430645	0.0613323
Q2 P5 C	1800	652.32	7.024	4.887333	35.71429	0.5178601	210.72	166.6227144	5.160498	52.92354	1.63910329	0.07383654
Bl post Q2 P5	1800	645.27	2.625			0.4964875	78.75	34.65271437				
Average blank			116.61									
			44.09729									
			10.79861									

Appendix 3B

^{3}H: data - Sample Oxidiser Measurements												
Sample	Counting time (sec)	SQP	CPM	Average	volume combusted (mL)	Efficiency	Gross count rate (Sample - Ra)	Nett to count rate (Ra-Rb)	Activity Value (Bq/L)	DL (CPM)	MDA (Bq/L)	uncertainty (Bq/ sample)
Bl before A	1800	863.26	4.907			0.4648029	147.21	95.88283789				
Bl before B	1800	859.45	3.237	4.072		0.4659677	97.11	45.78283789				
Total Activity A	1800	859.87	61191.01		0.1	0.4659193	1871561.9	1871510.613	23354759	55.61221	693.990019	3116.8731
Total Activity B	1800	855.35	61190.76	61190.88	0.1	0.4653974	1835722.7	1835671.383	22933208	55.61221	694.768312	3090.34688
Bl post total A	1800	856.08	3.68			0.4656373	110.4	59.07283789		55.61221		
Bl post total B	1800	867.79	3.237	3.4585		0.4612935	97.11	45.78283789		55.61221		
Combusted Activity A	1800	854.75	59202.08		0.1	0.4651554	1776062.5	1776011.163	22199413	55.61221	695.129819	3041.29494
Combusted Activity B	1800	863.93	57734.25		0.1	0.4644293	1732027.5	1731976.173	21682840	55.61221	696.216613	3008.05053
Combusted Activity C	1800	863.57	58463.97	58466.77	0.1	0.4646363	1675679.1	1675627.743	20968060	55.61221	695.9064	2957.39551
Bl post combusted A	1800	873.22	11.858			0.4540455	355.74	304.4128379		55.61221		
Bl post combusted B	1800	867.12	6.475	9.1665		0.461958	194.25	142.9228379		55.61221		
Q2 P1 A	1800	847.19	22.184		35.71429	0.4586367	665.52	614.1928379	21.80157	55.61221	1.97402733	0.16117393
Q2 P1 B	1800	846.35	22.593		35.71429	0.4575157	677.79	626.4628379	22.2916	55.61221	1.97886441	0.1631636
Q2 P1 C	1800	844.28	21.025	21.934	35.71429	0.4544143	630.75	579.4228379	20.75848	55.61221	1.99237022	0.15803307
Bl post Q2 P1	1800	856.7	2.864			0.465794	85.92	34.59283789		55.61221		
Q2 P2 A	1800	848.11	19.389		22.72727	0.4597735	581.67	530.3428379	29.50932	55.61221	3.09437311	0.23489818
Q2 P2 B	1800	845.35	17.686		22.72727	0.4560776	530.58	479.2528379	26.88268	55.61221	3.11944928	0.22520375
Q2 P2 C	1800	843.13	19.117	18.73067	22.72727	0.452483	573.51	522.1828379	29.52343	55.61221	3.14423024	0.2368545
Bl post Q2 P2	1800	858.95	2.556			0.4659994	76.68	25.35283789		55.61221		
Q2 P3 A	1800	845.02	3.135		28.02703	0.4555783	94.05	42.72283789	1.945422	55.61221	2.5323509	0.05701827
Q2 P3 B	1800	840.06	3.374		28.02703	0.446599	101.22	49.89283789	2.317594	55.61221	2.58326655	0.06244061
Q2 P3 C	1800	843.57	2.862	3.123667	28.02703	0.4532395	85.86	34.53283789	1.580598	55.61221	2.54541837	0.0520845
Bl post Q2 P3	1800	871.99	4.6			0.4559778	138	86.67283789		55.61221		
Q2 P4 A	1800	851.52	3.817		32.25	0.4631568	114.51	63.18283789	2.459434	55.61221	2.16474241	0.05838731
Q2 P4 B	1800	855.91	5.626		32.25	0.4655868	168.78	117.4528379	4.548069	55.61221	2.15344412	0.0780132
Q2 P4 C	1800	847.99	4.6	4.681	32.25	0.4596307	138	86.67283789	3.399681	55.61221	2.18134955	0.06831007
Bl post Q2 P4	1800	869.99	4.737			0.4587565	142.11	90.78283789		55.61221		
Q2 P5 A	1800	855.46	18.776		35.71429	0.4654374	563.28	511.9528379	17.90691	55.61221	1.94518417	0.14509995
Q2 P5 B	1800	855.22	18.538		35.71429	0.4653484	556.14	504.8128379	17.66054	55.61221	1.94555613	0.14412064
Q2 P5 C	1800	851.14	19.696	19.00333	35.71429	0.4628445	590.88	539.5528379	18.97801	55.61221	1.95608123	0.14976233
Bl post Q2 P5	1800	867.01	6.815			0.4620622	204.45	153.1228379				
Average Blank			129.432									
			51.32716									
			11.37682									

Appendix 4A

^{14}C: data - Sample Oxidiser Measurements												
Sample	Counting time (sec)	SQP	CPM	Average	volume combusted (mL)	Efficiency	Gross count rate (Sample - Ra)	Nett to count rate (Ra-Rb)	Activity Value (Bq/L)	DL (CPM)	MDA (Bq/L)	uncertainty (Bq/ sample)
Bl before A	1800	657.26	9.99			0.5329017						
Bl before B	1800	649.85	4.228	7.109		0.5103596						
Total A	1800	657.53	12071.05		0.5	0.5337253	362131.35	362118.86	829657.2	41.03063	319.003388	251.717753
Total B	1800	653.75	11967.58	12019.31	0.5	0.5222087	359027.28	359014.79	840685.6	41.03063	333.228978	256.164055
Bl post Total A	1800	655.46	4.296			0.5274147				41.03063		
Bl post Total B	1800	637.33	3.137	3.7165		0.4725484				41.03063		
Combusted A	1800	640.47	11034.4		0.5	0.4819988	331031.97	331019.48	839794.4	41.03063	391.146091	266.49375
Combusted B	1800	641.99	10836.77		0.5	0.4865814	325103.16	325090.67	816985.6	41.03063	383.813276	261.609211
Combusted C	1800	640.13	10892.53	10921.23	0.5	0.4809745	326775.84	326763.35	830762.1	41.03063	392.813933	265.338876
Bl post combusted A	1800	644.55	11.52			0.4943109				41.03063		
Bl post combusted B	1800	637.58	4.908	8.214		0.4733001				41.03063		
Q3P1 A	1800	652.87	9.751		33.3333333	0.5195321	292.53	280.04365	9.887124	41.03063	0.07575106	0.10830407
Q3 P1 B	1800	646.06	7.876		33.3333333	0.4988769	236.28	223.79365	8.228316	41.03063	0.0821536	0.10092807
Q3 P1 C	1800	649.37	5.796	7.807667	33.3333333	0.5089036	173.88	161.39365	5.817114	41.03063	0.07894825	0.08418378
Bl post Q3 P1	1800	654.34	2.216			0.5240042				41.03063		
Q3 P2 A	1800	654.4	8.251		26	0.5241868	247.53	235.04365	10.54446	41.03063	0.12230721	0.12617433
Q3 P2 B	1800	655.42	4.057		26	0.5272928	121.71	109.22365	4.871098	41.03063	0.12087056	0.08597309
Q3 P2 C	1800	640.63	3.512	5.273333	26	0.482481	105.36	92.873648	4.526623	41.03063	0.14436566	0.08679545
Bl post Q3 P2	1800	653.05	2.694			0.5200795				41.03063		
Q3 P3 A	1800	647.84	4.978		22.2222222	0.5042659	149.34	136.85365	7.466975	41.03063	0.18091594	0.11749476
Q3 P3 B	1800	644.13	3.75		22.2222222	0.4930418	112.5	100.01365	5.581147	41.03063	0.18924679	0.10303706
Q3 P3 C	1800	647.56	4.194	4.307333	22.2222222	0.5034177	125.82	113.33365	6.194101	41.03063	0.18152607	0.10728349
Bl post Q3 P3	1800	640.51	2.284			0.4821194				41.03063		
Q3 P4 A	1800	654.66	4.398		27.7777778	0.5249783	131.94	119.45365	5.008364	41.03063	0.10683	0.08445246
Q3 P4 B	1800	642.51	4.705		27.7777778	0.4881503	141.15	128.66365	5.801499	41.03063	0.12355744	0.09419743
Q3 P4 C	1800	641.86	3.103	4.068667	27.7777778	0.4861892	93.09	80.603648	3.649112	41.03063	0.12455618	0.07524262
Bl post Q3 P4	1800	644.18	2.523			0.4931929				41.03063		
Q3 P5 A	1800	650.98	4.33		29.4117647	0.5137893	129.9	117.41365	4.750593	41.03063	0.09948524	0.08081179
Q3 P5 B	1800	645.58	3.205		29.4117647	0.4974249	96.15	83.663648	3.49642	41.03063	0.10613868	0.07072811
Q3 P5 C	1800	654.21	3.17	3.568333	29.4117647	0.5236085	95.1	82.613648	3.279891	41.03063	0.09578895	0.0667795
Bl post Q3 P5	1800	640.42	1.602			0.4818482						
Average Blank			67.914	2.2638								
			12.48635									
			8.240995									

Appendix 4B

^{3}H: data - Sample Oxidiser Measurements

Sample	Counting time (sec)	SQP	CPM	Average	volume combusted (mL)	Efficiency	Gross count rate (Sample - Ra)	Nett to count rate (Ra-Rb)	Activity Value (Bq/L)	DL (CPM)	MDA (Bq/L)	uncertainty (Bq/ sample)
Bl before A	1800	870.37	3.987			0.4582632						
Bl before B	1800	871.65	2.896	3.4415		0.456482						
Total Activity A	1800	858.47	59303.88		0.1	0.4660033	1779116.46	1779093	21788948	55.86298	684.166325	2982.47345
Total Activity B	1800	853.69	59290.52	59297.2	0.1	0.4646288	1778715.6	1778692.2	21848481	55.86298	686.190237	2990.95924
Bl post total A	1800	868.23	3.68			0.4608296				55.86298		
Bl post total B	1800	860.32	4.26	3.97		0.4658455				55.86298		
Combusted Activity A	1800	861.18	57721.16		0.1	0.4656411	1731634.89	1731611.5	21223926	55.86298	684.698466	2944.69386
Combusted Activity B	1800	855.16	55396.29		0.1	0.4653252	1661888.58	1661865.1	20382895	55.86298	685.163426	2886.73984
Combusted Activity C	1800	857.77	60046.02	57721.16	0.1	0.4659626	1540596.9	1540573.5	18869393	55.86298	684.226054	2775.59707
Bl post combusted A	1800	863.36	30.04			0.4647503				55.86298		
Bl post combusted B	1800	861.3	28.038	29.039		0.465606				55.86298		
Q3 P1 A	1800	852.86	17.242		33.3333333	0.4641283	517.26	493.8274	18.21734	55.86298	2.06079062	0.15001335
Q3 P1 B	1800	845.38	17.345		33.3333333	0.4561224	520.35	496.9174	18.65309	55.86298	2.09696219	0.15312109
Q3 P1 C	1800	847.92	16.286	16.95767	33.3333333	0.4595466	488.58	465.1474	17.33041	55.86298	2.08133715	0.14706431
Bl post Q3 P1	1800	866.26	4.43			0.4627369				55.86298		
Q3 P2 A	1800	850.86	3.067		26	0.462604	92.01	68.577402	3.254055	55.86298	2.65074499	0.07291656
Q3 P2 B	1800	851.35	4.157		26	0.4630191	124.71	101.2774	4.801389	55.86298	2.64836878	0.08807453
Q3 P2 C	1800	844.75	6.168	4.464	26	0.4551607	185.04	161.6074	7.793808	55.86298	2.69409286	0.11271434
Bl post Q3 P2	1800	866.5	3.885			0.4625279				55.86298		
Q3 P3 A	1800	844.69	15.641		22.2222222	0.4550668	469.23	445.7974	25.15947	55.86298	3.15273913	0.2181082
Q3 P3 B	1800	842.59	17.038		22.2222222	0.4515249	511.14	487.7074	27.74066	55.86298	3.17747049	0.22986989
Q3 P3 C	1800	847.28	17.515	16.73133	22.2222222	0.4587521	525.45	502.0174	28.10475	55.86298	3.12741204	0.22952859
Bl post Q3 P3	1800	859.92	3.442			0.4659123				55.86298		
Q3 P4 A	1800	853.48	18.746		27.7777778	0.4645095	562.38	538.9474	23.83861	55.86298	2.47091936	0.18786992
Q3 P4 B	1800	845.1	17.246		27.7777778	0.4557005	517.38	493.9474	22.27052	55.86298	2.5186842	0.18336747
Q3 P4 C	1800	848.03	17.246	17.746	27.7777778	0.4596785	517.38	493.9474	22.07779	55.86298	2.49688792	0.18178064
Bl post Q3 P4	1800	861.93	5.521			0.465395				55.86298		
Q3 P5 A	1800	847.42	18.507		29.4117647	0.4589299	555.21	531.7774	22.4848	55.86298	2.36201853	0.17839635
Q3 P5 B	1800	847.57	19.564		29.4117647	0.4591178	586.92	563.4874	23.81582	55.86298	2.36105153	0.18354117
Q3 P5 C	1800	850.21	19.359	19.14333	29.4117647	0.4620118	580.77	557.3374	23.40834	55.86298	2.34626246	0.18139746
Bl post Q3 P5	1800	862.32	4.499			0.465242						
Average Blank			130.662	4.3554								
			23.4326									
			11.43075									

Appendix 5A

^{14}C: data - Sample Oxidiser Measurements												
Sample	Counting time (sec)	SQP	CPM	Average	volume combusted (mL)	Efficiency	Gross count rate (Sample - Ra)	Nett to count rate (Ra-Rb)	Activity Value (Bq/L)	DL (CPM)	MDA (Bq/L)	uncertainty (Bq/ sample)
Bl before A	1800	653.86	3.75			0.522543387						
Bl before B	1800	653.89	2.898	3.324		0.522634672						
Total A	1800	650.38	10718.34		0.5	0.511967869	321550.32	321482.364	667583.3	41.04247	85.22792	214.965029
Total B	1800	650.84	10919.35	10818.85	0.5	0.513364245	327580.5	327512.544	678255.6	41.04247	84.99609	216.381569
Bl post Total A	1800	657.29	4.875			0.532993193						
Bl post Total B	1800	644.13	2.489	3.682		0.493041791						
Combusted A	1800	646.97	11197.8		0.5	0.501631082	335933.91	335865.954	711823.9	41.04247	86.98415	224.248956
Combusted B	1800	662.66	11307.04		0.5	0.549405689	372731.31	372663.354	721131.7	41.04247	79.42028	215.673568
Combusted C	1800	643.91	11416.21	11307.01	0.5	0.492377169	342486.15	342418.194	739349.8	41.04247	88.61896	230.681283
Bl post combusted A	1800	654.61	47.135			0.524826106						
Bl post combusted B	1800	641.89	11.213	29.174		0.486279735						
Q4P1 A	1800	649.36	4.125		20.83333333	0.508873229	123.75	55.794	2.797565	41.04247	2.057909	0.06975375
Q4 P1 B	1800	646.99	4.807		20.83333333	0.501691633	144.21	76.254	3.878181	41.04247	2.087368	0.08227971
Q4 P1 C	1800	654.79	4.466	4.466	20.83333333	0.525374143	133.98	66.024	3.206531	41.04247	1.993275	0.07327384
Bl post Q4 P1	1800	641.54	2.046			0.485224167				41.04247		
Q4 P2 A	1800	647.42	5.455		55.55555556	0.5029937	163.65	95.694	1.820353	41.04247	0.780737	0.03437423
Q4 P2 B	1800	647.57	3.205		55.55555556	0.503448005	96.15	28.194	0.535841	41.04247	0.780032	0.01915039
Q4 P2 C	1800	650.13	4.023	4.227667	55.55555556	0.511209166	120.69	52.734	0.987019	41.04247	0.76819	0.02534268
Bl post Q4 P2	1800	642.43	2.046			0.487908857						
Q4 P3 A	1800	652.44	3.784		24.3902439	0.518224852	113.52	45.564	1.916234	41.04247	1.726077	0.05310221
Q4 P3 B	1800	652.57	3.409		24.3902439	0.518620025	102.27	34.314	1.442006	41.04247	1.724762	0.04640364
Q4 P3 C	1800	643.76	1.943	3.045333	24.3902439	0.491924079	58.29	-9.666	-0.42825	41.04247	1.818362	#NUM!
Bl post Q4 P3	1800	643.48	2.25			0.491078443						
Q4 P4 A	1800	643.54	2.387		22.22222222	0.491259636	71.61	3.654	0.177923	41.04247	1.998463	0.02162885
Q4 P4 B	1800	649.11	2.591		22.22222222	0.50811509	77.73	9.774	0.460133	41.04247	1.932169	0.02982288
Q4 P4 C	1800	643.82	2.523	2.500333	22.22222222	0.492105309	75.69	7.734	0.375941	41.04247	1.995028	0.02806322
Bl post Q4 P4	1800	642.75	2.12			0.488874568						
Q4 P5 A	1800	642.79	4.398		16.66666667	0.488995298	131.94	63.984	4.173294	41.04247	2.676955	0.09692533
Q4 P5 B	1800	642.48	2.796		16.66666667	0.488059735	83.88	15.924	1.040618	41.04247	2.682087	0.0508845
Q4 P5 C	1800	667.81	6.307	4.500333	16.66666667	0.565205759	189.21	121.254	6.842295	41.04247	2.316004	0.1145018
Bl post Q4 P5	1800	649.23	2.864			0.508478979						
Average of Bl post		Average Bl co	67.956	8.243543								
		STDEV Bl	10.34862									

Appendix 5B

^{3}H: data - Sample Oxidiser Measurements												
Sample	Counting time (sec)	SQP	CPM	Average	volume combusted (mL)	Efficiency	Gross count rate (Sample - Ra)	Nett to count rate (Ra-Rb)	Activity Value (Bq/L)	DL (CPM)	MDA (Bq/L)	uncertainty (Bq/ sample)
Bl before A	1800	863.36	4.566			0.464750338						
Bl before B	1800	865.82	3.135	3.8505		0.463103245						
Total Activity A	1800	862.3	57955.05		0.1	0.465250242	1738651.38	1738560.8	2321006	46.96618	627.0058	3213.81608
Total Activity B	1800	856.74	57027.84	57027.84	0.1	0.465802578	1710835.23	1710744.65	2281163	46.96618	626.2623	3184.22245
Bl post total A	1800	867.44	3.646			0.461646893						
Bl post total B	1800	863.4	3.408	3.527		0.464729						
Combusted Activity A	1800	859.27	51008.98		0.1	0.465982327	1530251.25	1530160.67	2039579	46.96618	626.0207	3010.31408
Combusted Activity B	1800	864.46	49546.68		0.1	0.464097959	1397868.39	1397777.81	1870688	46.96618	628.5625	2888.83136
Combusted Activity C	1800	864.73	52469.49	51008.38	0.1	0.463917029	1394074.95	1393984.37	1866339	46.96618	628.8077	2886.03383
Bl post combusted A	1800	866.8	30.642			0.462257512						
Bl post combusted B	1800	866.82	28.055	29.3485		0.462239127						
Q4 P1 A	1800	845.49	18.571		20.83333333	0.456285677	557.13	466.548	30.48412	46.96618	3.068757	0.25850305
Q4 P1 B	1800	846.09	19.048		20.83333333	0.457152578	571.44	480.858	31.35955	46.96618	3.062938	0.2619148
Q4 P1 C	1800	847.25	19.593	19.07067	20.83333333	0.45871378	587.79	497.208	32.31547	46.96618	3.052514	0.26539669
Bl post Q4 P1	1800	859.04	3.033			0.465995734						
Q4 P2 A	1800	843.04	20.684		55.55555556	0.452325625	620.52	529.938	13.09843	46.96618	1.160859	0.10417892
Q4 P2 B	1800	844.54	20.377		55.55555556	0.454830279	611.31	520.728	12.79991	46.96618	1.154466	0.10270613
Q4 P2 C	1800	846.1	19.491	20.184	55.55555556	0.457166683	584.73	494.148	12.08448	46.96618	1.148566	0.09955465
Bl post Q4 P2	1800	858.15	2.828			0.465991558				46.96618		
Q4 P3 A	1800	849.77	19.082		24.3902439	0.461583868	572.46	481.878	26.5854	46.96618	2.591143	0.22180456
Q4 P3 B	1800	843.41	22.422		24.3902439	0.452966951	672.66	582.078	32.72438	46.96618	2.640435	0.24828114
Q4 P3 C	1800	847.37	20.854	20.786	24.3902439	0.458866646	625.62	535.038	29.69306	46.96618	2.606487	0.23503037
Bl post Q4 P3	1800	866.06	3.033			0.462906114						
Q4 P4 A	1800	845.69	17.791		22.22222222	0.456579142	533.73	443.148	27.12802	46.96618	2.875111	0.23607917
Q4 P4 B	1800	847.47	18.2		22.22222222	0.458992797	546	455.418	27.73255	46.96618	2.859992	0.23804495
Q4 P4 C	1800	845.41	16.7	17.56367	22.22222222	0.456167031	501	410.418	25.1471	46.96618	2.877708	0.22746041
Bl post Q4 P4	1800	866.49	3.749			0.462536719						
Q4 P5 A	1800	848.65	17.45		16.66666667	0.460396448	523.5	432.918	35.04272	46.96618	3.801697	0.30856287
Q4 P5 B	1800	848.08	17.313		16.66666667	0.459737966	519.39	428.808	34.75975	46.96618	3.807142	0.30754473
Q4 P5 C	1800	850.34	18.54	17.76767	16.66666667	0.462134011	556.2	465.618	37.54793	46.96618	3.787403	0.31872351
Bl post Q4 P5	1800	870.2	2.454			0.458485901						
Average Blank			90.582	3.0194								
			14.143									
			9.517458									

Appendix 6

Quarter 1 data for ^{3}H: - Direct Method Measurements												
Sample	Counting time (sec)	SQP	CPM	Average	Volume (mL)	Efficiency	Gross count rate (Sample - Ra)	Nett to count rate (Ra-Rb)	Activity Value (Bq/L)	Detection Limit (CPM)	MDA (Bq/L)	uncertainty (Bq/ sample)
Bl x 01	1800	789.15	4.396		5	0.3989029	131.88	131.88	36.734086	2.71	0.75484815	0.584008471
Bl x 02	1800	800.39	2.658	3.527	5	0.4175274	79.74	79.74	21.220163	2.71	0.72117683	0.433860351
Cs x 01	1800	796.52	4573.43		0.5	0.4111149	137202.9	137202.9	370815.24	2.71	7.32425698	182.7743722
Cs x 02	1800	780.06	4203.726	4388.578	0.5	0.3838409	126111.78	126111.78	365058.05	2.71	7.84468592	187.6823661
Q1P1 A	1800	797.68	2.59		5	0.413037	77.7	77.7	20.902082	2.71	0.72901729	0.432930735
Q1P1 B	1800	796.76	2.317		5	0.4115126	69.51	69.51	18.768159	2.71	0.7317179	0.410995819
Q1P1 C	1800	795.93	2.045	2.317333	5	0.4101373	61.35	61.35	16.620452	2.71	0.73417154	0.387413644
Q1P2A	1800	792.2	2.113		5	0.4039567	63.39	63.39	17.435862	2.71	0.74540441	0.399827276
Q1P2B	1800	790.76	2.351		5	0.4015706	70.53	70.53	19.515039	2.71	0.74983348	0.424249999
Q1P2C	1800	789.89	1.976	2.146667	5	0.4001291	59.28	59.28	16.461355	2.71	0.75253497	0.390347015
Q1P3 A	1800	796.99	4.055		5	0.4118937	121.65	121.65	32.815912	2.71	0.73104087	0.54321005
Q1P3 B	1800	806.72	2.658		5	0.4280162	79.74	79.74	20.700153	2.71	0.70350406	0.423228405
Q1P3 C	1800	792.87	2.862	3.191667	5	0.4050669	85.86	85.86	23.551666	2.71	0.74336146	0.46405084
Q1P4 A	1800	791.98	2.318		5	0.4035922	69.54	69.54	19.144739	2.71	0.74607769	0.419151937
Q1P4 B	1800	788.89	2.045		5	0.3984721	61.35	61.35	17.107012	2.71	0.75566427	0.398755103
Q1P4 C	1800	791.77	2.726	2.363	5	0.4032442	81.78	81.78	22.533905	2.71	0.74672149	0.454938076
Q1P5 A	1800	794.94	2.828		5	0.4084969	84.84	84.84	23.076473	2.71	0.73711979	0.457412976
Q1P5 B	1800	800.51	3.135		5	0.4177263	94.05	94.05	25.016382	2.71	0.72083355	0.470960488
Q1P5 C	1800	790.43	3.103	3.022	5	0.4010238	93.09	93.09	25.792316	2.71	0.75085589	0.488065591
		Bl Average	105.81	3.527								
		Bl STDEV	36.86855									

Appendix 7

Quarter 2 data for ^{3}H: - Direct Method Measurements

Sample	Counting time (sec)	SQP	CPM	Average	Volume (mL)	Efficiency	Gross count rate (Sample - Ra)	Nett to count rate (Ra-Rb)	Activity Value (Bq/L)	Detection Limit (CPM)	MDA (Bq/L)	uncertainty (Bq/ sample)
Bl x 001	1800	792.75	2.044		5	0.404868	61.32	61.32	16.828528	2.71	0.74372654	0.392359735
Bl x 002	1800	783.84	1.0908	1.5674	5	0.3901043	32.724	32.724	9.3205845	2.71	0.77187337	0.297474217
Cs x 001	1800	788.11	4312.783		0.5	0.3971796	129383.49	129383.49	361950.67	2.71	7.58123256	183.7169945
Cs x 002	1800	783.72	4340.793	4326.788	0.5	0.3899054	130223.79	130223.79	371097.92	2.71	7.72266997	187.7512006
Q2P1 A	1800	792.8	4.089		5	0.4049509	122.67	122.67	33.658402	2.71	0.74357438	0.554834784
Q2P1 B	1800	795.33	5.895		5	0.4091431	176.85	176.85	48.027209	2.71	0.73595553	0.659362417
Q2P1 C	1800	795.75	3.033	4.339	5	0.409839	90.99	90.99	24.668223	2.71	0.73470583	0.472150443
Q2P2A	1800	795.85	2.726		5	0.4100047	81.78	81.78	22.162347	2.71	0.73440891	0.447436667
Q2P2B	1800	799.82	2.965		5	0.416583	88.95	88.95	23.724767	2.71	0.72281189	0.459270286
Q2P2C	1800	797.41	1.671	2.454	5	0.4125896	50.13	50.13	13.500098	2.71	0.72980779	0.34811876
Q2P3 A	1800	800.79	2.453		5	0.4181902	73.59	73.59	19.552505	2.71	0.72003383	0.416133217
Q2P3 B	1800	796.77	2.658		5	0.4115291	79.74	79.74	21.52946	2.71	0.73168844	0.440184137
Q2P3 C	1800	797.3	2.283	2.464667	5	0.4124073	68.49	68.49	18.45263	2.71	0.73013034	0.407084024
Q2P4 A	1800	791.2	1.5		5	0.4022997	45	45	12.428545	2.71	0.74847458	0.338262141
Q2P4 B	1800	792.26	3.305		5	0.4040561	99.15	99.15	27.265189	2.71	0.74522101	0.499921171
Q2P4 C	1800	788.18	2.113	2.306	5	0.3972956	63.39	63.39	17.728193	2.71	0.75790192	0.406530812
Q2P5 A	1800	795.06	1.602		5	0.4086957	48.06	48.06	13.065956	2.71	0.73676116	0.344103183
Q2P5 B	1800	781.08	1.567		5	0.385531	47.01	47.01	13.548413	2.71	0.78102956	0.360771881
Q2P5 C	1800	782.25	1.976	1.715	5	0.3874697	59.28	59.28	16.99918	2.71	0.77712174	0.403100409
		Bl Average	47.022	1.5674								
		Bl STDEV	20.22043									

Appendix 8

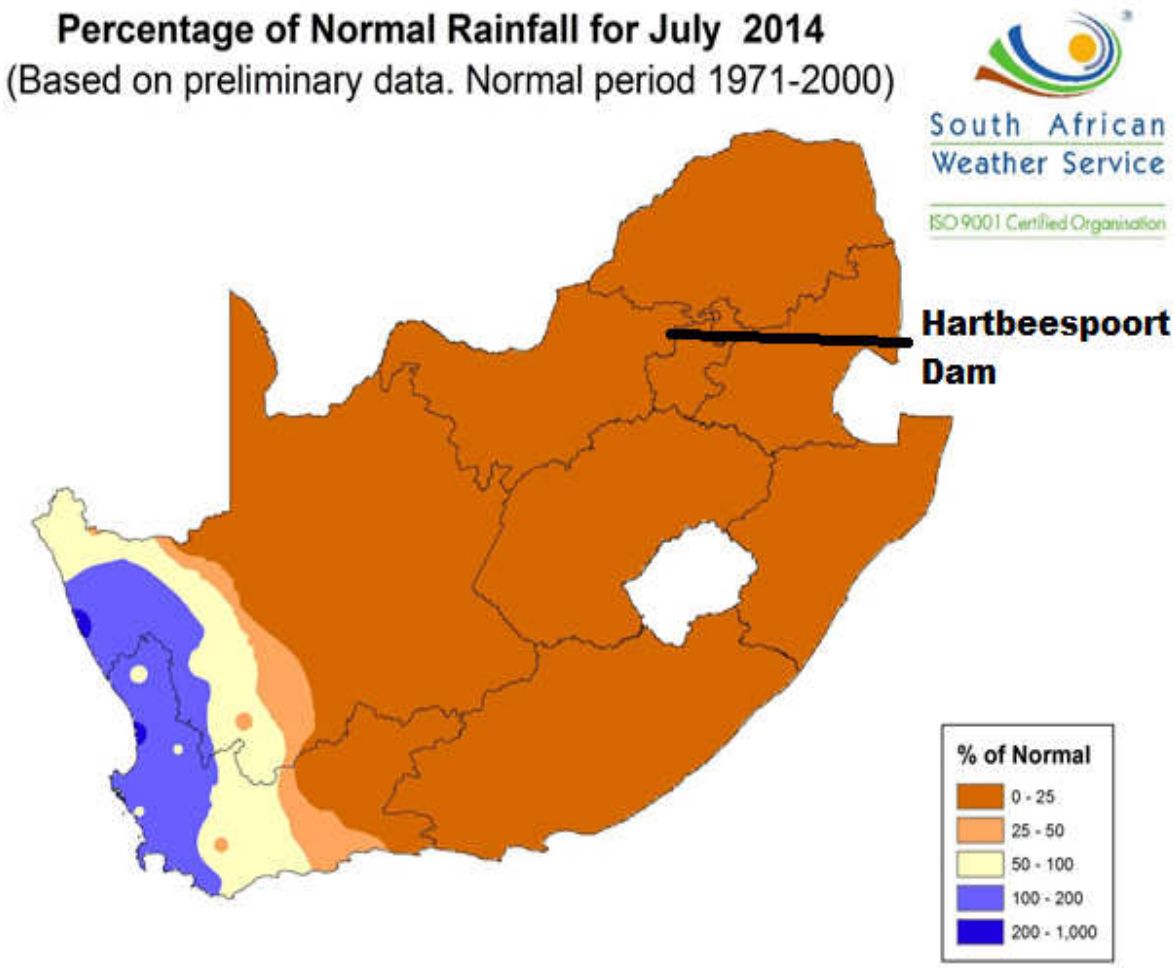
Quarter 3 data for ^{3}H: - Direct Method Measurements												
Sample	*Counting*	*SQP*	*CPM*	*Average*	Volume (mL)	Efficiency	Gross count rate (Sample - Ra)	Nett to count rate (Ra-Rb)	Activity Value (Bq/L)	Detection Limit (CPM)	MDA (Bq/L)	uncertainty (Bq/ sample)
Bl x 01	1800	802.02	1.908		5	0.4202283	57.24	57.24	15.13463	2.71	0.716541686	0.36522572
Bl x 02	1800	797.03	2.08	1.994	5	0.41196	62.4	62.4	16.83011	2.71	0.730923255	0.38898617
Cs x 01	1800	786.33	4342.658		0.5	0.3942302	130279.74	130279.74	367184.6	2.71	7.637951648	185.731441
Cs x 02	1800	785.8	4296.253	4319.456	0.5	0.393352	128887.59	128887.59	364072	2.71	7.655004251	185.148872
Q3P1 A	1800	799.38	2.351		5	0.4158539	70.53	70.53	18.84476	2.71	0.724079126	0.40967839
Q3P1 B	1800	803.86	2.385		5	0.4232772	71.55	71.55	18.78202	2.71	0.71138045	0.40539354
Q3P1 C	1800	797.94	2.249	2.328333	5	0.4134678	67.47	67.47	18.1312	2.71	0.728257681	0.40300507
Q3P2A	1800	794.3	1.397		5	0.4074364	41.91	41.91	11.42919	2.71	0.739038355	0.32232641
Q3P2B	1800	797.19	2.215		5	0.4122251	66.45	66.45	17.91093	2.71	0.73045317	0.40115291
Q3P2C	1800	796.73	2.079	1.897	5	0.4114629	62.37	62.37	16.84235	2.71	0.731806297	0.38936248
Q3P3 A	1800	796.58	1.704		5	0.4112143	51.12	51.12	13.81275	2.71	0.732248619	0.35271511
Q3P3 B	1800	792.7	1.567		5	0.4047852	47.01	47.01	12.90396	2.71	0.743878759	0.34361124
Q3P3 C	1800	306.33	1.295	1.522	5	-0.4011239	38.85	38.85	-10.7614	2.71	-0.75066866	-0.3152201
Q3P4 A	1800	793.48	1.09		5	0.4060776	32.7	32.7	8.947386	2.71	0.741511166	0.28566804
Q3P4 B	1800	795.68	2.147		5	0.409723	64.41	64.41	17.46708	2.71	0.73491382	0.39735908
Q3P4 C	1800	791.03	2.317	1.851333	5	0.402018	69.51	69.51	19.21141	2.71	0.748999023	0.42070239
Q3P5 A	1800	792.66	1.738		5	0.4047189	52.14	52.14	14.31446	2.71	0.744000581	0.36193357
Q3P5 B	1800	795.93	1.806		5	0.4101373	54.18	54.18	14.67801	2.71	0.734171543	0.36407187
Q3P5 C	1800	795.9	1.772	1.772	5	0.4100876	53.16	53.16	14.40343	2.71	0.734260537	0.36067227
		Bl Average	59.82	1.994								
		Bl STDEV	3.648671									

Appendix 9

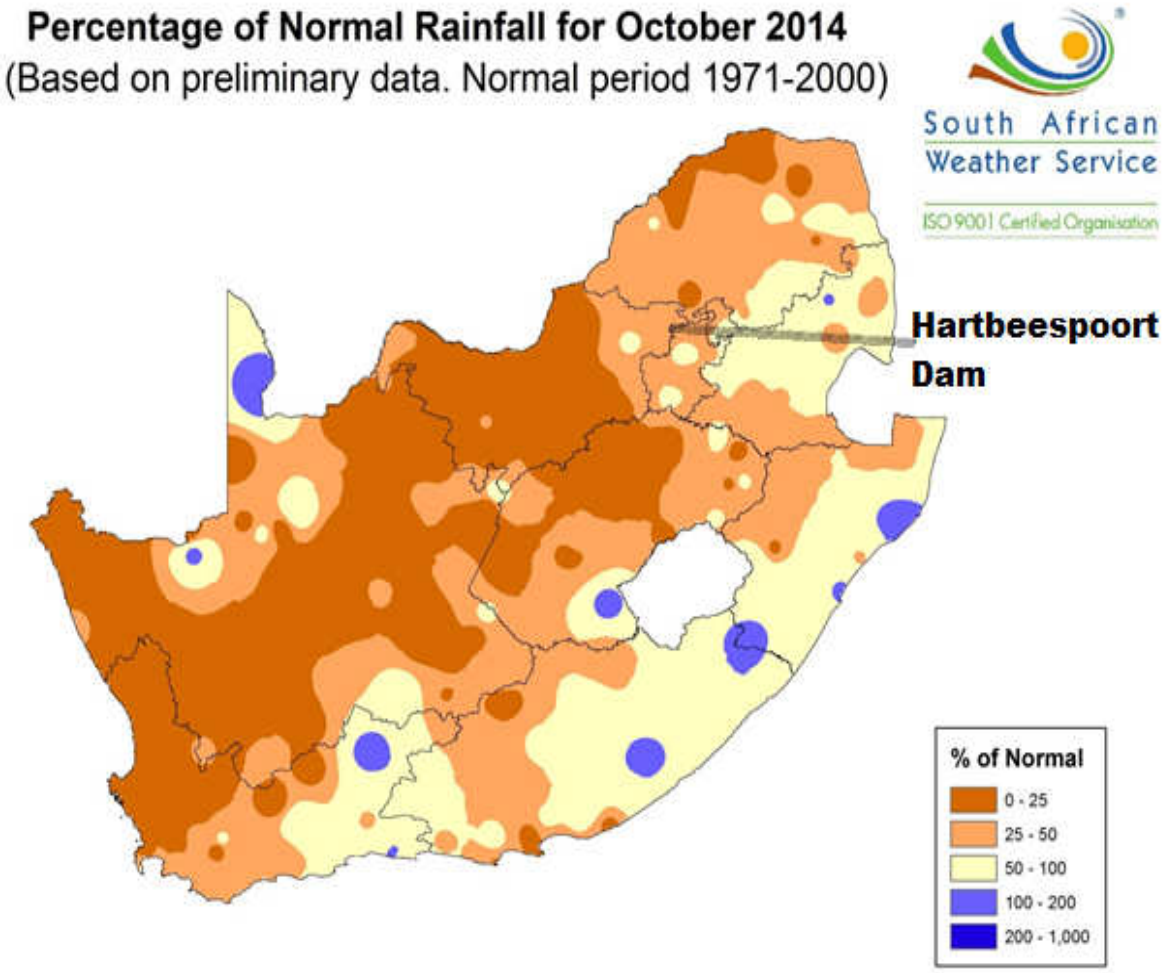
Quarter 4 data for ^{3}H: - Direct Method Measurements												
Sample	Counting time (sec)	SQP	CPM	Average	Volume (mL)	Efficiency	Gross count rate (Sample - Ra)	Nett to count rate (Ra-Rb)	Activity Value (Bq/L)	Detection Limit (CPM)	MDA (Bq/L)	uncertainty (Bq/ sample)
Bl x 01	1800	797.93	2.385		5	0.413451	71.55	71.55	19.22839	2.71	0.72828687	0.41502798
Bl x 02	1800	800.58	4.225	3.305	5	0.417842	126.75	126.75	33.7049	2.71	0.72063345	0.54658598
Cs x 01	1800	788.16	4463.122		0.5	0.397262	133893.7	133893.7	374489.8	2.71	7.57965149	186.852678
Cs x 02	1800	786.3	4348.791	4405.957	0.5	0.39418	130463.7	130463.7	367749.6	2.71	7.63891486	185.885985
Q4P1 A	1800	797.08	2.079		5	0.412043	62.37	62.37	16.81864	2.71	0.73077629	0.38881445
Q4P1 B	1800	801.29	2.045		5	0.419019	61.35	61.35	16.26817	2.71	0.71861016	0.37920209
Q4P1 C	1800	796.21	2.215	2.113	5	0.410601	66.45	66.45	17.98176	2.71	0.73334197	0.4027394
Q4P2A	1800	794.5	3.305		5	0.407768	99.15	99.15	27.01701	2.71	0.73843773	0.4953707
Q4P2B	1800	795.51	3.135		5	0.409441	94.05	94.05	25.52258	2.71	0.73541943	0.48049025
Q4P2C	1800	797.03	3.478	3.306	5	0.41196	104.34	104.34	28.14189	2.71	0.73092325	0.50299918
Q4P3 A	1800	794.75	2.862		5	0.408182	85.86	85.86	23.37193	2.71	0.73768832	0.46050933
Q4P3 B	1800	789.79	7.531		5	0.399963	225.93	225.93	62.76408	2.71	0.75284673	0.76236614
Q4P3 C	1800	793.66	3.578	4.657	5	0.406376	107.34	107.34	29.34885	2.71	0.74096694	0.51718951
Q4P4 A	1800	794.12	2.487		5	0.407138	74.61	74.61	20.36164	2.71	0.73957975	0.43038152
Q4P4 B	1800	791.27	2.83		5	0.402416	84.9	84.9	23.44176	2.71	0.74825884	0.46448938
Q4P4 C	1800	795.46	3.169	2.828667	5	0.409358	95.07	95.07	25.8046	2.71	0.73556827	0.48318652
Q4P5 A	1800	791.17	3.339		5	0.40225	100.17	100.17	27.66936	2.71	0.74856707	0.50474223
Q4P5 B	1800	791.49	2.556		5	0.40278	76.68	76.68	21.15297	2.71	0.74758163	0.44103165
Q4P5 C	1800	791.13	3.237	3.044	5	0.402184	97.11	97.11	26.82853	2.71	0.74869044	0.49705488
		Bl Average	99.15	3.305								
		Bl STDEV	39.03229									

Data highlighted in red colour, represents the results of which the spout tips were observed to have noticeable cracks after combustion of sample, hence could not be used as part of the data.

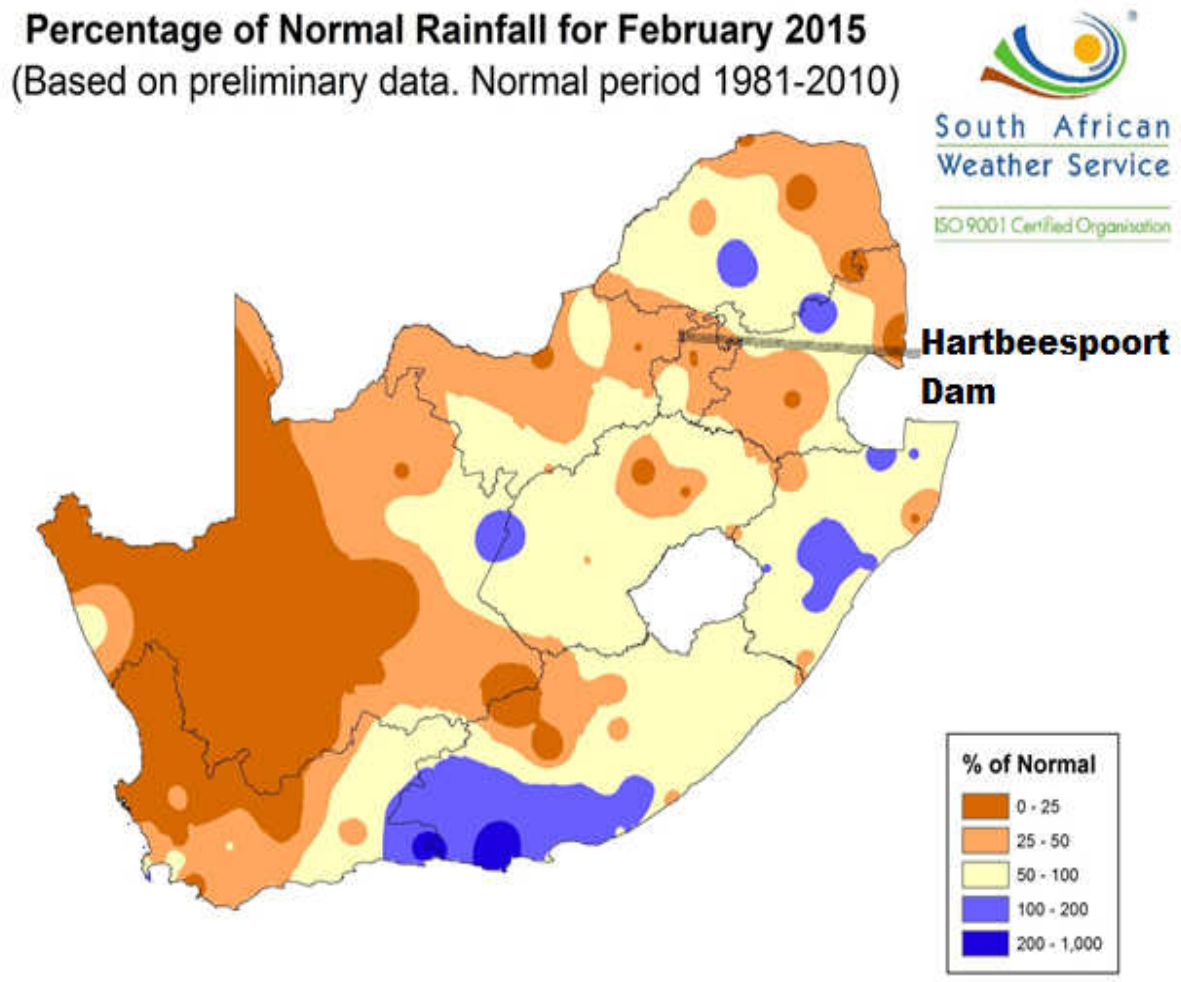
Appendix 10: Percentage of Normal Rainfall for July 2014 (South African Weather Services, 2016).



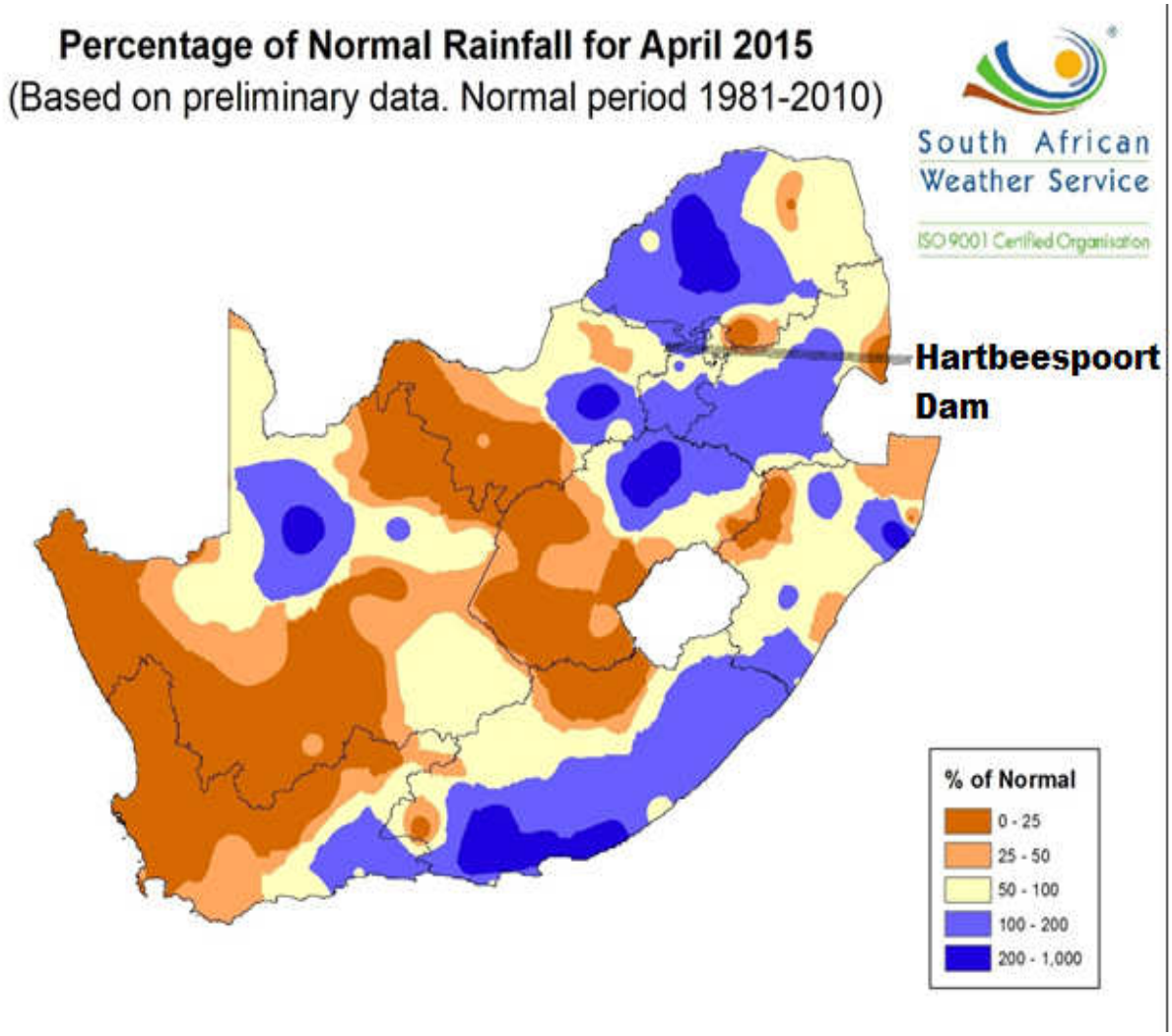
Appendix 11: Percentage of Normal Rainfall for October 2014 (South African Weather Services, 2016)



Appendix 12: Percentage of Normal Rainfall for February 2015 (South African Weather Services, 2016)



Appendix 13: Percentage of Normal Rainfall for April 2015 (South African Weather Services, 2016)



Appendix 14: Draft Article

Title: APPLICATION OF BIOLOGICAL SAMPLE OXIDISER AND LOW-LEVEL LIQUID SCINTILLATION COUNTER FOR THE DETERMINATION OF ^{14}C AND ^{3}H CONTENT IN WATER FROM THE HARTBEESPOORT DAM IN NORTH-WEST PROVINCE

Authors: L H N Khumalo, M S Sonopo and S J Moja

Journal: ProQuest

Year: 2016

6.2.2. Annexure

Annexure A: Ethical Clearance Certificate

UNISA university of south africa

CAES RESEARCH ETHICS REVIEW COMMITTEE

Date: 02/10/2014

Ref #: **2014/CAES/140**
Name of applicant: **Ms LHN Khumalo**
Student #: **45665583**

Dear Ms Khumalo,

Decision: Ethics Approval

Proposal: Measurements of ^{14}C and ^{3}H by liquid scintillation counter in water from the Hartbeespoort Dam in North West Province

Qualification: Postgraduate degree

Thank you for the application for research ethics clearance by the CAES Research Ethics Review Committee for the above mentioned research. Final approval is granted for the duration of the project.

The application was reviewed in compliance with the Unisa Policy on Research Ethics by the CAES Research Ethics Review Committee on 02 October 2014.

The proposed research may now commence with the proviso that:

1) *The researcher/s will ensure that the research project adheres to the values and principles expressed in the UNISA Policy on Research Ethics.*
2) *Any adverse circumstance arising in the undertaking of the research project that is relevant to the ethicality of the study, as well as changes in the methodology, should be communicated in writing to the CAES Research Ethics Review Committee. An amended application could be requested if there are substantial changes from the existing proposal, especially if those changes affect any of the study-related risks for the research participants.*
3) *The researcher will ensure that the research project adheres to any applicable national legislation, professional codes of conduct, institutional guidelines and scientific standards relevant to the specific field of study.*

University of South Africa
Preller Street, Muckleneuk Ridge, City of Tshwane
PO Box 392 UNISA 0003 South Africa
Telephone: +27 12 429 3111 Facsimile: +27 12 429 4150
www.unisa.ac.za

Note:
The reference number [top right corner of this communiqué] should be clearly indicated on all forms of communication [e.g. Webmail, E-mail messages, letters] with the intended research participants, as well as with the CAES RERC.

Kind regards,

Signature
CAES RERC Chair: Prof EL Kempen

Signature
CAES Executive Dean: Prof MJ Linington

University of South Africa
Preller Street, Muckleneuk Ridge, City of Tshwane
PO Box 392 UNISA 0003 South Africa
Telephone: +27 12 429 3111 Facsimile: +27 12 429 4150
www.unisa.ac.za

Annexure B: Sampling Approval Letter

water & sanitation

Department:
Water and Sanitation
REPUBLIC OF SOUTH AFRICA

Provincial Operations: North West , Cnr Dr. James Moroka Drive and Sekame Road, Megacity Shopping Centre, Unit no. 99, Ground Floor,Private Bag x5, Mmabatho, 2735, Tel (012) 207 9911/2, Fax: (012) 207 9914, www.dwa.gov.za

Enquiries: Mr P.S Venter
Telephone: 012 207 9911/2
Reference: 16/3/4/1/4/4

Ms Lamlile Khumalo

REQUEST TO HAVE ACCESS TO INFORMATION AND TO TAKE WATER SAMPLES FROM THE HARTBEESPOORT DAM COMPLETION OF MASTERS DEGREE IN ENVIRONMENTAL CHEMISTRY WITH UNISA: MS LAMLILE KHUMALO

Your email dated 9 September 2014 with regards to the above-mentioned, has reference.

Please take note that there is a significant amount of recent water quality and biological data available for the Hartbeespoort Dam (2008 – 2013) that is available for background reference to yourself and the University on request.

You are free to update / obtain further samples as and when required. The Department is also available for advice and guidance if you might need it to take your own samples. Please make contact with the Metsi a Me Office at the number given above.

Yours sincerely

MR P.S. VENTER
DEPUTY REGIONAL DIRECTOR: NORTH WEST
(PROGRAMME LEADER: HARTIES METSI A ME)
DATE: 2014-09-18

Page 1 of 1

Annexure C: RadioAnalysis Approval Letter

Memorandum

necsa
We're in your world
OPERATIONS

Date 13 August 2014
Ref nr **RA-2014-MEM-0024**

To Mrs. A Steyn;
Cc Ethics Review Committee

Request to approve supervisory and financial support for Ms. LHN Khumalo to pursue her MSc studies on: *Measurements of ^{14}C and ^{3}H by Liquid Scintillation Counting in water from the Hartbeespoort dam in North-West Province*

1. **Background:**

In 2012 Ms. Lamlile Khumalo registered for an Honours degree in Environmental Management. She utilised soil samples and instruments (Sample preparation, Gamma spectrometry, Alpha spectrometry, INAA and Gross Alpha-Beta counters) in RadioAnalysis laboratory at NECSA. During the analysis process, the provision of services were not interrupted nor delayed. A Senior Scientist in RadioAnalysis was assigned to her to ensure that the project produced high quality results and it was completed on time.

Currently Ms. Khumalo is registered for her Masters degree in Environmental Science with UNISA. She will be utilising the instruments from RadioAnalysis and analysing samples collected from Hartbeespoort dam for her project. Dr M. Sonopo and Dr D. Kock have both been assigned to her from Necsa R&D and Prof S.J. Moja of UNISA.

2. **Elaboration:**

Ms. Khumalo will get time to conduct the analysis using a catalytic oxidiser in P1600 R&D laboratory for sample preparation and RadioAnalysis's ultra low-level Quantulus liquid scintillation counter (LSC) for the determination of radioactivity for tritium (^{3}H) and carbon-14 (^{14}C). She will get practical training on operating the LSC from competent RadioAnalysis personnel and allocated time to analyse samples.

Currently RadioAnalysis is an ISO/IEC 17025 SANAS accredited laboratory and offers ^{3}H services to clients by direct and distillation methods but is not capable of measuring ^{14}C since it did not have the appropriate separation method. The outcome of the project has an advantage for RadioAnalysis for determining ^{14}C and ^{3}H in water samples accurately with improved separation, reduced turn-around times and even eliminating repeats of analysis due to quenching. It is therefore also envisaged that RadioAnalysis will utilise the information gained to offer services of ^{14}C and ^{3}H measurements to various clients.

3. **Financial implication:**

RadioAnalysis wil incur the costs of analysing approximately 50 samples on the LSC and it is anticipated that this will not have a significant interruption on the services provided to clients. It is anticipated that the costs of consumables that will be incurred by RadioAnalysis will be R50 000. Travelling and sampling costs will be incurred within Necsa via the routine S&LD sampling schedules. Once the project proposal has been approved by UNISA, it is possible that NRF will

fund part of the project and RadioAnalysis will save some of the costs.

4. Recommendation:

It is recommended that Necsa should invest in the supervisory and financial support to Ms. Khumalo to ensure that this project meets its objectives.The benefits of this investments far outweighs the costs that will be incurred since a more accurate method will established for the determination of tritium in aqueous and also solid samples. RadioAnalysis will have the capability to pursue the ^{14}C market that is requested by clients on numerous occassions.

APPROVED/NOT APPROVED

A Sleyn
Business Unit Head: ACS

Date: 2014/08/13

COMPILER

AS Makhaba
Manager: RA

Date: 2014/08/13

Annexure D: Turn-it-in Report


Turnitin Originality Report

dissertation by Lamlile Khumalo

From dissertation (Lamlile Khumalo)

- Processed on 22-Feb-2016 13:07 SAST
- ID: 635190345
- Word Count: 23935

Similarity Index

22%

Similarity by Source

Internet Sources:

15%

Publications:

11%

Student Papers:

6%