RE-ASSESSMENT OF RADIOLOGICAL HAZARDS OF NATURALLY OCCURRING RADIOACTIVE MATERIALS (NORM) FROM THE JUBILEE OILFIELDS OF GHANA

A dissertation presented to the:

DEPARTMENT OF NUCLEAR SAFETY AND SECURITY

UNIVERSITY OF GHANA

By

BAAFI EUNICE NYARKO (ID: 10598881)

BSc (KNUST), 2014

In partial fulfillment of the requirements for the degree of

MASTER OF PHILOSOPHY

In

RADIATION PROTECTION

July, 2018

DECLARATION

This thesis is the outcome of the research work undertaken by Eunice Nyarko BAAFI in the department of Nuclear Safety and Security, University of Ghana under the supervision of Prof. Augustine Faanu (Ag Director, Radiological and Non-ionizing Radiation Directorate, NRA) and Dr. David Okoh Kpeglo (Head, Department of Nuclear Safety and Security, SNAS; Senior Research Scientist, RPI, GAEC)

Sign: Date:……

Baafi Eunice Nyarko

(Student)

Sign: Date:…….

Dr. David Okoh Kpeglo

(Principal Supervisor)

Sign: Date:……...

Prof. Augustine Faanu

(Co-Supervisor)

DEDICATION

This research work is dedicated to the Adusei and Baafi families.

ACKNOWLEDGEMENTS

Thanks and praise to the Most High for a successful completion of this research work. My utmost appreciation goes to my supervisors (Prof. Augustine Faanu and Dr. David Okoh Kpeglo) for their constructive criticisms, encouragement and insightful contributions towards this research work. I will like to also thank the management of Tullow Ghana Limited for their help in obtaining the samples, especially Mr. Emmanuel Arthur.

Lastly, I express my profound gratitude to the management of the Radiation Protection Institute (RPI), Ghana Atomic Energy Commission (GAEC), especially to all the scientists in the radiochemistry laboratory (Mr. Maruf Abubakar, Mrs. Bernice Konadu Agyeman and Mrs. Patience Nyarko) and all who assisted me in various ways till the completion of this thesis.

ABBREVIATIONS

ALARA	As Low As Reasonably Achievable
AMAD	Activity Median Aerodynamic Diameter
API	American Petroleum Institute
APPEA	Australian Petroleum Production and Exploration Association
ASTM	American Society for Testing and Materials
BSS	Basic Safety Standard
DRL	Derived Release Limit
EPA	Environmental Protection Agency
E&P	Exploration and Production
ESRF	Environmental Studies Research Fund
FPSO	Floating Production Storage and Offloading
GAEC	Ghana Atomic Energy Commission
GNPC	Ghana National Petroleum Commission
IAEA	International Atomic Energy Agency
IARC	International Agency for Research on Cancer
ICRP	International Commission on Radiological Protection
MCA	Multi-Channel Analyzer
MDA	Minimum Detectable Activity
NORM	Naturally Occurring Radioactive Materials
NRA	Nuclear Regulatory Authority

NRPA	Norwegian Radiation Protection Authority
OECD/NEA	Organization for Economic Co-operation and Development/Nuclear Energy Agency
PCG	Petroleum Commission of Ghana
PIPS	Passivated Implanted Planar Silicon
RPI	Radiation Protection Institute
SDWA	Safe Drinking Water Act
SEM	Scanning Electron Microscopy
SRM	Standard Reference Material
TEN	Tweneboa, Enyera, Ntome
TGL	Tullow Ghana Limited
UKOOA	United Kingdom Offshore Operation Association
UNSCEAR	United Nations Scientific Committee on the Effects of Atomic Radiation
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

ABSTRACT

This study re-assesses the radiological hazards of Naturally Occurring Radioactive Materials (NORM) on workers and the general public due to continuous exploration and production of crude oil and waste generated from the Jubilee Oilfields of Ghana. The specific activities of ^{234}U, ^{238}U, ^{230}Th, ^{232}Th, ^{226}Ra, ^{210}Pb, ^{234}Th, ^{228}Ra, ^{224}Ra and ^{40}K in crude oil and NORM waste samples have been estimated using Sodium Iodide detector and alpha spectrometry after radiochemical separation. A trend analysis of an increase in the activity concentrations of radionuclides has also been established between the previous study and this study using a statistical test of association (paired t-test) at 95% confidence interval. An annual effective dose of 1.32 mSv obtained for occupationally exposed workers in this study was below the International Commission on Radiological Protection (ICRP) recommended dose limit of 20 mSv per year (averaged over 5 years and not exceeding 50 mSv per year in any single year). From the study, radium concentrations are of radiological importance for sludge and produced water due to the high levels of activity concentrations recorded. There is also tendency for possible increase levels of activity concentration of these radionuclides with time as exploration and production continues with more wells being drilled. As a result it is recommended that a national guideline for monitoring of NORM is established to ensure regulatory monitoring of these facilities in Ghana.

CHAPTER ONE

INTRODUCTION

1.1 Background

It is a well-known fact that naturally occurring radioactive materials (NORM) are extant in the earth's crust. They form part of soil, rocks, water, and food and can as well be detected in the human body. Uranium-238 and Thorium-232 are parents of two complex series of radioactive elements. The Uranium-238, Uranium-235 and Thorium-232, as well as Potassium-40 are of specific importance (Kpeglo, 2015). They contain a number of radionuclides, specifically, Radium-226 from the Uranium-238 decay series and Radium-228 from the Thorium-232 decay series, which are found in oil and gas products, produced water and all sludge and scale deposits in subsurface and/or surface production facilities (Smith, 1996).

Naturally Occurring Radioactive Materials (NORM) presents a considerable waste issue in the oil and gas industry. Oil and gas extraction and processing tend to accumulate NORM at concentrations higher than normal in by-product waste streams such as produced water, scale and sludge (Smith, 1992).

Produced water is the largest generated waste which mainly contains radium isotopes, solid residues and production equipment. This is the water from the formation process in the reservoir that is generated along with oil or gas. Occasionally, it may also encompass injection water and condensation water. The characteristics and composition or naturally-occurring chemical substances in produced water are closely linked to the geological characteristics of oil reservoirs. (Bakke et al, 2013). Produced water is normally detached

from the oil and discarded by some means such as down an injection well or disposal well. This water is discharged into the environment for it to be evaporated, by some companies. Usually, unlined lagoons or pits are constructed to collect this water and it ends up becoming highly contaminated with NORM such as ^{226}Ra and ^{228}Ra (Al-Masri & Suman, 2003).

Sludge and scales form the solid residues found in pipes and other production equipment. Sludge is formed from the combination of oil, sediment and corrosion products that build up within piping, bottom of storage tanks, separators and any other equipment where produced water is handled or managed. Sludge is made up of mainly carbonates and silicates which contain radium. Scales usually precipitate inside piping, filters, injection wellhead equipment, as well as other water-handling equipment. The presence of these scales lead to the gradual loss of productivity and the need for frequent maintenance work. Scales are basically formed from the precipitates of barium and strontium sulfates and calcium carbonate. The precipitates form deposits within the surface of pipes and equipment (Gazineu et al, 2005).

Unrestrained clearance of these types of wastes could lead to human exposure and environmental pollution and subsequently lead to radiation exposure of members of the public. Seven environmental pathways are known; for which radiation exposure from NORM generated by the oil and gas industry can take place. They are through radon inhalation, dust inhalation, external gamma exposure, ground water ingestion, food ingestion, skin beta exposure and surface water ingestion, (Smith, 1992). People at peril from exposure to NORM radiation from the oil and gas industry consists of oilfield workers, workers at NORM disposal facilities, workers at equipment cleaning facilities,

and the general public. Coastal communities close to shallow water offshore oilfields and land disposal facilities are also at a major risk of exposure. The general population may be at risk to NORM through radon inhalation; and ingestion of groundwater, surface water and food. Inappropriate disposal of NORM contaminated waste, such as scales, sludge and drilling mud produced by the oil and gas industry is likely to cause soil and water contamination and higher indoor radon levels in neighboring buildings (Kpeglo, 2015).

Previous work conducted, according to Kpeglo, (2015), on oil fields (Saltpond and Jubilee) of Ghana from 2012 to 2013 suggested that the radioactivity associated with NORM scales, sludge and produced water were significant, specifically with ^{226}Ra, ^{228}Ra and ^{228}Th with activities in scales exceeding the Exempt level of $1Bqg^{-1}$. It was recommended from this study among other things that analysis for radionuclides in oil waste should be carried out at least once in a year with the aim of monitoring the levels of radioactivity in the wells as production increases with time.

This study therefore, seeks to make comparison of natural radioactivity levels in the production oil wells/reservoirs and to assess the potential hazard of NORM waste generated from the Jubilee Oil Field on the public and workers eight years after drilling oil in commercial quantities in Ghana.

This is particularly necessary because there has been significant increased interest in the exploration and production activity after the Jubilee Field discovery in 2007 and commercial production of oil and gas commencing in October 2010. The Jubilee field contains up to 3 billion barrels ($480,000,000m^3$) of pure crude oil. There are currently

seventeen (17) active Petroleum Agreements (Pas) for offshore concessions mostly in the Western Basin (PCG, 2015).

Hence the need to re–assess the radiological hazard resulting from the oil and gas activities since the previous study in 2013 cannot be overemphasized.

1.2 Problem Statement

The exploration and extraction of oil and gas constantly exposes workers, the public and the environment in general to the radiological hazards of NORM. Therefore, for purposes of radiological protection of the worker and the public it is important to conduct regular monitoring of the production wells to establish radioactivity levels as production increases with associated NORM.

However, since the commencement of commercial production from the Jubilee Oil Field in 2010, only one study has been conducted in 2012 and 2013 to assess NORM.

Based on recommendations from previous studies carried out on radioactivity levels associated with NORM in the crude oil and petroleum waste generated in the Jubilee Oil Fields of Ghana (Kpeglo,2015), this research work seeks to re-assess the radiological hazards of NORM from the Jubilee Oilfields after eight (8) years of operation. This study will provide more data in comparison with the data from the previous study to aid in realistic decisions on the controls to be enforced if needed. Any remedial actions can then be justified based on the data obtained.

1.3 Objectives of Research

The research work is aimed at re-assessing radiological hazards of naturally occurring radioactive materials (crude oil and petroleum waste) from the Jubilee Oil Fields of Ghana and to establish effective controls by making comparisons with the previous study. The specific objectives of this research are to:

a. Determine and re-assess the radioactivity concentration of NORM from the Jubilee oil field.

b. Compare activity concentration with previous work to establish the differences in radioactivity levels in the oil wells/reservoirs.

c. Make a statistical analysis of the results obtained from the previous and current studies.

d. Provide an estimate of radiation hazard indices, radium equivalent activity, and radon emanation coefficient and radon mass exhalation rate for petroleum waste samples.

e. Re-assess the current state of Radiological protection of workers of the jubilee oil fields and the public.

f. Make appropriate recommendations from the findings to the relevant stakeholders.

1.4 Relevance of Work

This research work aims at re-assessing radiological hazards from Naturally Occurring Radioactive Materials and make a comparison of the current and previous radioactivity levels of NORM in crude oil and petroleum waste from the Jubilee Oil Fields of Ghana after a period of eight (8) years of operation.

It is imperative that radiation exposure is monitored periodically from the Jubilee Oil Field to ensure radiological conditions remain acceptable for the protection of workers and the public. The data from the study will help to put in place the appropriate control measures with respect to basic radiological protection. In addition, the assessment of radiological hazards and consequences associated with NORM which may pose serious health implications to workers and the public will form the basis for optimization of the protection of workers and the public.

The data from this study will also serve as a useful database for Regulatory Bodies, Oil Field Operators, Oil Exploration Companies, Oil Refineries and Service Companies in the Oil and Gas industry in Ghana.`

1.5 Scope and Limitation

This research work is envisioned to cover the measurement of activity concentrations due to uranium series as well as the thorium series at the Jubilee oil field.

1.6 Structure of Thesis

The thesis of the study was structured into five chapters.

a. The first chapter was based on the background of the study, the objectives, the relevance of the work and the problem statement.

b. The second chapter focused on a review of related research from literature. Thus, relevant books, internet data and journals.

c. The third chapter describes the method and materials used throughout the study.

d. The presentation of results from the study as well as the discussion is captioned in the fourth chapter.

e. Lastly, the fifth chapter provides the summary of the results and findings from the study, conclusions and recommendations to regulatory bodies, oil field operators, and service companies in the petroleum industry in Ghana.

CHAPTER TWO

LITERATURE REVIEW

Overview

This Chapter seeks to review some of the works done and reported in a number of publications, as well as discussions on some radiological aspects of NORM in view of occupational radiation protection, public health and environmental radiation protection.

2.1 Origin and Radiological characteristics of NORM

Naturally occurring radioactive elements exist in the earth's rocks, soils, and water in varying concentrations. Naturally occurring radionuclides have two types of sources. They are the Primordial (^{238}U, ^{235}U and ^{232}Th decay series, ^{40}K, ^{87}Rb) and Cosmic ray interactions (^{3}H, ^{14}C, ^{7}Be). All minerals and raw materials contain primordial natural radionuclides of terrestrial origin (Zaidan, 2010).

The NORM which occurs in reservoir rock has minute quantities of natural uranium and thorium and their radioactive daughters. One of the daughter products, radium, is known to be water absorbent, therefore dissolves in the reservoir water. Radium can precipitate with barium and calcium ions to make any scales slightly radioactive. Clay and fine particles can absorb the radium from the formation water (Kinsey et al., 1997).

According to a research that was done in the USA between 1959 and 1989, (Alnabhani et al., 2015), uranium and thorium could be found in alluvial formations of common shale, black shale, sandstones, orthoquartzites, siltstones, claystone, carbonates, bentonites, carbonate rocks, halite, anhydrite, phosphate rock and chert. Different levels of activity

concentration of uranium, thorium, potassium and their daughter products were roughly found in all rocks and soil. Their concentrations differ depending on the type of the rock for example, black shale, such as the Marcellus, often contains levels of Uranium-238, Uranium-235, Potassium-40, and Thorium-232 in higher concentrations than found in less organic-rich grey shale, sandstone, or limestone.

The presence of ^{238}U and ^{232}Th in subsurface formations from which hydrocarbon are produced have extensive half-lives. They are abundant in the earth's crust and have activity concentrations that depend on the rock type. Radioactive decay of ^{238}U and ^{232}Th produces numerous series of daughter radioisotopes of diverse elements of different physical characteristics with regard to their half-lives, modes of decay, and types and energies of emitted radiation (Zaidan, 2010).

Figure 2.1 and Figure 2.2 shows the transport of ^{238}U and ^{232}Th progenies in the production of oil and gas. The elements of these primordial radionuclides are not gathered from the reservoir rock from which oil, gas and formation water are found.

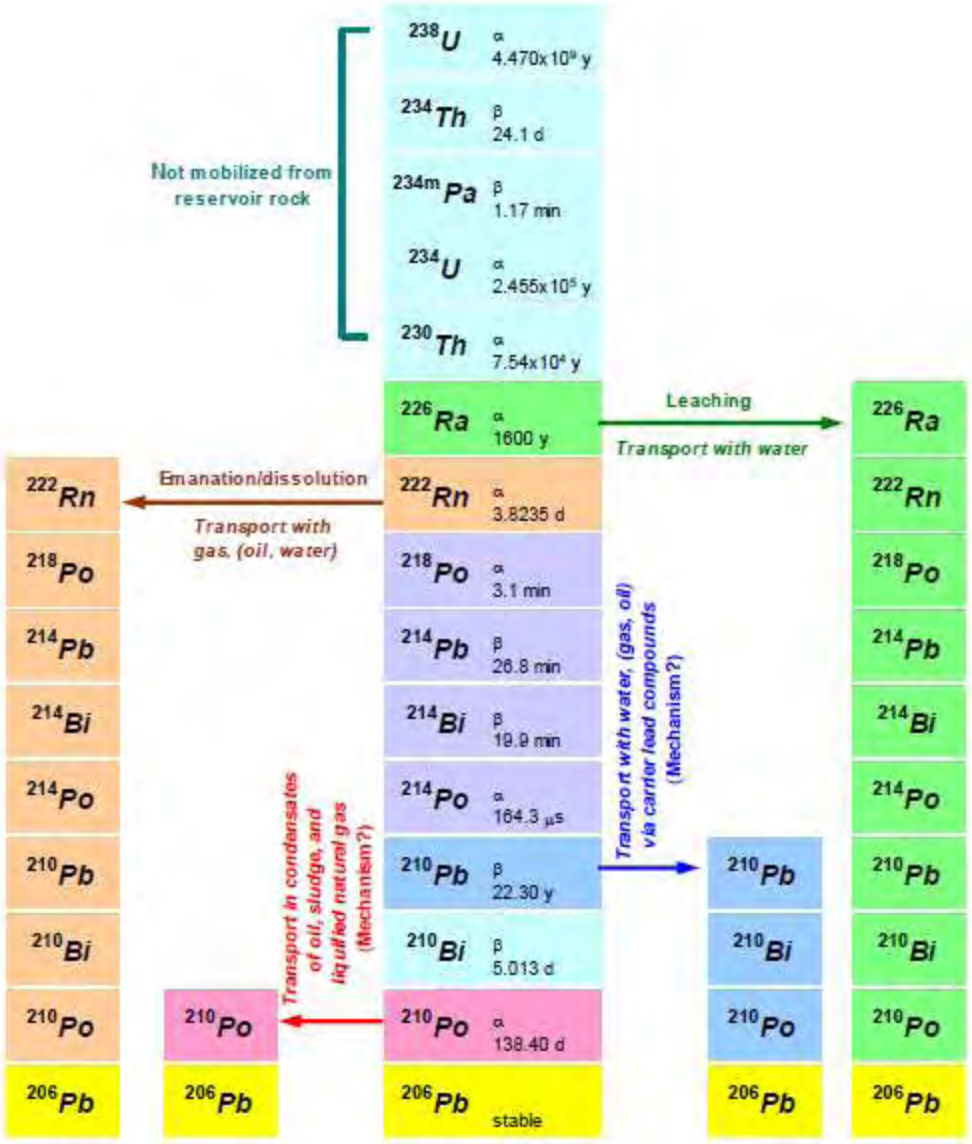

Figure 2.1: U-238 decay series (IAEA, 2010)

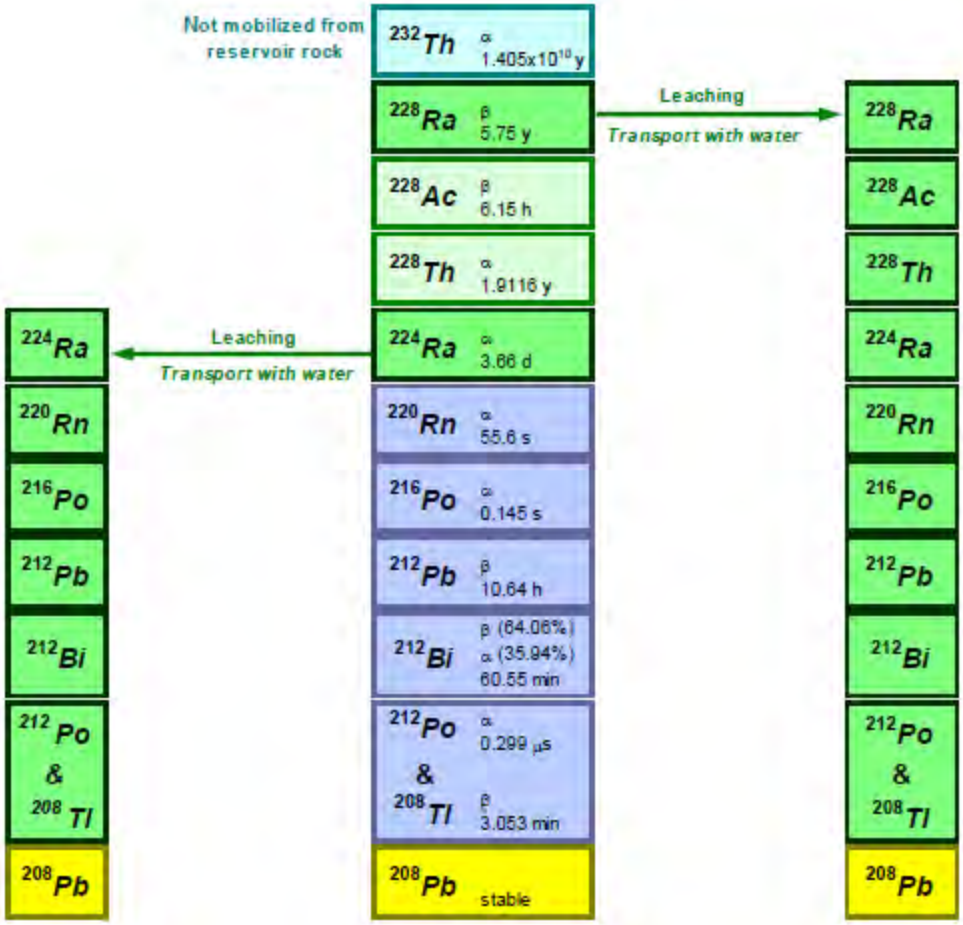

Figure 2.2: Th-232 decay series (IAEA, 2010)

Table 2.1: Radioactive decay characteristics of naturally occurring radionuclide in oil and gas production (IAEA, 2003)

Radionuclide	Half-life	Mode of decay	Main decay product(s)
Ra-226	1600 a	Alpha	Rn-222 (Noble gas)
Rn-222	3.8235 d	Alpha	Short lived progeny
Pb-210	22.30 a	Beta	Po-210 (Alpha emitter)
Po-210	I38.40 d	Alpha	Pb-206 (Stable)
Rn-228	5.75 a	Beta	Th-228
Th-228	1.9116 a	Alpha	Ra-224
Ra-224	3.66 d	Alpha	Short lived progeny

*a = years; d = days

The formation water consists of Group II (Periodic Table) cations of calcium, strontium, barium and radium dissolved from the reservoir rock. As a result, formation water contains the radium isotopes ^{226}Ra from the ^{238}U series as shown in Figure 2.1, and ^{228}Ra and ^{224}Ra from the ^{232}Th series as shown in Figure. 2.2. All three radium isotopes, as a result appear in the water co-produced with the oil or gas, but not their parents. They are known as 'unsupported' because their long lived parents ^{238}U and ^{232}Th and also ^{228}Th remain in the reservoir. The ^{228}Th radionuclide sometimes detected in aged sludge and scale is likely to be present as a product of the decay of the mobilized ^{228}Ra (IAEA, 2003).

In a situation where the ions of the Group II elements, radium inclusive, are available in the produced water, decrease in pressure and temperature may result in an increase in the dissolved products of mixture of their carbonates and sulphates. This may lead to their precipitation as sulphate and carbonate scales inside the walls of wellheads (W), pumps

(P), production tubulars (T), separators (S), valves (V), oil storage tanks (O), water treatment vessels (H), and gas treatment (G) as shown in Figure 2.3 (Kpeglo, 2015; Zaidan, 2010). Opportunities are created for deposition to take place where there is turbulent flow, nucleation and centripetal forces. Producing particles of clay or sand together which will bring about deposition of scale in the well completion may be mixed from dissimilar producing wells and combined in the uppermost part of the plant and equipment (Zaidan, 2010).

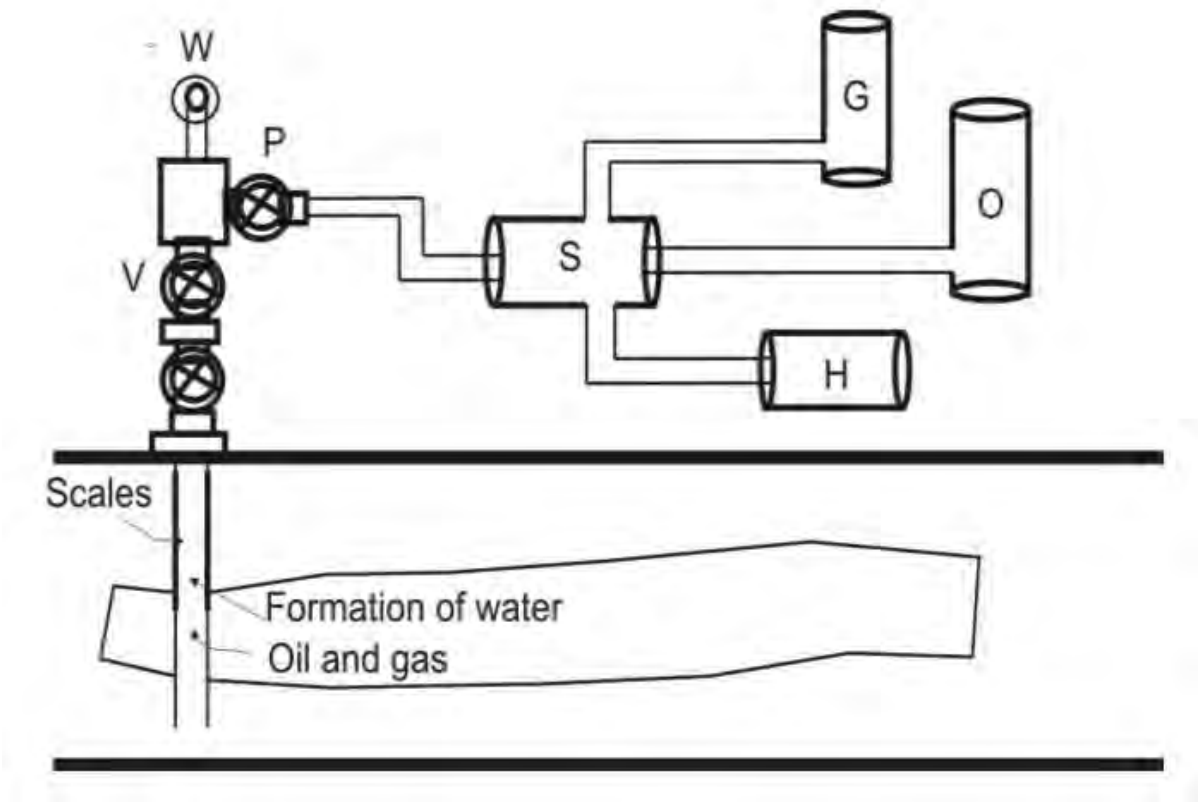

Figure 2.3 Precipitation of scales in production plant and equipment (IAEA, 2003)

^{226}Ra decays in the reservoir rock to produce ^{222}Rn, which is a noble gas. This originates from a mixture of oil, gas and water in the reservoir rock. ^{222}Rn formed from the production area comes with the stream of gas and water followed by the release of dry gases. Thus, equipment from treatment of gas and transfer facilities may mount up a thin layer of ^{210}Pb created by the decay of ^{222}Rn remaining in the inner surfaces of gas lines. Chances of ^{210}Pb deposits being run into again in liquefied natural gas processing plants are high.

In 2003, the IAEA reported a slightly dissimilar procedure leads to the mobilization of stable lead that encompasses comparatively increased concentrations of the radionuclide ^{210}Pb from the reservoir rock. Although not well understood, this method has been seen in a number of gas production fields and results in the deposition of thin, active lead films on the internal surfaces of production equipment and the appearance of stable lead and ^{210}Pb in sludge. Condensates extracted as liquids from natural gas, may contain relatively high levels of ^{222}Rn and unsupported ^{210}Pb. In addition, ^{210}Po is observed at levels in excess of its grandparent ^{210}Pb, indicating direct emanation from the reservoir (IAEA, 2003).

2.2 NORM in oil and gas industry

Earlier accounts of NORM related to mineral oil and natural gases came into sight in 1904 (IAEA, 2003). Several observations prompted renewed interest when later accounts described the existence of ^{226}Ra in reservoir water from oil and gas fields in the 1970s and 1980s. The radiological viewpoint of these events, the outcome of monitoring and

studies and the progress of putting in place instructions for radiation safety have currently been recounted comprehensively (IAEA, 2005).

Some important work has been done in Ghana, to assess the dangers associated with NORM in the mining industry and most workers in the mining industry are privy to the potential problems associated with NORM (Kpeglo, 2015). Moreover, recent work has been carried out to evaluate the potential hazards related to NORM in the oil and gas industry in Ghana and per its recommendation, analysis for radionuclides in oil waste should be carried out at least once in a year with the objective of monitoring the levels of radioactivity in the wells as production increases with time.

The sources for most radioactivities in oil and gas NORM wastes are long-lived isotopes of uranium and thorium (primarily Uranium-238 and Thorium-232). NORM that is generated in elevated concentrations by most industrial processes is largely unregulated. Management and disposal of NORM is normally not addressed by most federal regulations, and very few states have developed regulations specific to oil and gas NORM (Smith, 1992).

El Afifi (2005) reported that natural radionuclides ^{238}U, ^{235}U and ^{232}Th, as well as the radium-radionuclides (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) and ^{210}Pb are brought to the slurry surfaces in the exploration and extraction processes of oil and gas. They may contain levels of radioactivity above the surface background. The petroleum waste, scale or sludge, have been manufactured in two ways: incorporation or precipitation onto the production equipment such as: pipelines, tank storage, pump etc. The production of oil

and gas waste in equipment is due to the precipitation of alkaline earth metals as sulfate, carbonates and/or silicates.

In dealing with these materials, their radioactive constituents may be divided, leading to NORM waste. Nuclear spectroscopic analysis indicate that the major radionuclides found in NORM waste associated with petroleum industries are ^{238}U, ^{235}U and ^{232}Th series (Kpeglo, 2015).

Naturally occurring radioactive materials (NORM) exist in many industries, as well as the petroleum industry. NORM waste can be found in petroleum reservoirs, in oil and gas production and in processing facilities (Gazineu et al., 2005).

Over the years, a vast amount of data has been taken on the radionuclide concentrations in NORM. However, only few have been reported in literature. Normally, the specific activities of radium isotopes found in scales are higher than in sludge. The concentrations of ^{226}Ra, ^{228}Ra and ^{224}Ra in scales and sludge range from less than 0.1 Bq g^{-1} up to 15 000 Bq g^{-1} (Zaidan, 2010).

The volume of NORM waste produced by the petroleum industry is rather remarkable. The American petroleum industry produces 25,000 t of scale contaminated with NORM and 225,000 t of NORM contaminated sludge yearly as estimated by the Environmental Protection Agency (EPA) of the United States of America (USEPA, 1993).

According to Vandenhove, (2002), the overall production of natural gas and oil is 140 Mt and 0.23×10^{12} m^3, respectively, which produces sludge of 10,000 m^3 yearly in the European Union. Even though concentrations as high as 15,000 kBq kg^{-1} (410,000 pCi g^{-1}) have been reported in literature, the leading radionuclides found in scales and other

precipitates are ^{226}Ra and ^{228}Ra, with typical concentrations ranging from 1 to 1000 kBq kg^{-1} (USEPA, 1993). Generally, values for ^{228}Ra in scales and sludge are not much less than for ^{226}Ra. Moreover, radium concentrations in sludge that have been reported are, on average, lower than in scales (Vandenhove, 2002).

In a study that was conducted in Brazil, (Godoy and Cruz, 2003) reported activity concentration values for scales taken from an offshore oil producing facility which was in the range of 19.1 to 323.0 kBq kg^{-1} and 4.21 to 235 kBq kg^{-1} for ^{226}Ra and ^{228}Ra, respectively. The sludge taken from the same facility had concentrations that ranged from 0.36 to 367 kBq kg^{-1} for ^{226}Ra, and from 0.25 to 343 kBq kg^{-1} for ^{228}Ra, respectively.

In another study that was done in New York State, activity concentrations that were as high as 7.4 kBq kg^{-1} for ^{226}Ra, 4.7 kBq kg^{-1} for ^{228}Ra and 4.2 kBq kg^{-1} for ^{40}K were obtained for scale and sludge samples from the oil industry (Kpeglo, 2015). Concurrently, the values that were obtained for sludge samples from the Red Sea Region were 18.0 kBq kg^{-1} for ^{226}Ra, 13.3 kBq kg^{-1} for ^{228}Ra and 1.3 kBq kg^{-1} for ^{40}K (Shawky et al., 2001).

In a research conducted at the oilfields of Syria, Al-Masri and Aba, (2005) reported the radioactivity content of 152 scale samples taken from equipment. The mean ^{226}Ra activity concentration in these samples was estimated to be 174 kBq kg^{-1}, whilst 1520 kBq kg^{-1} recorded for this isotope was the highest activity concentration. Conversely, the average and maximum values for ^{228}Ra were found to be 91 kBq kg^{-1} and 868 kBq kg^{-1} respectively. A steady increase in ^{226}Ra specific activity was reported from downhole tubes to the equipment and tubing at the surface installations.

Table 2.2 gives a summary of the major appearance of NORM in oil and gas production facilities

Table 2.2: NORM in Oil and Gas production (IAEA, 2010)

Type	Radionuclide	Characteristics	Occurrence
Ra scales	Ra-226,Ra-228,Ra-224 and their progeny	Hard deposits of Ca, Sr, Ba, sulphates and carbonates	Wet parts of production installations, well completions
Ra sludge	Ra-226,Ra-228,Ra-224 and their progeny	Sand, clay, paraffin, heavy metals	Separators, skimmer tanks
Pb deposits	Po-210 and its progeny	Stable lead deposits	Wet parts of gas production installations, well completions
Pb films	Po-210 and its progeny	Very thin films	Oil and gas treatment and transport
Po films	Po-210	Very thin films	Condensates treatment facilities
Condensates	Po-210	Unsupported	Gas productions
Natural gas	Rn-222,Pb-210,Po-210	Noble gas plated on surfaces	Consumers domain gas treatment and transport systems
Produced water	Ra Ra-226,Ra-228,Ra-224 and / or Pb-210	More or less saline, large volumes in oil production	Each production facility

2.3 NORM in the petroleum industry

According to the IAEA (2003), petroleum production and natural gas production facilities are known to have naturally occurring radioactive materials in their components. NORM

can be related to the occurrence of crude oil, produced water and natural gas. The major petroleum residues of NORM are in scale, sludge and sand. It is present in the form of thin layers created by the decay products of ^{222}Rn on the internal walls of the constituents of the gas plant where natural gas and its fractions only are available. Taking into consideration that formation water forms part of natural gas, minute amount of sludge can be found in gas plants also. NORM in oil installations principally contain ^{226}Ra and ^{228}Ra, whose activity is mostly in equilibrium with the specific activity of the products of their decay (Kpeglo, 2015).

The formation of scale is brought about by the following events (IAEA, 2003; APPEA, 2002): combination of incompatible waters; variations in pressure; variation in temperature; impurities; additives; flow rates variation; variations in the acidic nature of water; expansion of fluid; evaporation of gas; etc. The most significant of these procedures are combining incompatible waters and temperature variations. APPEA, (2002) reported that "Trace concentrations of barium, strontium, calcium and radium percolate out from reservoir sand under high temperature and pressure in the oil reservoir. They are available in solution in the formation water. This water also comprises sulphates, carbonates and other ions.

Minute quantities of solid scale contains high concentration of radium; in that, the concentration of radium in scale is in higher degree compared to that of radium in produced water, when scale precipitates from huge quantities of formation water. Scale is made up of virtually no uranium and/or thorium as they are significantly insoluble in the formation water compared to radium. It can be established that NORM in petroleum production facilities encompasses primarily ^{226}Ra, ^{228}Ra and their decay products are

short- lived. Radium-226 has a half-life of 1,600 years whilst Radium-228 is 5.8 years. The products of radon decay are produced incessantly in solid NORM in petroleum production installations by radium decay (E & P forum, 1987; APPEA, 2002).

Consequently, in the course of routine work conditions and shutdowns, scale and sludge gives off nearly the same amount of radiation. Produced water itself is not a source of external radiation exposure, since radium concentration and its decay products in produced water is normally low compared to scale and sludge (APPEA, 2002; E & P forum, 1987). Nonetheless, it is necessary that radium in produced water from the discharge made from onshore facilities, especially, be considered for treatment based on the concentration of radium and on environmental factors. Below is a summary of the decay series radionuclides of Radium-226 and Radium-228 in Table 2.3 and Table 2.4.

Table 2.3: Properties of Radium-226 decay series (IAEA, 2003)

Nuclide	Atomic No.	Half- life	Radiation
^{226}Ra	88	1602y	α , γ
^{222}Rn	86	3.824d	α
^{218}Po	84	3.05m	α
^{214}Pb	82	26.8m	β , γ
^{214}Bi	83	19.8m	β , γ
^{214}Po	84	162ms	α
^{210}Pb	82	22.3y	β , γ
^{210}Bi	83	5.012d	β
^{210}Po	84	138.4d	α
^{206}Pb	82	Stable	-

Table 2.4: Properties of Radium-228 decay series (IAEA, 2003)

Nuclide	Atomic No.	Half- life	Radiation
^{228}Ra	88	5.75y	β
^{228}Ac	89	6.13h	β , γ
^{228}Th	90	1.913y	α , γ
^{224}Ra	88	3.64d	α , γ
^{220}Rn	86	55.3s	α
^{216}Po	84	0.15s	α
^{212}Pb	82	10.64h	β , γ
^{212}Bi	83	60.6m	α , β , γ
^{212}Po	84	0.305ms	α
^{208}TI	81	3.07m	β , γ
^{208}Pb	82	Stable	-

2.4 Concentrations of radionuclide in NORM

A vast amount of data has been gathered on the concentration of radionuclides in NORM in past years, though only a few has been reported in literature. The concentrations of ^{226}Ra, ^{228}Ra and ^{224}Ra in scales and sludge ranges from less than 0.1 Bq g^{-1} up to 15 000 Bq g^{-1} as shown in Table 2.5 (IAEA, 2003). Generally, the activity concentrations of radium isotopes are higher in scales than in sludge. The opposite applies to ^{210}Pb, which normally has quite low concentration in hard scales but may reach a concentration of more than 1000 Bq g^{-1} in Lead deposits and sludge. Even though thorium isotopes are not mobilized from the reservoir, the decay product ^{228}Th starts to grow in from ^{228}Ra after deposition of the latter. Due to this, the concentration of ^{228}Th increases to about 150% of the concentration of ^{228}Ra when scales containing ^{228}Ra are kept for longer periods (Zaidan, 2010).

Table 2.5: Concentration of NORM in oil and gas (IAEA, 2003)

Radio-nuclide	Crude oil Bq/g	Natural gas Bq/m^3	Produced water Bq/L	Hard scale Bq/g	Sludge Bq/g
^{238}U	<0.01	—	0.0003–0.1	0.001–0.5	0.005–0.01
^{226}Ra	0.000–0.04	—	0.002–1200	0.1–15 000	0.05–800
^{210}Po	0–0.01	0.002–0.08	—	0.02–1.5	0.004–160
^{210}Pb	—	0.005–0.02	0.05–190	0.02–75	0.1–1300
^{222}Rn	—	5–200 000	—	—	—
^{232}Th	0.000 03–0.002	—	0.0003–0.001	0.001–0.002	0.002–0.01
^{228}Ra	—	—	0.3–180	0.0 –2800	0.5–50
^{224}Ra	—	—	0.5–40	—	—

2.5 NORM in scale, sludge and produced water

NORM accumulates in elevated concentrations in oil and gas waste streams primarily when radium isotopes are dissolved from the subsurface formation and carried to the surface in the produced water (Smith, 1992). The oil and gas waste streams most likely to be contaminated by increased NORM concentrations comprise produced water, scale, and sludge. Their existence is dependent on some parameters of the reservoir and that can be activated if the reservoir is flooded with water (Kpeglo, 2015).

2.5.1 Produced water

Produced water is known to be the highest volume of waste generated when it comes to oil and gas production operations (Kpeglo et al, 2016). Produced water is made up of formation water from the reservoir, injected water, addition of chemicals in the course of the separation of oil/water and/or condensed water. Volumes of produced water vary between installations and over the lifetime of a field, with a distinctive range of 2400–40 000 m^3 d^{-1} for oil producing facilities and 1.5–30 m^3 d^{-1} for gas production. It may contain ^{226}Ra, ^{228}Ra, ^{224}Ra and ^{210}Pb in concentrations of up to a few hundred Becquerel per litre but is virtually free of ^{228}Th (IAEA, 2003).

Since Radium-226 is an intermediary constituent of the uranium series, it is one of the Naturally Occurring Radioactive Materials of key interest. Due to its solubility in water it is categorized as water borne pollutant. Radium emerges at the surface dissolved in the water that comes with the hydrocarbons. The content of radium depends on the amount of radium available in sub-surface formation, formation water chemistry, extraction and treatment processes and the age of the waste after production (Kpeglo et al, 2016). Radium concentrations in produced water vary from undetectable levels to 103.6 Bq L^{-1}

(Snavely, 1989).

A recent study of oil-field produced water discharged to the Gulf of Mexico offshore Louisiana recorded average total radium concentrations of 19.9 Bq L^{-1} (9.7 Bq L^{-1} of Ra-226 and 10.2 Bq L^{-1} of Ra-228). Brine produced at oil and gas facilities in Michigan measured as high as 1073 Bq L^{-1} of Radium-226, although only a limited number of samples were collected. The Nuclear Regulatory Commission's limit for total radium content in liquid wastes discharged to areas of unrestricted access is 1.1 Bq L^{-1}. The current drinking water standard under the Safe Drinking Water Act (SDWA) is 0.19 Bq L^{-1} (Smith, 1992).

A study of the Norwegian offshore oil production installations recorded mean concentrations of 4.1 Bq L^{-1} for ^{226}Ra and 2.1 Bq L^{-1} for ^{228}Ra even though concentrations at different facilities may be higher. There is a significant variation between the activity concentration ratios of ^{226}Ra and ^{228}Ra. As a result, the principal radionuclide may be ^{226}Ra or ^{228}Ra or ^{210}Pb (IAEA, 2003).

The activity concentrations of ^{226}Ra and ^{228}Ra in produced water primarily depend on the uranium and thorium concentrations in reservoir sand. High levels of radium leaches out to the formation water from the reservoir sand and host rocks than to low aquifer portable water under increased temperature and pressure conditions where the reservoir temperature may exceed 150^{o}C. In the Norwegian offshore oil production facilities, mean concentration of radium were measured at 4 Bq L^{-1} for ^{226}Ra and 2 Bq L^{-1} for ^{228}Ra (Lysebo and Strand, 1997). The activity concentration of ^{226}Ra in the produced water of one Australian offshore petroleum production facility was estimated at 17 Bq L^{-1} and that of ^{228}Ra at 23 Bq L^{-1} (APPEA, 2002).

2.5.2 Scale

Generally, the utmost concentrations of radium that form when dissolved radium co-precipitates with strontium, barium or calcium sulfates are found in scale deposits. These sulfates form hard, insoluble deposits on the inside of piping, filters, brine disposal/injection wells, and other water handling equipment. A significant drop in temperature and pressure involving the reservoir and crude oil can accumulate scale in the well tubing. Forming of scales can be expected based on the concentrations of cations and anions in the formation water, temperature and pressure in the reservoir and well tubing (Odo and Tomson, 1994).

The water chemistry of a number of reservoir wells can be considerably dissimilar. A number of them may have higher concentration of barium and strontium and low concentration of sulfate while the formation water of others may be lacking in barium and strontium though they may have higher concentration of sulfate. This occurs when a portion of the reservoir is drowned by water from the sea, which has higher concentration of sulfate, to maximize the pressure of production. In such situations rigorous forming of scale takes place when the two types of incompatible water combine in a production header (Kpeglo, 2015).

From a management viewpoint, the most ‘difficult’ type of NORM is the insoluble barium sulfate scale that is created inside pipes and vessels. They are normally high in radioactivity compared to carbonate scales. The accumulation of scale in pipes and vessels can also lead to difficulties in production such as clogging of pipes and valves and detrimental accretion of enormous amounts of NORM solids in vessels and separators (Kvasnicka, 1998).

In Michigan, radioactive scale deposits have also been detected on exterior surfaces of downhole casing and tubing. Scale deposits can solidify and may need to be gotten rid of by cleaning processes to be certain that equipment will function. In general, radium concentrations are highest in wellhead piping and in production piping near the wellhead. Radium content in most scale ranges from background levels to several thousand picocuries per gram. On the other hand, much higher concentrations have been measured in Michigan (i.e., from 2812 to 58 883 Bq g^{-1} of Radium-226), suggesting that the range of NORM concentration is much greater (Smith, 1992).

2.5.3 Sludge

Sludge deposits are made up of accrued heavy hydrocarbons, tight emulsions, produced formation sand, and marginal quantities of corrosion and scaly debris that settle out of suspension in some oilfield equipment. Normally, sludge consists of fine sand particles, corrosive particles, and flakes of paint, bacteria growth obtained from scale. In gas plants, sludge containing radium solids buildup in separators containing Lead-210/Polonium-210 and must be occasionally gotten rid of (APPEA, 2002). Generally, radium concentrations in sludge are much lower than radium concentration in scale collected from pipes. NORM in sludge add up when radium co-precipitates with sulphates and carbonates inside piping, separators, heater/treaters, storage tanks, and any other equipment where produced water is managed.

Typically, NORM - contaminated sludge is characterized by trace radium concentrations that range from background to 11.1 Bq g^{-1} (Baird et al. 1990), even though in Michigan

one sludge sample recorded as high as 244.2 Bq g^{-1} (Smith, 1992).

2.6 Radiation protection aspects of NORM

During production in the petroleum industry, it is likely that NORM could cause external exposure as a result of the accumulations of radionuclides that emit gamma rays as well as internal exposures of workers and other persons. This usually occurs when waste and contaminated equipment are being transported, during maintenance, decontaminating equipment, managing and discarding of waste in the absence of suitable radiation protection measures. Similar exposures may result from the decommissioning of petroleum production installations and facilities that manage waste (Zaidan, 2010; Kpeglo, 2015).

2.6.1 Radiation Exposure Pathway

There are seven environmental pathways through which exposure to radiation from oil and gas NORM can take place. It includes inhalation of radon, external gamma exposure, ingestion of ground water, ingestion of surface water, inhalation of dust, skin beta exposure and ingestion of food (Smith, 1992). Persons at risk from exposure to NORM radiation consist of oilfield workers, workers at NORM disposal facilities, workers at equipment cleaning facilities and the general public. Workers that are considered to be at the greatest risk of exposure to NORM are those in charge of cleaning the facilities equipment.

Exposure pathways of interest are external gamma exposure, dust inhalation, and skin

beta exposure. External exposure results from high concentration of Naturally Occurring Radioactive Materials within equipment such that its walls are not able to block the gamma radiations. When NORM are gotten rid of from the equipment, it eliminates the shielding factor the equipment walls provide. It is likely to inhale dust during dry cleaning processes if appropriate measures are not put in place to control it. Skin beta exposures are possible if scale and sludge are handled directly (Kpeglo, 2015).

Workers at NORM disposal facilities are at risk of exposure via radon inhalation, external gamma exposure, dust inhalation, and skin beta exposure pathways. Risk is increased at facilities where NORM contaminated waste and equipment are buried without control features (i.e., not at licensed NORM or low level waste facilities) and at smelter facilities where NORM detection systems have not been installed.

2.6.2 External Exposure

Dose rates inside and outside the components in Table 2.6 may increase if contaminated scales and sludge are deposited in pipes and vessels. Short lived progeny of the radium isotopes, ^{226}Ra specifically, emit gamma radiation which has the ability of penetrating the walls of these components, and the high energy photon emitted by ^{208}Tl (one of the progeny of ^{228}Th) can add up to the dose rate on outer surfaces when scale has been building up for a number of months. The dose rates depend on the quantity and activity concentrations of the radionuclides present inside and the shielding reached several hundred microsieverts per hour, which is about 1000 times higher than normal background values because of cosmic radiation and terrestrial radiation (Zaidan, 2010).

Table 2.6: Dose rates of external gamma radiation in some oil production and processing facilities (Zaidan, 2010)

Location	Dose rate (μSv/h)
Down hole tubing, safety valve (internal)	Up to 300
Wellheads, production manifold	0.1 – 22.5
Production lines	0.3 - 4
Separator (scale measured internally)	Up to 200
Separator (scale measured externally)	Up to 15
Water outlets	0.2 – 0.5

The accumulation of radium scales can be checked without opening the equipment (Plate 2.1). Disassembling the system for repairs or other intentions can cause an escalation in dose rates where scales are available. External exposures can be controlled by increasing the distance from, and decreasing the period of exposure to, the radioactive materials of concern. Practically, limiting occupancy time is very efficient since it restricts yearly doses to low values. Deposits made up of solely ^{210}Pb can't be estimated by external readings of closed plant or equipment. The low energy gamma emissions of ^{210}Pb and beta particles radiated does not penetrate the steel wall. Thus, ^{210}Pb doesn't make a significant contribution to external dose. Workers can only be exposed when equipments are opened.

Plate 2.1: Monitoring the outside of equipment/plant with a dose rate meter (Zaidan, 2010)

2.6.3 Internal exposure

Internal exposure to Naturally Occurring Radioactive Materials may be due to ingestion or inhalation of radionuclides. This may happen while operating on or in open plant or equipment, handling waste materials and surface contaminated objects, and during the cleaning of contaminated equipment. Ingestion can also occur if precautions are not taken before eating, drinking, smoking, etc. Efficient precautions are needed during the afore-mentioned activities to avoid radioactive contamination and avert its transfer to parts where additional persons might also be exposed. The non-radioactive characteristics of scales and sludge demand conventional safety measures, therefore the risk of ingesting NORM is likely to be very low. On the other hand, cleaning contaminated surfaces in the

course of reparation, renovation or other forms of operation may produce aerial radioactive material, especially if arid abrasive methods are applied. The exposure from inhalation could become relevant if efficient personal protective equipment (respiratory protection inclusive) and/or engineered controls are not used. Both the physical and chemical characteristics of NORM are dependent on the potential committed dose from inhalation. It is imperative to note the components of radionuclide and activity concentrations, the activity aerodynamic size distribution of the particles which is quantified by AMAD, and the chemical forms of the elements and the respective lung absorption types". The BSS (IAEA, 2014) estimated the subsequent lung absorption types for the elements of importance for dose calculations:

a. Radium (all compounds): medium (M)
b. Lead (all compounds): fast (F)
c. Polonium (all unspecified compounds): fast (F)

   (Oxides, hydroxides, nitrates): medium (M)

d. Bismuth (nitrate): fast (F)

   (All unspecified compounds): medium (M)
e. Thorium (all unspecified compounds): medium (M)

   (Oxides, hydroxides): slow (S).

Table 2.7: Dose per unit intake for inhalation of radionuclides in particles of NORM Scale (IAEA, 2003)

Committed effective dose per unit intake (Sv / Bq)			
Radionuclides	5μm AMAD		1μm AMAD
	Slowest lung absorption type listed in BSS	Slow (S) absorption type	Slowest lung absorption type listed in BSS
Ra-226	2.26×10^{-6}	3.8×10^{-5}	3.2×10^{-6}
Pb-210	1.1×10^{-6}	4.5×10^{-6}	8.9×10^{-7}
Po-210	2.2×10^{-6}	2.8×10^{-6}	3.0×10^{-6}
Ra-228	1.7×10^{-6}	1.2×10^{-5}	2.6×10^{-6}
Th-228	3.2×10^{-6}	3.2×10^{-5}	3.9×10^{-5}
Ra-224	2.4×10^{-6}	2.8×10^{-6}	2.9×10^{-6}

Table 2.7 illustrates the effective dose per unit intake of dust particles of 5 μm AMAD and 1 μm AMAD for the default size distribution for routine work conditions and a size distribution likely to be suitable for operations like the ones that involve the usage of high temperature cutting torches respectively. In every instance, values are estimated for the slowest lung absorption type enumerated in the (BSS, 2014) (S represents thorium; M represents radium, polonium and bismuth, and F for lead (Table 2.7). Additionally, based on a more conventional assumption that all radionuclides are of lung absorption type S, values for 5 μm AMAD calculated by Silk are cited. Table-2.7 shows that the inhalation of particles of 5 μm AMAD merging ^{226}Ra in addition to its whole decay chain in equilibrium, ^{228}Ra, and ^{224}Ra including its whole decay chain also in equilibrium, every

single one at a concentration of 10 Bqg^{-1}, would give a committed effective dose per unit intake around 0.1–1.0 $mSvg^{-1}$, the true value reliant on the magnitude of in growth of ^{228}Th from ^{228}Ra and the lung absorption types assumed. Based on the slowest lung absorption types enumerated in the BSS, the committed effective dose per unit intake for 1 μm AMAD particles would be about 25–30% higher (IAEA, 2003).

2.7 Practical Radiation Protection Measures

The conventional conditions for radiation protection and safety in the BSS apply to equipments in the oil and gas industry associated with NORM. The main objective in all circumstances is to keep radiation doses as low as reasonably achievable, economic and social factors being taken into account (ALARA), and below the regulatory dose limits for workers. The feasible precautions that must be considered to be able to meet these objectives differ primarily for each of the types of radiation exposure; internal contamination and external radiation (IAEA, 2014).

2.7.1 Measures against External Exposure

The availability of NORM in equipments is not likely to bring about external exposures that exceed the dose limits for workers in a year. External dose rates from NORM in practical work are normally very low and may not require protective measures. In special situations where there are significant but localized dose rates, the following fundamental rules can be applied to reduce any external exposure and its contribution to total dose:

a. Reducing the period of any needed external exposure;

b. Maintaining optimal distances between any build-up of NORM and potentially exposed people;

c. Protecting people likely to be exposed by keeping shielding material between them and the NORM.

Practically, rule (a) and (b) include designating supervised or controlled areas with restricted access. An effective method to minimize dose rates from sources of radiation is using a shielding material though it is unlikely that it can be included in shielding a mass build-up of NORM. Nevertheless, the principle can be used practically by making sure that NORM are sealed off and behind thick steel walls of installations for as long as possible whilst plans are being put in place to dispose of the material. If enormous quantities of high specific activity NORM waste are stockpiled, some forms of confined shielding using wastes with low activity may be needed to minimize gamma dose rates on the outside of the waste storage facility to low levels.

2.7.2 Measures against Internal Exposure

Internal exposure may arise from ingestion or inhalation of NORM whilst working with uncontained/uncontrolled material or due to uncontrolled spreading of radioactive contamination, where suitable control measures are absent. The risk of ingestion or inhalation of any contaminated (radioactive) substance is reduced by adhering to the fundamental guidelines, where workers:

a. Use the correct protective clothing to minimize the dangers associated with the transfer of contamination

b. Abstain from smoking, drinking eating, chewing for instance gum, usage of cosmetics (medical or barrier creams, etc.), licking labels, or any other activities that maximize the danger of transferring radioactive materials to the face in the course of work;

c. Wear appropriate respiratory protective equipment to avoid inhaling any likely airborne radioactive contamination

d. Use feasible work procedures which will keep NORM contamination wet or that confine it to avoid airborne contamination;

e. Put into practice the habit of keeping the house clean at all times to avoid the spreading of NORM contamination;

f. Comply with the rules of industrial hygiene like washing protective clothing carefully as well as hand washing after work.

2.8 Health effects of NORM

The primary health risk of concern when dealing with NORM; is the potential for developing cancer. Ingested radium has been associated with bone cancer, bone sarcoma, and head carcinoma, the last of which is presumably caused by production of radon gas that accumulates in head cavities (Mays et al., 1985). Radon which is a decay product of radium exists as a gas and is associated with occurrences of lung cancer (Wanty and Schoen, 1993). The immediate decay products of ^{222}Rn are radionuclides with short half-lives, which attach themselves to fine particles in the air, and when inhaled, irradiate the tissues of the lung with alpha particles, and increase the risk of lung cancer

Radon has been recognized as a radiation hazard causing excess lung cancer among underground miners (ICRP, 1981). As a result radon has been classified as a human carcinogen (IARC, 1988). Since the 1970s, evidence has been increasing that radon can also represent a health hazard in non- mining environments (WHO, 1993; ICRP, 1993). Since environmental radon on the average accounts for about half of all human exposure to radiation from natural sources, increasing attention has been paid to exposure to radon and its associated health risks in the oil and gas industry (Kathren, 1998).

2.8.1 Potential effects of NORM on the receiving environment

Fauna or flora does not have radiation protection dose limits. The ICRP recommended a recent principle of environmental radiation protection for flora and fauna (ICRP, 2007). It stated that when man is protected by some radiological standards then biota is also protected. This indicates that, as long as radiation exposure to the public due to discharges from NORM or by disposal of NORM waste does not exceed the public limit of 1 $mSvy^{-1}$, then biota would receive up to standard radiation doses. This idea of environmental radiation protection applies to the oil and gas industry NORM due to the radioactivity levels in the oil and gas industry (APPEA, 2002):

a. Oil and gas industry NORM are Low Specific Activity (LSA) radioactive materials and they have a low rate of generation. As a result of this, exposures to radiation and the impact on marine life radiologically as a result of discharges of small quantities of NORM are possible to insignificant.

b. The content of radionuclide in creek and river sediments may be increased by

release of produced water from onshore petroleum facilities and this might cause a likely pollution of portable water.

c. The radiological impact because of offshore and onshore discharges should be projected for a critical group of the public considering site specific conditions.

NORM discharged to the environment can lead to an increase in the radiation doses of humans through different pathways and the potentially highest radiation exposures are estimated putting into consideration all essential exposure pathways, to be received by the "critical group of the public" (APPEA, 2002). The critical group for every petroleum facility that discharges NORM to the environment must be defined.

2.8.2 Personal exposures due to NORM radiation in petroleum production

Alpha, beta and gamma radiation are natural radionuclides produced by NORM. Therefore, external and internal radiation exposure can result from NORM. Workers get exposed to all forms of radiation externally such as radiations from gamma during regular tasks. Gamma rays penetrate through steel walls of pipes and vessels and the dose rate at the surface of the production pipes and vessels could be increase every hour in the order of tens of μSv. During shutdowns and maintenance periods, workers may be exposed to radon gas and NORM dust through inhalation as well as external gamma radiation (Kvasnicka, 1996). Considering that the specific activity of radium in barium (radium) sulphate scale can exceed 500 Bqg^{-1} (Kvasnicka, 1996), scale dust inhaled must be a hundred milligrams to cause the radiation dose to exceed the public dose limit of 1mSv in a year. Though a tiny proportion of radon gas is released from scale, the radon gas

concentrations in non-ventilated vessels with scale, sludge or sand could lead to high radiation exposures. The potential of inhaling dust from NORM and radon gas makes management of radiation exposures of workers during shutdowns dissimilar from managing radiation exposures at periods of normal task (Kvasnicka, 1996).

2.9 Overview of Ghana's Upstream Oil and Gas Industry

Twenty-four other discoveries as shown in Table 2.8 have been made in the offshore Western Basin following the success story of the Jubilee Field discovery in 2007.

Currently, there are two producing oil fields. They are the Jubilee and TEN oil fields both operated by Tullow Oil Ghana and its partners (Kosmos Energy, Anadarko Petroleum, Petro SA and GNPC).

Table 2.8: Oil and Gas Discoveries in Ghana (Courtesy: Petroleum Commission of Ghana, 2015)

Contact Area	Operator	Discoveries	Discovery Date	Hydrocarbon Type	Status
Expanded Shallow Water Tano	Erin (CAMAC) Energy	North Tano South Tano West Tano	Philips-1980 Philips-1978 Dana-2000	Oil	Appraised
Shallow Tano	Interoil	Ebony	November 2008	Gas/Condensate	Marginal/Relinquished
Deepwater Tano	Tullow Oil	Tweneboa-1	March 2009	Gas condensate	Development
		Tweneboa-2	January 2010	Oil	Development
		Owo/Enyera-1	September 2010	Oil	Development
		Ntomme	January 2012	Oil and Gas	Development
		Wawa	2012	Oil and Gas	Appraisal
West Cape Three Points	Kosmos Energy	Odum-1	February 2008	Heavy Oil	Relinquished
		Teak-1	February 2011	Oil and Gas	Appraised
		Teak-2	March 2011	Gas	Appraised
		Banda-1	June 2011	Oil	Relinquished
		Mahogany Deep	January 2009	Light Oil	Appraised
		Akasa-1	August 2011	Light Oil and Gas	Appraised
Offshore Cape Three	ENI	Sankofa-1	September 2009	Gas	Development
		Gye Nyame-1	July 2011	Gas	Development
Deepwater Tano Cape Three Points	Hess	Paradise-1	July 2011	Oil and Condensate	Appraisal
		Hickory North-1	May 2012	Oil and Condensate	Appraisal
		Almond-1	September 2012	Oil and Condensate	Appraised
		Beech-1	August 2012	Oil	Appraised
		Cob-1	January 2013	Oil	Appraisal
		Pecan	December 2012	Oil	Appraised
		PN-1	February 2013	Oil	Appraised
Deepwater Cape Three Points	Lukoil	Dzata-1	February 2010	Oil and Gas	Relinquished
		Lynx-1X	July 2014	Oil and Gas	Relinquished

CHAPTER THREE

MATERIALS AND METHOD

Overview

This Chapter highlights on detailed description of the study area, sampling, sample preparation and measurement procedures and mathematical formalisms that are used in the calculation of the activity concentration, the radiation hazard indices, the radium equivalent activity, the radon emanation coefficient and radon mass exhalation rate. The chapter also highlights how results generated were summarized and analyzed.

3.1 Description of Study Area

3.1.1 Jubilee Oil Field

The Jubilee oil field is situated off the coast of the Western Region of Ghana in the South Atlantic Ocean. It is located 60 km offshore, between the Deepwater Tano and West Cape Three Points blocks. It forms the southern-most tip of Ghana, and its closest location in the sea is at 0 latitude, 0 longitude, and 0 altitude. Its temperature ranges from 23.8 to 26.4 ºC with average temperature around 24.9 ºC (GNPC, 2013).

The offshore oil and gas production facility (Floating Production Storage Offloading (FPSO) Kwame Nkrumah) has been in operation in the field since June 2010. It has two main oil blocks. They are West Cape Three Points and Deep Water Tano. Figure 3.2 shows the Ghana offshore activity map for Cape Three Points. The Jubilee Field is a reserve of oil and gas located offshore Ghana. It is approximately 60 km from the nearest

coast and lies in deep water (1,100–1,700 m), on both sides of two oil concession blocks".

Tullow is the designated operator of the Jubilee fields offshore the west coast of Ghana. Tullow Ghana limited (TGL) is oil and gas exploration and production company that is registered accordingly with the Ghana National Petroleum Corporation and the Petroleum Commission of Ghana.

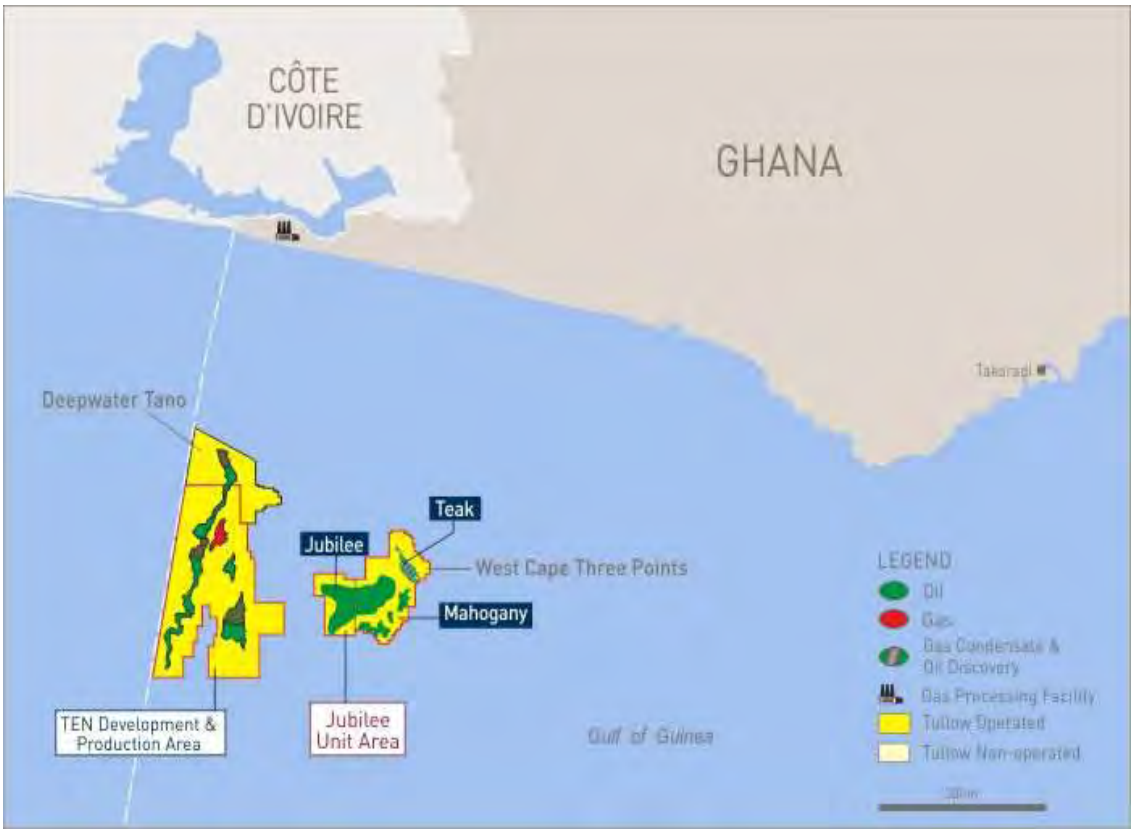

Figure 3.1: The Jubilee Unit Area (Tullow Ghana Limited, 2018).

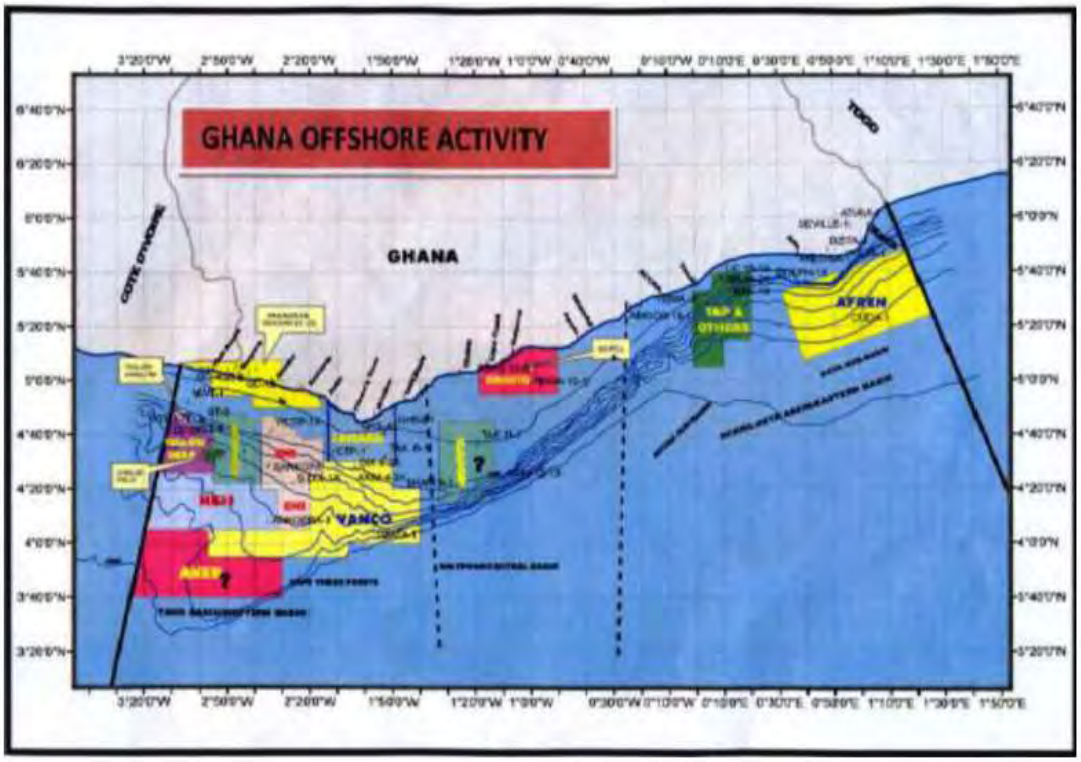

Figure 3.2: Ghana offshore activity map (PC, 2018)

3.1.2 Geology of Jubilee Oilfield

The Tano-Cape Three Points Basin is a Cretaceous wrench modified pull-apart basin. It was formed from trans-tensional movement at the period of the separation of southern West Africa and northern South America. Active rifting led to the creation of a deep basin. As time went by, there was further thinning of the continental crust and sea floor widened. New oceanic crust was created at the trailing edges of the two continental plates as they began dividing and the two plates finally separated. Existing conditions at the time were best for the shale deposition; consequently, thick organic rich shale was built-up. A number river systems added significant clastic into the deep basin leading to deposition of large turbidite fan/channel complexes. Some sandstone was in tilted fault

blocks as reservoirs. Trapping is both stratigraphic and structural. Since the 1890's the hydrocarbon potential of the basin of Ghana's quota has been known based on onshore oil seeps although the main discovery was made in 2007 at the Jubilee Field with oil production beginning in December, 2010 (Kpeglo, 2015).

3.2 Sampling and sample preparation

A total number of twenty-five (25) samples were collectively taken from the Jubilee Oil field on the FPSO Kwame Nkrumah. They included five (5) sludge samples, ten (10) crude oil samples and ten (10) produced water samples received from Tullow Ghana in May, 2018. In the laboratory, each of the samples were homogenized and transferred into 1 or 0.5 litre Marinelli beakers. The Marinelli beakers with the samples were completely sealed using radon impermeable tapes and stored for 1 month, to allow the short-lived daughters of ^{238}U and ^{232}Th decay series to attain secular equilibrium with their long-lived parent radionuclides (ASTM, 1983; 1986).

The sealed samples were weighed and each counted using a Sodium Iodide (NaI) detector.

3.3 Preparation of sample and Gamma spectroscopy measurement

3.3.1 Instrumentation and calibration

Direct gamma spectrometry analysis without pre-treatment (non-destructive) was used for the measurement of gamma rays for the crude oil, sludge and produced water samples using a Sodium Iodide (NaI) detector. The gamma spectrometry system is made up of

NaI detector coupled to a computer based multi-channel analyzer (MCA). The relative efficiency of the detector is 7% with energy resolution of 2.0 keV at gamma ray energy of 1332 keV of ^{60}Co. The identification of individual radionuclides was done using their characteristic gamma-ray energies and the quantitative analysis of radionuclides was also done by using the Maestro gamma acquisition and analysis software (Figure 3.4). The detector is housed in a 100 mm passive shielding of lead lined with copper, cadmium and plexiglass (3mm each) to minimize the background radiation (Figure 3.3). So as to determine the background distribution in the environment around the detector (quality control), ten (10) empty Marinelli beakers were thoroughly cleaned using nitric acid and counted for 36000 s in the same geometry as the samples. The background spectra were used to correct the net peak area of gamma rays of measured isotopes. The background spectra were also used to determine the minimum detectable activities of radionuclides at each photo peak for the detector.

Energy and efficiency calibrations were undertaken by counting standard radionuclides of known activities with well-defined energies in the energy range of 60 keV to ~2000 keV. For the analysis of waste water samples, the efficiency calibration was carried out using standard radionuclides uniformly distributed in solid water with volume and density of 1000cm^3 and 0.98 gcm^{-3} respectively (source number: AJ-9177 and manufactured by Eckert & Ziegler Nuclitec GmbH).

Figure 3.3: Gamma spectrometry system with NaI detector

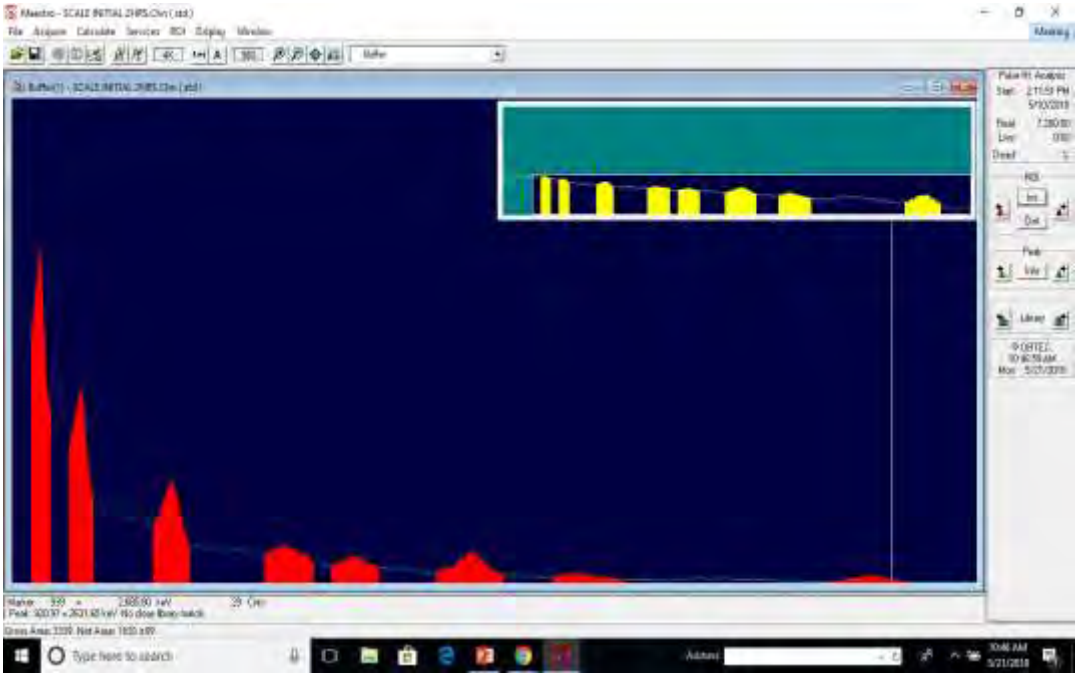

Figure 3.4: Maestro gamma acquisition and analysis software interface

3.4 Preparation of sample and alpha-particle spectrometry measurement

The preparation of the sample and conditioning prior to the beginning of the alpha-particle spectrometry measurement is a very tedious task. It is inevitable to steer clear of self-absorption effects in dealing with the application of radiochemical procedures for the isolation of the radionuclides of interest specific source preparations (Figure 3.5).

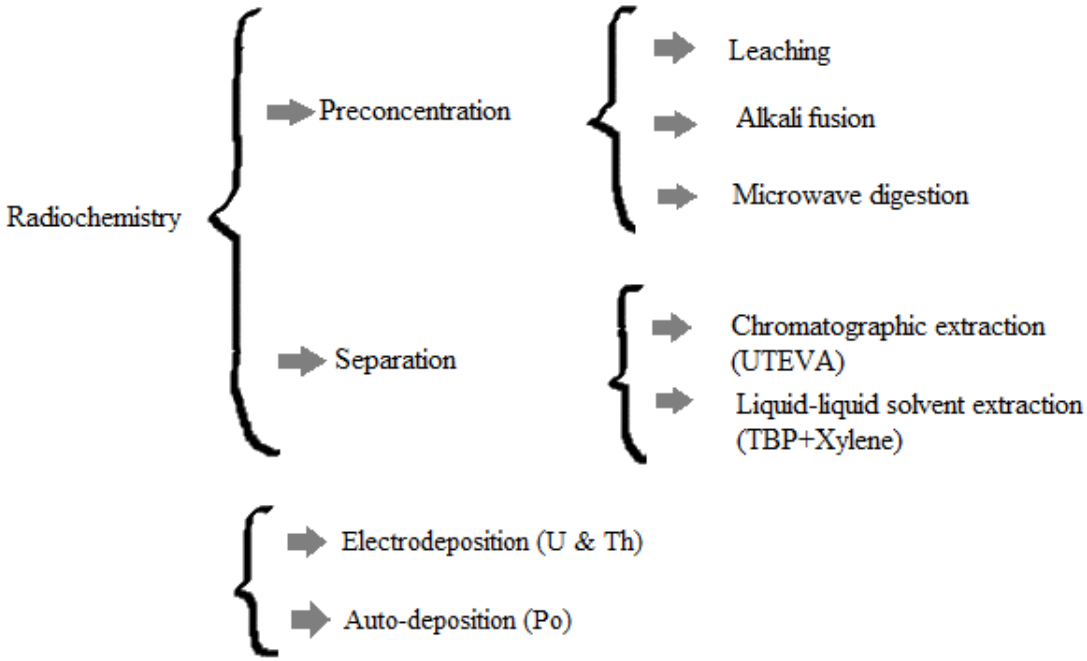

Figure 3.5: Summary of the analytical steps in Alpha Spectrometry.

After sampling, water samples were acidified with concentrated HNO_3 (65%) to pH 2-3. This is to prevent the growth of microorganisms and make the interactions with the walls of the storage containers minimal before the laboratory analysis is conducted.

Three major steps are involved in the liquid and solid matrix sample preparations for U and Th determination in Alpha-particle spectrometry. These are pre-concentration, radiochemical separation and electrodeposition.

For the water samples, the pre-concentration of U and Th was done by the co-precipitation of actinides with iron hydroxide. 0.5L of the water sample was taken from an already homogenized sample/storage container. After filtration known concentrations of 0.352 Bqg^{-1} of ^{232}U tracer and 0.1137 Bqg^{-1} of ^{229}Th tracer were added while gently warming at 30°C and stirring to ensure complete homogenization. Afterwards, 2ml of Fe^{3+} solution (5 mg/mL) were added and the pH was adjusted to 8.0-8.5 with concentrated NH_3 (25%) leading to the co-precipitation of actinides with iron hydroxide. Carefully, the supernatant was removed after the precipitate had settled down. The remained fraction was then centrifuged at 4500rpm for 10 minutes. The precipitate, incorporated with U and Th, was dried and dissolved in 5ml of 3M HNO_3 before the radiochemical separation stage began.

For solid samples, after adding the same tracers indicated earlier, 0.63g of dried homogenized solid sample aliquot was taken and calcinated at 600°C for a duration of 24hrs. Afterwards the ashed material was wet digested with aqua regia for 4hrs at 50°C using the leaching technique. 12mL of H_2O_2 was then added in drops and 45mL of concentrated HNO_3 (65%) was also added while the sample was stirred for 12hrs at constant room temperature. Lastly, 30mL of 8M HNO_3 was added, after which filtration was done. The filtered fraction was evaporated to 10mL and topped to 50mL with distilled water. The final solution of 50mL obtained was then submitted to the same

actinides co-precipitation iron hydroxide procedure for water samples described earlier (Lehritani et al, 2011).

In the case of crude oil, the samples were digested using a microwave digester with the application of the digestion programme code for light crude oil (0.4g crude + 8mL Conc. HNO_3 + 2mL H_2O_2 + 1mL HCl with digestion time of 30mins). The digested solution was then diluted with distilled water to the 50mL mark and submitted to the same actinides co-precipitation iron hydroxide procedure for water samples described above.

In the radiochemical separation stage, the commercial extraction chromatographic resin known as UTEVA from TRISKEM Co. was applied (Lehritani et al, 2011). For UTEVA technique, the dissolved solution formed by 5mL of 3M HNO_3 obtained from the pre-concentration of U and Th step was directly loaded into an UTEVA resin after releasing the preconditioned 0.1M HNO_3 that these resin contain from the manufacture. The column was then rinsed with 5mL of 3M HNO_3 (this is to extract Po) and afterwards, the Th fraction initially retained in the column was also extracted by loading 4mL of 9M HCl followed by 20mL of 5M HCl. The U fraction was also stripped after by loading 10mL of 0.01M of HCl. Both solutions that were obtained are free from other interfering alpha emitters, that is, 24mL in the case of Th and 10mL in the case of U.

Source preparation for U and Th were electrodeposited independently onto stainless steel discs. The U isotopes were electroplated at 1.2A for 1hr, while Th was electroplated at 1.5A for 2hrs.

The measurement of U and Th isotopes electroplated on stainless steel discs were with 450mm^2 active surface PIPS detectors in an 8-chamber Alpha Analyst System

(Canberra). The efficiency values for all alpha chambers were measured at a source to detector distance of 0.5cm and the same source to detector distance was used for measurements of all samples in this study. Each chamber was exclusively devoted to the measurement of one element to prevent cross contamination. The Genie 2000 software was used in accumulating and analyzing the alpha spectra for 200,000s.

In determining the minimum detectable activity (MDA) of U and Th, the background spectrum was used at a 95% confidence level (~0.1mBq) with a measurement time of 2-3 days.

The accuracy and precision of analytical procedures used in this study for the gamma and alpha spectrometric techniques were validated with the analysis of IAEA SRMs (IAEA381 and IAEA375) under the same experimental conditions as the samples.

3.5 Calculation of activity concentration and estimation of doses

The activity concentrations of ^{226}Ra were determined using the γ-ray emissions and the respective γ-yield of ^{214}Pb at 351.9 keV (35.8%) and ^{214}Bi at 609.3 keV (44.8%). The ^{228}Ra activity concentrations were determined through the gamma emissions of ^{228}Ac at 911 keV (26.6%), and the ^{228}Th activity concentrations were determined through the gamma emissions of ^{212}Pb at 238.6 keV (43.3%) and ^{208}Tl at 583 keV (30.1%) and 2614.7 keV (35.3%) taking into consideration a branching ratio of 33.7% from ^{212}Bi towards ^{208}Tl. The ^{40}K activity concentration was determined directly from its emission line at 1460.8 keV (10.7%) while the ^{137}Cs and ^{210}Pb activity concentrations were determined directly from the gamma emission lines at 661.67 keV (85.1%) and 46.5 keV

(4.3%) respectively. Finally, the ^{238}U activity concentrations were determined through the gamma-ray emission of its daughter ^{234}Th (4.8%) (Kpeglo, 2015). The same procedures were adopted in this work.

3.5.1 Calculation of Activity Concentration

The activity concentrations of radionuclides in the soil/sediments, water and petroleum samples for gamma measurements were calculated from the expression as shown in Equation 1 (Kpeglo, 2015).

$$A_{sp} = \frac{N.e^{\lambda_p t_d}}{p.T_c.\eta.m} \qquad (1)$$

Where;

Asp is the activity concentration

N is the net counts of the radionuclide in the samples,

td is the delay time between sampling and counting,

p is the gamma emission probability (gamma yield),

η is the absolute counting efficiency of the detector system,

Tc is the sample counting time,

m is the mass of the sample (kg) or volume (l),

exp (λpTd) is the decay correction factor for delay between time of sampling and counting, and

λp is the decay constant of f gthe parent radionuclide.

For alpha measurements the activity concentrations were calculated using the isotopic dilution techniques whiles the yield was calculated using Equation 2 (Kpeglo, 2015)

$$A(Bq) = \frac{N}{t.\varepsilon.I.C_1} \quad (2)$$

Where:

A is activity of tracer

N is the net counts of the tracer peak in the samples

t is the sample measurement time

I is the Intensity of alpha emission

ε is the detector efficiency for the measured alpha ray energy for the same chamber

C_1 is the Radiochemical yield calculated for tracer (%)

3.6 Determination of radium equivalent activity and hazard indices

The radiological risk of NORM in sludge in the study area which may be used for road construction, housing/building, cement production, block making etc. was assessed by calculating the radium equivalent activity (Ra_{eq}) and the external hazard and internal hazard indices (OECD/NEA, 1979; Beretka and Mathew, 1985).

The Ra_{eq} is a widely used hazard index used to determine the potential radiological impact on human health and it was calculated using Equation (3).

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K \quad (3)$$

Where; C_{Ra}, C_{Th} and C_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K respectively. The maximum recommended value of Ra_{eq} in raw building materials and products must be less than 370 Bq/kg for safe use. This means that the external gamma dose must be less than 1.5 mSv/year.

The term external hazard index (H_{ex}) is another criterion that is used to estimate the level of gamma ray radiation associated with natural radionuclides in specific construction materials. It is defined as shown in Equation (4).

$$H_{ex} = \frac{C_{Ra}}{370} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \quad (4)$$

Where C_{Ra}, C_{Th} and C_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K respectively. The value of the external hazard index must be less than one for the external gamma radiation hazard to be considered negligible. The radiation exposure due to the radioactivity from construction materials is limited to 1.5 mSv/y.

Also internal hazard index (H_{in}) due to radon and its daughters was calculated from Equation (5). This is based on the fact that, radon and its short-lived products are also hazardous to the respiratory organs.

$$H_{in} = \frac{C_{Ra}}{185} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \quad (5)$$

Where C_{Ra}, C_{Th} and C_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K respectively. For construction materials to be considered safe for construction of dwellings, the internal hazard index should be less than one.

3.7 Determination of radon emanation fraction and radon mass exhalation rate

The waste samples were air-dried and then oven dried to remove any additional moisture from the samples. The dried samples were each transferred into measuring containers without any treatment and vacuum sealed. The emanation fraction measurements were carried out on sludge sample.

The samples were each counted on a Sodium Iodide (NaI) detector after sealing for 2 – 10 hours. The samples were then allowed to stay for 4 weeks for secular equilibrium to be established between ^{226}Ra and its short-lived daughter nuclides of ^{214}Pb and ^{214}Bi. The activity concentration of ^{226}Ra was determined from the average of the peak areas of ^{214}Pb and ^{214}Bi.

The radon emanation fraction was determined using the following method described by White and Rood (2001). In this method, the emanation fraction is determined from the net count rates after sealing the sample container (C_1) and the net count rate after secular equilibrium (C_2). The emanation fraction (EF) determination is based on the increase of ^{222}Rn concentration during the time interval between initial counting time (t_1) at sealing

and counting time after 30 days (t_2). The net count rates at t_1 and t_2 were expressed in Equation 6 and Equation 7;

$$C_1 = A_0 + N\left(1 - e^{-\lambda t_1}\right) \quad (6)$$

$$C_2 = A_0 + N\left(1 - e^{-\lambda t_2}\right) \quad (7)$$

Where:

A_0 is the count rate of ^{222}Rn present in a sample at sealing time t_1;

N is the net count rate of ^{222}Rn emanated after time t_2;

λ is ^{222}Rn decay constant (s^{-1}).

A_0 and N are determined by solving equations (6) and (7) as follows:

In order to simplify equations (6) and (7), x was put in place of $1-e^{-\lambda t1}$ and y put in place of $1-e^{-\lambda t2}$.

The results for N, A_0 and EF are given in equations (8), (9) and (10).

$$N = \frac{C_1 - C_2}{x - y} \quad (8)$$

$$A_0 = \frac{xC_2 - yC_1}{x - y} \quad (9)$$

$$EF = \frac{N}{A_0 + N} \quad (10)$$

The emanation fraction (EF) was calculated from equation (10).

The mass exhalation rate or radon mass exhalation rate is the product of the emanation fraction and ^{222}Rn production rate. The mass exhalation rate (ERn, in Bq/kg) was calculated using the equation:

$$ERn = CRa \times EF \times \lambda_{Rn} \quad (11)$$

Where, CRa is the specific activity of ^{226}Ra (in Bq/kg) and λ_{Rn} is the decay constant of ^{222}Rn (2.1×10^{-6} per s)".

3.8 Determination of annual effective dose using external gamma dose rate measurement

The annual effective dose was calculated from the measured average outdoor external gamma dose rate using Equation 12 (UNSCEAR, 2000).

$$E_{\gamma,ext}(mSv) = D_{\gamma,ext}.T_{exp}.DCF_{ext}.10^{-3} \quad (12)$$

Where;

$D_{\gamma,ext}$ is the average outdoor external gamma dose rate μGy/h

T_{exp} is the exposure duration per year, 2000 hours and applying an outdoor occupancy factor of 0.2

DCF_{ext} is the effective dose to absorbed dose conversion factor of 0.7 Sv/Gy for environmental exposure to gamma rays".

3.9 Data analysis

Results obtained from the research were subjected to descriptive statistical analysis, where results were summarized into tables and appropriate graphs such as bar charts and pie charts. Statistical test of significance was also generated. It was measured at 95% confidence interval at a p-value <0.05, using SPSS version 16. Since the analysis involved comparing means of radionuclides in crude oil and produced water for both alpha and gamma spectrometry of this research and a previous one (Kpeglo, 2015), the most appropriate statistical test of significance is the paired t-test.

3.9.1 Paired T-Test

The paired t-test is a statistical procedure test used to find if the mean difference between two sets of observations is equal or zero. Each subject is measured twice in a paired t-test; therefore pairs of observations are made. General applications of the paired t-test are case-control studies and repeated-measures designs. In a paired t-test, there are two competing hypotheses; the null hypotheses and the alternate hypothesis. An assumption is made in the null hypothesis that the true mean difference between the paired samples is zero. On the other hand, the alternative hypothesis assumes that the true mean difference between the paired samples is not zero.

The statistical significance is determined by considering the p-value. The probability of observing the test results under the null hypothesis is given by the p-value. A low p-value indicates a low probability of accepting the null hypothesis and a high probability of accepting the alternate hypothesis (Statistical Solutions, 2018).

For the purpose of this research, an assumption is made in the null hypothesis that there is no significant difference between the mean activity concentration of radionuclides in the previous study (Kpeglo, 2015) and this study while the alternative hypothesis indicates that there is significant difference between the mean activity concentration of radionuclides in the previous study and this study.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

Overview

This section focuses on the results, analysis and discussions of the total samples that were collected from the Jubilee Oilfields of Ghana.

4.1 Quality control and validation of Gamma Spectrometry technique

Prior to the analysis, the gamma and alpha detectors were calibrated for energy and efficiency and results are presented in Figure 4.1 to Figure 4.3.

Analytical quality control procedures which were carried out for the gamma and alpha spectrometry systems were necessary in order to authenticate the quality and reliability of measurements.

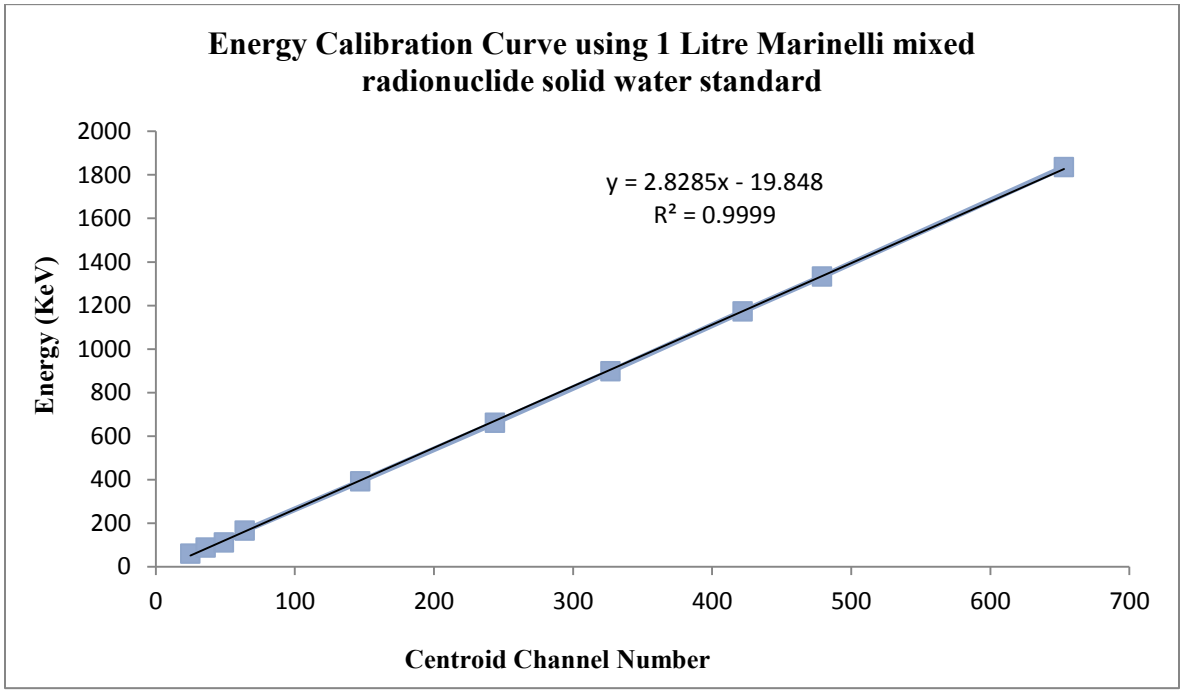

Figure 4.1: Energy calibration curve for gamma spectrometry system

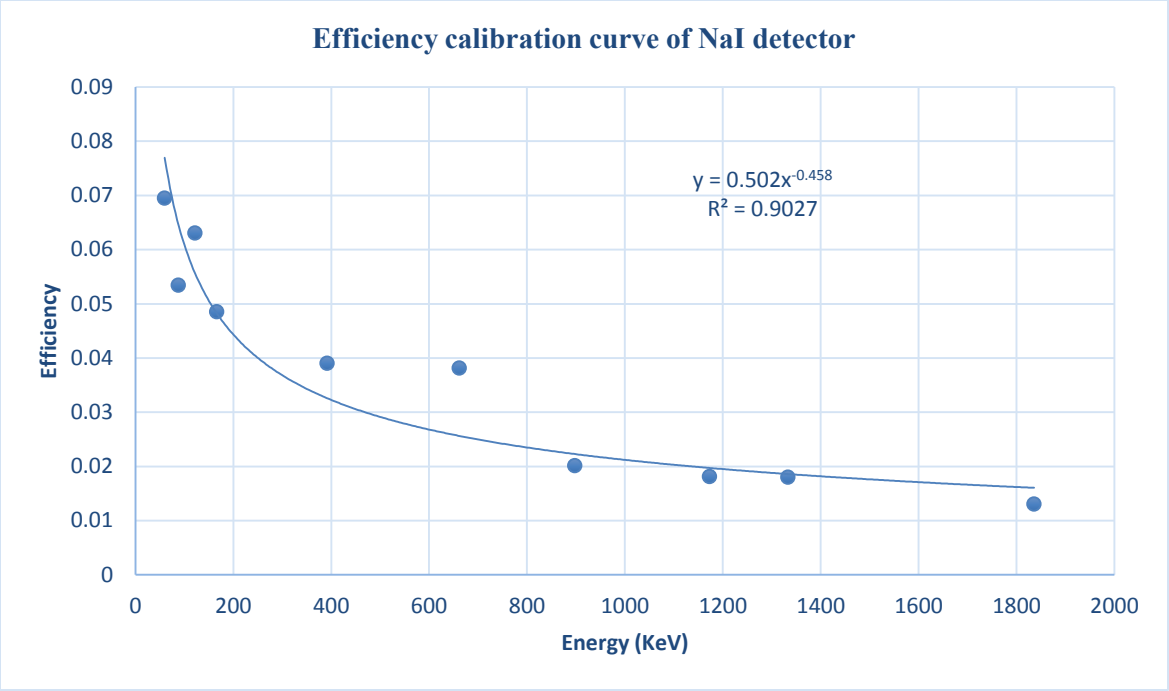

Figure 4.2: Efficiency calibration curve for mixed radionuclide solid water standard in 1L marinelli beaker geometry of NaI detector

The IAEA reference materials IAEA-RGU-1(U-ore), IAEA-RGTh-1 (Th-ore) and IAEA-RGK-1 (K-ore) with mean densities (1.33 ± 0.03 g/cm^3) similar to the mean densities of solid matrix samples to be measured were prepared. 0.5L Marinelli beakers of the same type as that of solid matrix samples were used to estimate the efficiencies for photo peaks of natural radionuclides measured and quantified in the samples.

For liquid matrix samples, a multi-gamma certified cocktail standard (^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{60}Co and ^{88}Y,) uniformly distributed in solid water with volume and density of 1000cm^3 and 0.98 gcm^{-3} respectively was used for efficiency calibration of the gamma system.

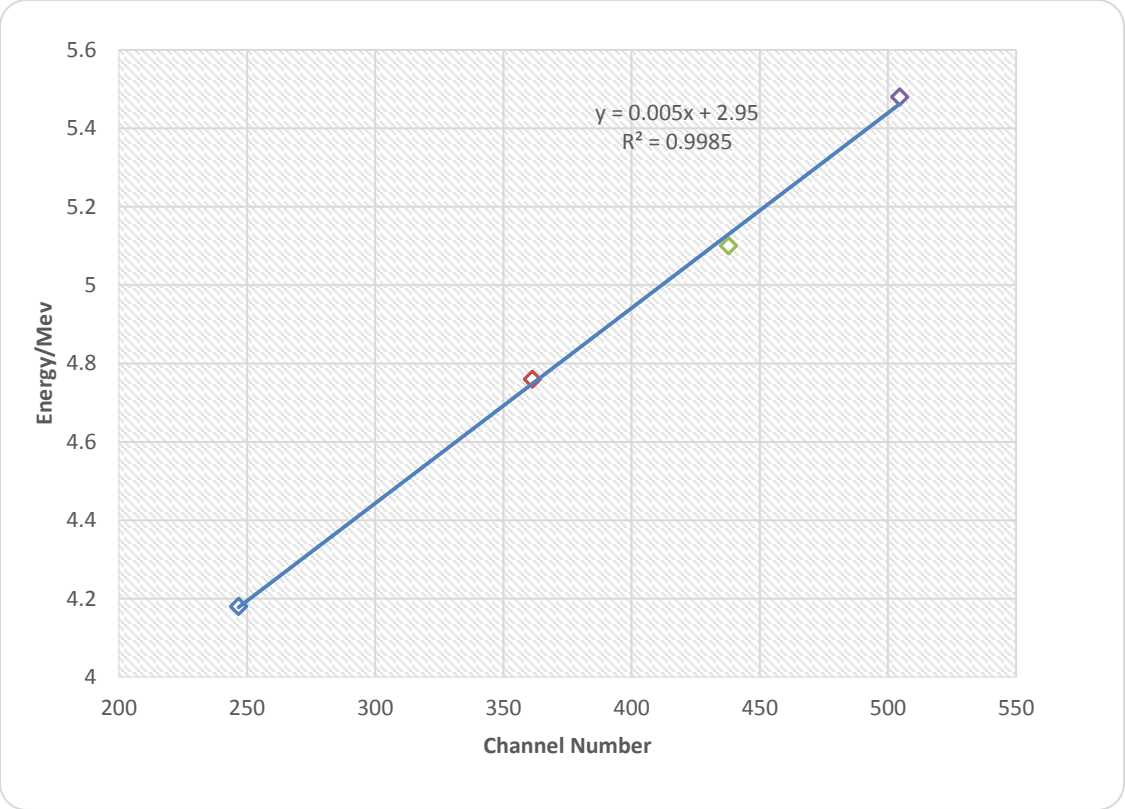

Figure 4.3: Energy calibration curve for alpha spectrometry system with PIPS detection system

The energy calibration for alpha system was done using an Eckert & Ziegler Certified mixed standard radionuclide calibration source (^{241}Am, ^{238}U, ^{234}U and ^{239}Pu) in a 24.1mm diameter by 0.65mm thick stainless steel disk geometry as was used for samples in alpha measurements.

Table 4.1: Results of experimental efficiencies for the alpha chambers at a source to detector distance of 0.5 cm

Chamber	1A	1B	2A	2B	3A	3B	4A	4B
E (%)	20.1±1.2	19.5±1.1	19.0±1.2	19.9±1.1	18.9±1.3	19.3±1.3	19.5±1.3	19.4±1.3

Table 4.1 shows the results of experimental efficiencies for the alpha chambers at a source to detector distance of 0.5 cm. The efficiency values were used for estimation of the radiochemical yields but not the activity concentrations which were calculated based on isotopic dilution method.

The sensitivity of the method used in this work was in good agreement with the reference values for IAEA SRMs as shown in Table 4.2 and Table 4.3

Table 4.2: Analysis of reference material via gamma spectrometry

Sample	Matrix	Density (g.cm-3)	Radionuclide	Reference Value ($Bq.Kg^{-1}$)	Measured value($Bq.kg^{-1}$)	Error (%)
IAEA381	liquid	1.02 ± 0.02	^{137}Cs	0.49 ± 0.01	0.52 ± 0.05	6.12
			^{40}K	11.4 ± 0.9	12.8 ± 1.8	12.3
IAEA375	Solid	1.69 ± 0.17	^{134}Cs	463 ± 9	455 ± 20	1.73
			^{137}Cs	5280 ± 106	5182 ± 108	1.86
			^{40}K	424 ± 8	417 ± 13	1.65
			$^{226}Ra(^{214}Pb)$	20 ± 2	21 ± 2	5.0

Table 4.3: Analysis of reference material via alpha spectrometry

Sample	Matrix	Radionuclide	Reference value ($Bq.kg^{-1}$)	Measured value ($Bq.kg^{-1}$)	Error (%)
IAEA 381	liquid	^{238}U	0.042 ± 0.004	0.044 ± 0.002	4.76
		^{234}U	0.051 ± 0.006	0.053 ± 0.004	3.92
IAEA 375	Solid	^{238}U	24 ± 5	26 ± 5	8.33
		^{234}U	25 ± 7	22 ± 4	12.0
		^{232}Th	21 ± 1	19 ± 2	9.52

4.2 Results of Measurement of radionuclide concentration

4.2.1 Crude oil

Table 4.4 and Table 4.5 show the activity concentrations of the ^{40}K, ^{232}Th and ^{238}U series radionuclides by gamma and alpha spectrometry in crude oil samples. For gamma-ray spectrometry, the specific activities of ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th and ^{40}K for crude oil were below the Minimum Detectable Activity (MDA) as shown in Table 4.4.

Table 4.4: Activity Concentration of ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K and ^{210}Pb in crude oil determined by gamma-ray spectrometry

Sample ID	Activity Concentration ($Bq.L^{-1}$)				
	Ra-226	Pb-210	Ra-228	Th-228	K-40
MDA	<0.45	<1.20	<0.48	<0.20	<1.50

The activities of ^{234}U, ^{238}U, ^{230}Th and ^{232}Th for alpha-particle spectrometry (Table 4.5) were in the range of 160 – 188mBq/L with an average of 171.1 ± 42.4 mBq/L, 139 – 241mBq/L with an average of 207.4 ± 42.5 mBq/L, 93 – 242mBq/L with an average of 176.1 ± 45 mBq/L, 59 – 81mBq/L with an average of 67.6 ± 24.2 mBq/L respectively.

Table 4.5: Activity Concentrations of ^{238}U, ^{234}U, ^{230}Th and ^{232}Th in the Crude oil samples determined by alpha-particle spectrometry

Sample ID	Concentration (mBq/L)			
	^{234}U	^{238}U	^{230}Th	^{232}Th
CO1	160 ± 40	235 ± 51	135 ± 46	72 ± 31
CO2	170 ± 45	230 ± 48	147 ± 67	68 ± 22
CO3	168 ± 40	216 ± 50	93 ± 29	81 ± 30
CO4	172 ± 42	148 ± 33	118 ± 39	62 ± 21
CO5	165 ± 41	139 ± 50	127 ± 49	60 ± 25
CO6	162 ± 42	236 ± 38	237 ± 45	70 ± 24
CO7	175 ± 41	220 ± 29	222 ± 43	59 ± 19
CO8	180 ± 48	200 ± 38	242 ± 47	71 ± 30
CO9	188 ± 45	241 ± 47	215 ± 41	66 ± 19
CO10	171 ± 40	209 ± 41	225 ± 43	67 ± 21
Mean	171.1	207.4	176.1	67.6
SD	8.4	36.08	57.05	6.52
Range	160 - 188	139 - 241	93 - 242	59 - 81

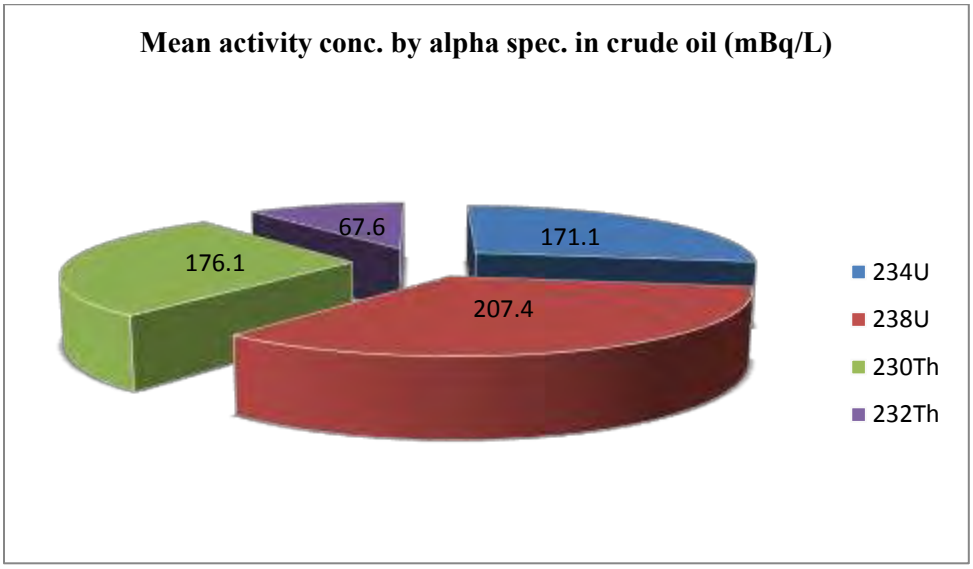

Figure 4.4: Comparison of the mean activity concentration of the various radionuclides in crude oil by alpha spectrometry

In addition, Figure 4.4 gives a pictorial representation of the activity concentrations of the different radionuclides in crude oil. ^{238}U recorded the highest mean activity concentration of 207.4 ± 42.5 mBq/L with ^{232}Th recording the lowest of 67.6 ± 24.2 mBq/L.

A clear observation can be made from Table 4.4 and Table 4.5 that the activity concentrations in crude oil were not significant compared with the worldwide range reported by the IAEA, 2003 in the literature review in Table 2.5 therefore, might not have any significant impact on the health of workers and the public.

Table 4.6: Comparison of mean activity concentration of crude oil from previous study (Kpeglo, 2015) and current study (Alpha Spectrometry)

Sample ID	Concentration (mBq/L)			
	^{230}Th		^{232}Th	
	KPEGLO, 2015	**CURRENT**	**KPEGLO, 2015**	**CURRENT**
CO1	237	135	61	72
CO2	222	147	58	68
CO3	242	93	67	81
CO4	215	118	64	62
CO5	225	127	59	60
CO6		237		70
CO7		222		59
CO8		242		71
CO9		215		66
CO10		225		67
Mean	228.2	176.1	61.8	67.6

In comparing the mean concentration of each of the radionuclides in crude oil from the previous study and this research, it is evident that ^{230}Th from Kpeglo, 2015 was higher than the current study while ^{232}Th was higher in this study than that of the previous work

as shown in Table 4.6. The observed difference seen in ^{230}Th can be attributed to the 'unsupportive' nature of parent radionuclides and the characteristics of the reservoir rocks in oil wells.

Table 4.7: Paired T-test results for ^{230}Th in crude oil

Sample Pair	Mean	SD	Standard Error	p-value
$^{230}Th_1$- $^{230}Th_2$	1.04E+02	27.179	8.573	0.001

Table 4.7 shows the paired t-test results for ^{230}Th. The p-value of 0.001 is less than 0.05 which is statistically significant. This implies that there is a significant difference between the activity concentrations of ^{230}Th in crude oil from the previous study and this research work.

Table 4.8: Paired T-test results for ^{232}Th in crude oil

Sample Pair	Mean	SD	Standard Error	p-value
$^{232}Th_1$- $^{232}Th_2$	-6.80000	6.90652	3.08869	0.092

The p-value 0.092 of ^{232}Th is greater than 0.05 as shown in Table 4.8, this indicates that the test is statistically insignificant, and therefore there is no statistical significant difference between the activity concentrations of ^{232}Th in crude oil from the previous study and this research work.

A statistical association could not be established for ^{238}U and ^{234}U sample pair. This is because the activity concentrations for each of these radionuclides in the previous study

were below detection limit therefore a comparison between their activities could not be made.

4.2.2 Sludge

For sludge samples (gamma-particle spectrometry), the average specific activity of ^{226}Ra was 350 ± 50 Bq.kg^{-1} (in the range of 320 – 380 Bq.kg^{-1}); ^{210}Pb had an average of 190 ± 40 Bq.kg^{-1} (in the range of 170 – 200 Bq.kg^{-1}); for ^{228}Ra, the average was 220 ± 500 Bq.kg^{-1} (in the range of 200 – 250 Bq.kg^{-1}); while for ^{228}Th , the average was 140 ± 30 Bq.kg^{-1} (in a range of 120 – 160 Bq.kg^{-1}); and ^{40}K ranged from 60 – 100 Bq.kg^{-1} with an average of 80 ±10 kBq.kg^{-1}.

Table 4.9: Activity Concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K, ^{210}Pb, and ^{234}Th in Sludge determined by gamma-ray spectrometry

Sample ID	Activity Concentration (kBq.kg^{-1})				
	Ra-226	Pb-210	Ra-228	Th-228	K-40
SL1	0.35 ± 0.05	0.20 ± 0.05	0.25 ± 0.5	0.12 ± 0.02	0.08 ± 0.01
SL2	0.34 ± 0.04	0.18 ± 0.04	0.22 ± 0.6	0.15 ± 0.03	0.06 ± 0.01
SL3	0.36 ± 0.05	0.19 ± 0.05	0.21 ± 0.5	0.16 ± 0.04	0.09 ± 0.02
SL4	0.38 ± 0.06	0.17 ± 0.03	0.20 ± 0.5	0.14 ± 0.02	0.10 ± 0.01
SL5	0.32 ± 0.04	0.20 ± 0.04	0.24 ± 0.5	0.13 ± 0.04	0.07 ± 0.01
Mean	0.35	0.188	0.224	0.14	0.08
SD	0.02	0.01	0.02	0.02	0.02
Range	0.32 – 0.38	0.17 – 0.2	0.2 – 0.25	0.12 – 0.16	0.06 – 0.1
DRLs	300	300	300	300	300

The mean activity concentrations of the radionuclides determined by the gamma spectrometry were all within the aqueous Derived Release limits of the Canadian guidelines except ^{226}Ra which exceeded the DRL of 300 Bq/kg as shown in Table 4.9 and represented in Figure 4.5.

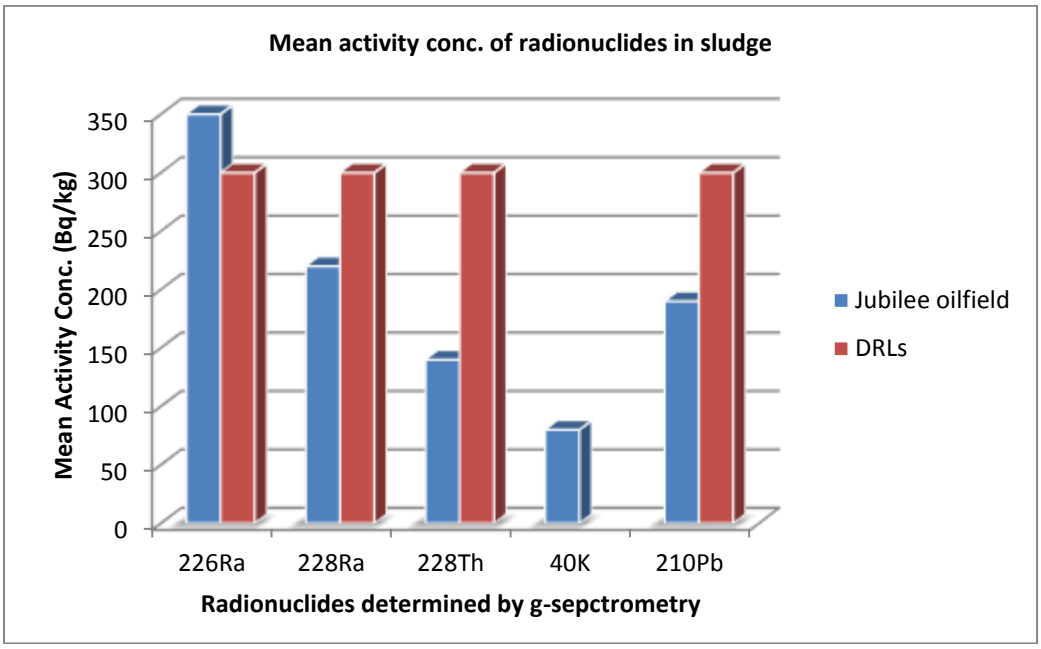

Figure 4.5: Comparison of the mean specific activity of radionuclides in sludge for Jubilee Oilfields with the Canadian Derived Release Limits – Aqueous NORM Sources

The activity concentrations of ^{234}U, ^{238}U, ^{230}Th and ^{232}Th in the sludge samples that were determined by alpha-particle spectrometry are represented in Table 4.10. ^{234}U activities were in the range of 10.1 – 15.8 Bq/kg with an average of 12.18 ± 1.5 Bq/kg, ^{238}U activities ranged from 7.1 – 13.2 Bq/kg with an average of 10.4 ± 1.6 Bq/kg, ^{230}Th activities ranged from 4.7 – 9.8 Bq/kg with average of 6.6 ± 0.7 Bq/kg and ^{232}Th activities also ranged from 3.3 – 10.4 Bq/kg with an average of 5.58 ± 0.7 Bq/kg.

Table 4.10: Activity Concentrations of ^{238}U, ^{234}U, ^{230}Th and ^{232}Th in Sludge samples determined by alpha-particle spectrometry

Sample ID	Concentration (Bq.kg^{-1})			
	^{234}U	^{238}U	^{230}Th	^{232}Th
SL1	10.2 ± 1.0	7.1 ± 1.8	6.9 ± 0.8	4.5 ± 0.5
SL2	12.4 ± 1.7	10.2 ± 1.5	4.7 ± 0.5	3.3 ± 0.6
SL3	15.8 ± 1.0	11.2 ± 1.2	6.5 ± 0.7	10.4 ± 1.1
SL4	12.4 ± 1.7	10.3 ± 1.5	5.1 ± 0.5	3.3 ± 0.5
SL5	10.1 ± 1.9	13.2 ± 2.1	9.8 ± 0.9	6.4 ± 1.0
Mean	12.18	10.4	6.6	5.58
SD	2.32	2.20	2.01	2.98
Range	10.1 – 15.8	7.1 – 13.2	4.7 – 9.8	3.3 – 10.4

Figure 4.6 gives a pictorial presentation of the activity concentrations of the different radionuclides in sludge. ^{238}U recorded the highest mean activity concentration of 12.18 ± 1.5 Bq/kg with ^{232}Th recording the lowest of 5.58 ± 0.7 Bq/kg.

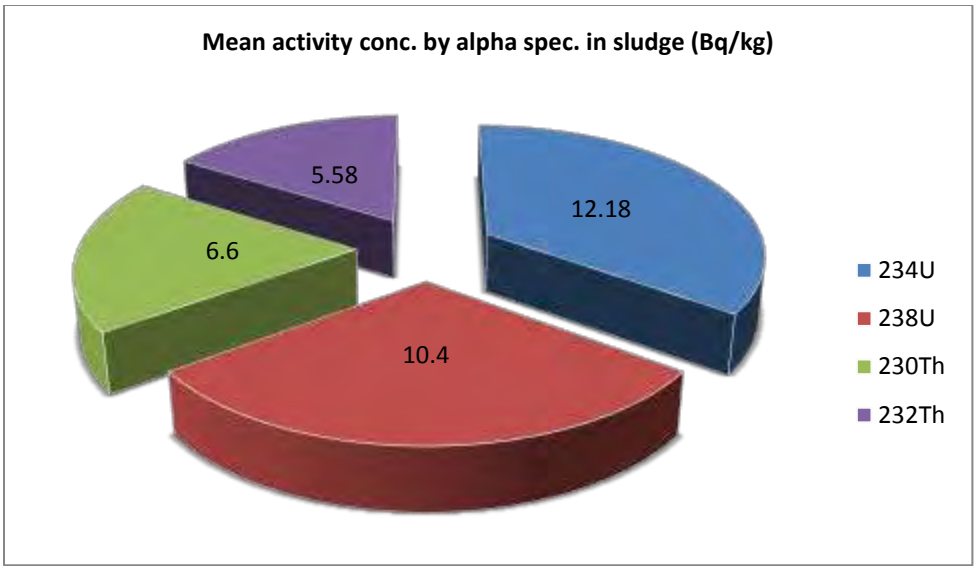

Figure 4.6: Comparison of the mean activity concentrations of the radionuclides in sludge by alpha spectrometry

In Table 4.11, a comparison of the results of ^{226}Ra and ^{228}Ra in sludge was made with data from other countries. The range of activity concentration of ^{226}Ra and ^{228}Ra from this study was lower than the values recorded for other studies in Malaysia, Norway, Syria and Brazil, with Brazil recording the highest (Omar et al., 2004; Lysebo et al., 1996; Al-Masri and Suman, 2003; Godoy and Crux, 2003). Previous study conducted by Kpeglo, 2015, in Ghana also recorded higher values of activity concentration for ^{226}Ra and ^{228}Ra compared to this present work. This can be attributed to the difference in the source of the sludge sample, which could be from either crude oil or produced water storage tanks. However, this study recorded higher values than that of Algeria (Heaton and Lambley, 1995).

Table 4.11: Comparison of ^{226}Ra and ^{228}Ra in Sludge from Ghanaian oilfields with others published in literature

Country	^{226}Ra (kBq/kg)	^{228}Ra (kBq/kg)	Reference
Ghana	0.32- 0.38	0.2 – 0.25	Present Study
	0.6 – 8.4	0.3 – 5.6	Kpeglo, 2015
Algeria	0.069 – 0.393		Heaton and Lambley, 1995
Brazil	0.36 - 367	0.25 - 343	Godoy and Crux, 2003
Malaysia	0.006 – 0.56	4.52	Omar et al., 2004
Norway	0.1 – 4.7	0.1 – 4.6	Lysebo et al., 1996
Syria	0.47 - 1	0.359 – 0.66	Al-Masri and Suman, 2003

In all, the mean activity concentrations of the radionuclides were all within the aqueous Derived Release limits of the Canadian guidelines except ^{226}Ra which exceeded the DRL of 300 Bq/kg.

The geochemical and geological characteristics of reservoir rocks, the type of hydrocarbons, operating conditions and age of the oilfields may be the reasons for the disparity in the activity concentrations of natural radionuclide content in NORM waste of different sources.

No statistical test of association (paired t-test) could be established between the sludge samples. This is as a result of the different sources from which the sludge samples were obtained for the different studies conducted.

4.2.3 Produced water

The activity concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th, ^{224}Ra and ^{40}K in the produced water

samples from the Jubilee Oilfields that was determined by gamma-ray spectrometry are presented in Table 4.12. The activity concentration of ^{226}Ra was in the range of 8.0 - 9.0 Bq/L with an average of 7.64 ± 0.3 Bq/L; while for ^{228}Ra, the range was from 7.8 - 8.9 Bq/L with an average of 7.62 ± 0.4 Bq/L. For ^{228}Th, the range was from 3.0 - 3.7 Bq/L with an average of 2.91 ± 0.6 Bq/L. In the case of ^{40}K, the range was from 12.0 – 13.2 Bq/L with an average of 11.11 ± 0.8 Bq/L; whiles ^{224}Ra was in the range of 2.8 -3.5 Bq/L also with an average of 2.78 ± 0.6 Bq/L.

Table 4.12: Activity Concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th, ^{224}Ra and ^{40}K in produced water, determined by gamma-ray spectrometry

Sample ID	Concentration (Bq/L)					^{228}Ra/^{226}Ra
	^{226}Ra	^{228}Ra	^{228}Th	^{40}K	^{224}Ra	
PW1	8.6 ± 0.3	8.3 ± 0.4	3.4 ± 0.5	12.3 ± 0.8	3.0 ± 0.6	0.97
PW2	8.4 ± 0.3	8.5 ± 0.3	3.1 ± 0.7	12.2 ± 0.8	3.2 ± 0.5	1.01
PW3	8.3 ± 0.1	8.6 ± 0.2	3.0 ± 0.5	11.8 ± 0.5	3.1 ± 0.4	1.04
PW4	8.7 ± 0.3	8.8 ± 0.4	3.2 ± 0.6	12.8 ± 1.0	2.8 ± 0.7	1.01
PW5	8.5 ± 0.2	8.2 ± 0.3	3.1 ± 0.5	13.2 ± 1.2	3.3 ± 0.5	0.96
PW6	8.8 ± 0.3	8.9 ± 0.5	3.7 ± 0.8	12.1 ± 0.7	3.5 ± 0.8	1.01
PW7	8.3 ± 0.2	7.8 ± 0.5	3.4 ± 0.6	12.2 ± 0.8	3.2 ± 0.7	0.94
PW8	8.0 ± 0.4	8.2 ± 0.3	3.2 ± 0.5	12.3 ± 0.8	3.0 ± 0.6	1.03
PW9	8.4 ± 0.5	8.5 ± 0.4	3.3 ± 0.5	12.5 ± 0.9	2.9 ± 0.6	1.01
PW10	9.0 ± 0.5	8.7 ± 0.6	3.1 ± 0.6	12.0 ± 0.7	2.8 ± 0.7	0.97
Mean	7.64	7.62	2.91	11.11	2.78	0.90
SD	0.29	0.33	0.21	0.41	0.23	0.03
Range	8.0-9.0	7.8-8.9	3.0-3.7	12.0-13.2	2.8-3.5	0.94-1.04

The radium isotopic ratios for ^{226}Ra and ^{228}Ra were calculated for the Jubilee Oilfield as shown in Table 4.12. The ratio was in the range of 0.94 – 1.04 with an average of 0.90. This represents the different U and Th concentrations from the oil producing wells of the oilfield as well as the lithological properties of the reservoir.

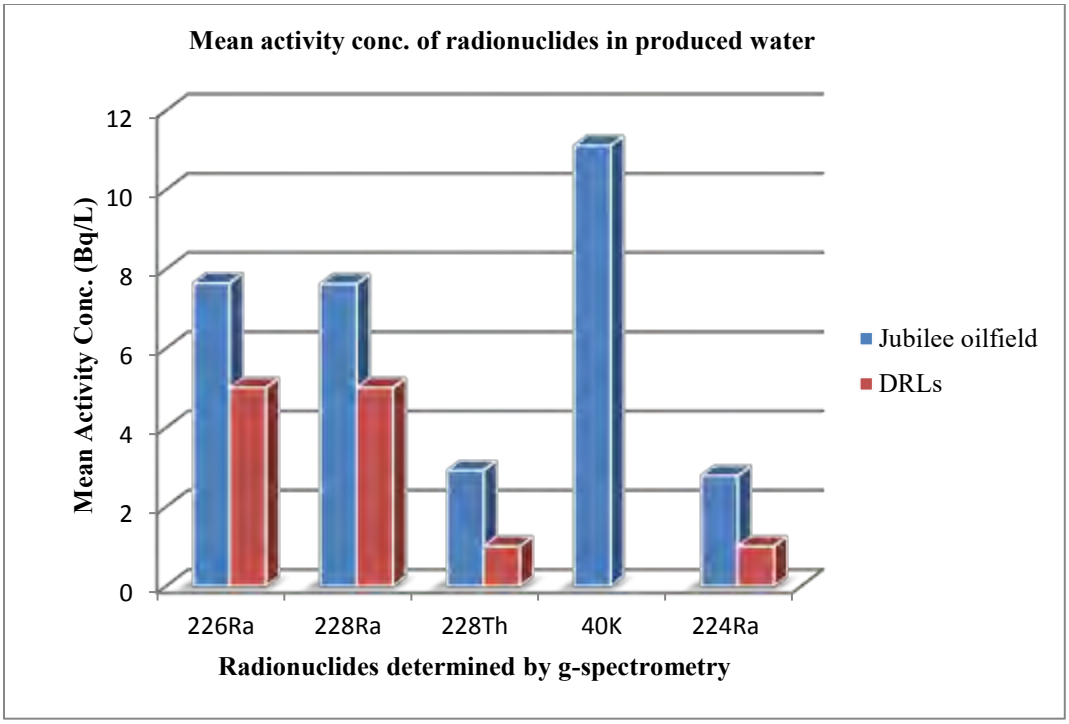

Figure 4.7: Comparison of the mean specific activity of radionuclides in produced water for Jubilee Oilfields with the Canadian Derived Release Limits – Aqueous NORM Sources

Figure 4.7 shows a comparison of the mean specific activity concentrations of the different radionuclides present in produced water and the aqueous Derived Release Limit (DRL) of the Canadian guideline governing liquid discharges (Health Canada, 2011). It is observed from the figure that all the radionuclides exceeded the DRLs of Canada. This may be due to factors such as the operating conditions of the oilfield, the type of hydrocarbons produced and the geological properties of the reservoir rocks.

Table 4.13: Activity Concentrations of ^{238}U, ^{234}U, ^{230}Th and ^{232}Th in Produced water samples determined by alpha-particle spectrometry

Sample ID	Concentration (mBq/L)			
	^{234}U	^{238}U	^{230}Th	^{232}Th
PW1	10.2 ± 2.2	11.5 ± 2.5	7.5 ± 1.2	4.8 ± 1.1
PW2	7.0 ± 1.5	6.2 ± 1.2	9.1 ± 2.0	3.8 ± 1.8
PW3	9.1 ± 1.1	12.3 ± 2.0	8.5 ± 0.9	5.5 ± 1.2
PW4	6.8 ± 1.6	7.4 ± 1.2	10.2 ± 2.1	7.1 ± 1.9
PW5	5.9 ± 1.5	5.0 ± 2.1	5.8 ± 1.0	4.7 ± 1.1
PW6	7.0 ± 1.5	6.3 ± 1.2	9.1 ± 2.0	3.8 ± 1.8
PW7	12.5 ± 2.8	10.4 ± 2.5	11.1 ± 0.9	5.6 ± 1.5
PW8	7.8 ± 1.2	5.3 ± 0.8	7.0 ± 1.3	4.5 ± 1.0
PW9	10.2 ± 2.2	11.5 ± 2.5	7.9 ± 1.2	5.7 ± 1.1
PW10	9.0 ± 1.1	12.4 ± 2.0	8.8 ± 0.9	6.5 ± 1.2
Mean	8.55	8.83	8.5	5.2
SD	2.03	3.06	1.54	1.09
Range	6.8 – 12.5	5 – 12.4	5.8 – 11.1	3.8 – 7.1
*DRLs	10000	10000	5000	1000

*DRLs: Canadian Derived Release Limits – Diffuse NORM Sources

The activity concentrations of ^{234}U, ^{238}U, ^{230}Th and ^{232}Th in the produced water samples that were determined by alpha-particle spectrometry are presented in Table 4.13. ^{234}U activities were in the range of 6.8 – 12.5 mBq/L with an average of 8.55 ± 1.7 mBq/L, ^{238}U activities ranged from 5 – 12.4 mBq/L with an average of 8.83 ± 1.6 mBq/L, ^{230}Th

activities ranged from 5.8 – 11.1mBq/L with average of 8.5 ± 1.4 mBq/L and ^{232}Th activities also ranged from 3.8 – 7.1 mBq/L with an average of 5.2 ± 1.4 mBq/L.

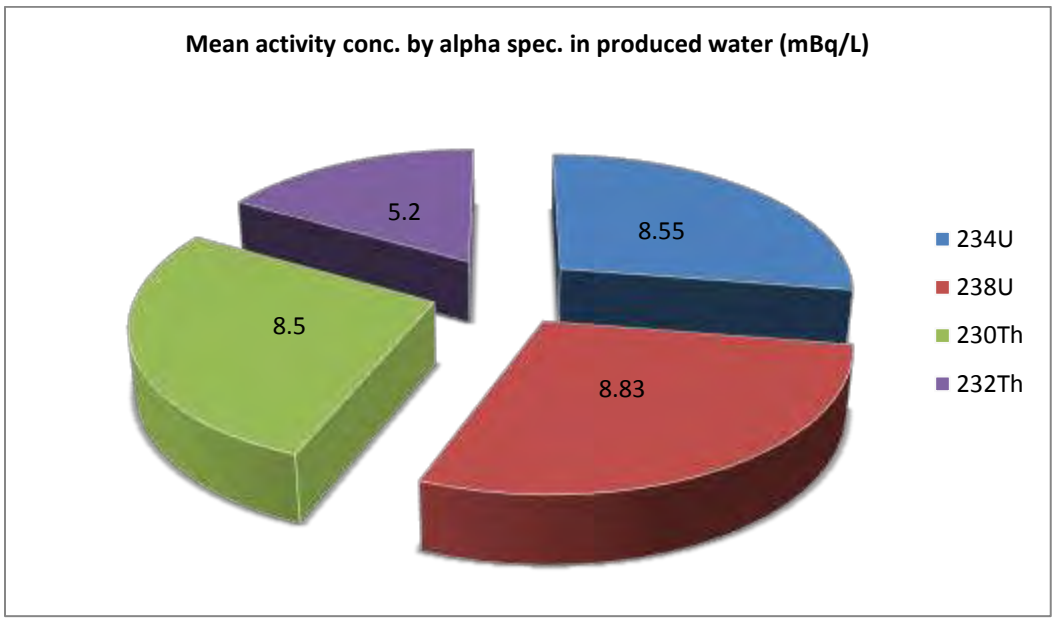

Figure 4.8: Comparison of the mean activity concentrations of the radionuclides in produced water by alpha spectrometry

Figure 4.8 gives a pictorial presentation of the activity concentrations of the different radionuclides in produced water. ^{238}U recorded the highest mean activity concentration of 8.83 ± 1.6 mBq/L with ^{232}Th recording the lowest of 5.2 ± 1.4 mBq/L.

Table 4.14 also shows results of the comparison of ^{226}Ra and ^{228}Ra in produced water of Ghanaian oilfields with other countries published in literature. It gives an indication of relatively high concentrations of radium compared to radium concentrations in other oilfields in other countries. The Al Jafra, Attala and Qahar oilfields of Syria are reported to have higher radium concentration in produced water (Al-Masri, 2005), as well as the

Gulf of Mexico (Stephenson, 1992). However, all the results were within the worldwide range of 0.002 – 1200 Bq/L for ^{226}Ra and 0.3 – 180 Bq/L for ^{228}Ra as reported by the IAEA in 2003 (Table 2.5, literature review). Comparatively, there has been a relative increase in the Radium concentration of the Jubilee oilfields of Ghana from 2015 to the present time. This increase can be attributed to the maturity of the oilfields from the commencement of production in 2010 to the present year (2018).

Table 4.14: Comparison of ^{226}Ra and ^{228}Ra in produced water from Ghanaian oilfields with others published in literature

Country	Field	^{226}Ra (Bq/L)		^{228}Ra (Bq/L)		Reference
		Range	Mean	Range	Mean	
Ghana	Jubilee	8.0 – 9.0	7.64	7.8 – 8.9	7.62	Present Study
	Saltpond	18.7 - 22.3	20.5	31.6 –33.5	33.3	Kpeglo, 2015
	Jubilee	6.2 – 7.6	6.8	6.4 – 6.9	6.6	Kpeglo, 2015
Norway	Brage		9		17	Røe, 1998
	Oseberg F		6		11	Røe, 1998
	Oseberg C		7		<2	Røe, 1998
	Troll		6		7	Røe, 1998
	Continental Shelf	<1 - 16	3.3	<1 - 21	2.8	NRPA, 2004
		<DL - 16	4.1	<DL – 10.0	2.1	Strand et al., 1997
USA	Gulf Coast	<0.002 -58	11.7	0.02 - 59	15.5	Kraemer and Reid, 1984
	Louisiana	<DL – 34.4	5.9	<DL -34.3	6.1	Hamilton et al.,1991
	Gulf Coast	2 - 55		2.6 - 22		Lagera et al., 1999
	Gulf of Mexico	3.4-55.3		6.0-22.2		Hart et al., 1995
	Gulf of Mexico	0.2 – 21.6	9.7	0.7-21.7	10.3	Stephenson snd Supernaw, 1990
	Santa Barbara channel, CA		6.1		5.1	Neff, 1997
Nigeria	Delta state	3.5-10.8	6.0	3.4-9.3	5.2	Avwiri et al.,2013
Brazil	Barcia de Campos	<0.01 – 6.0		<0.05-12.0		Jeres veguira et al, 2002
Netherlands	Dutch North Sea	<2 - 302		<1 - 20		NRPA, 2004
Australia			17	23		APPEA, 2002
Denmark		<DL -11.1				NRPA, 2004
Syria	Al Jafra	13.8-111.2	51.9	12.4-67.4	37.5	Al-Masri, 2005
	Attala	9.9-58	41.0	8.8-50.5	35.0	Al-Masri, 2005
	Qahar	13.9-20.9	18.7	20.7-57.5	26.1	Al-Masri, 2005
Algeria		5.1-14.8				Hamlat et al., 2001
UK			1.7			UKOOA, 1992
Canada	Scotian Shelf		0.04		0.34	Nelson, 2007
	Grand Banks		1.2		8.5	Nelson, 2007
Indonesia	S. Java sea	0.3-2.1		0.02-0.66		Neff & Foster, 1997
World-wide		0.002-1200		0.3-180		Jonkers et al., 1997

In general, the activity concentrations that were obtained for all the radionuclides in the samples were below the aqueous Derived Release Limit (DRL) of the Canadian guidelines governing liquid discharges (Health Canada, 2011). Also, the activity concentrations of U and Th isotopes in produced water were lower compared to that of the radium isotopes earlier discussed.

As reported by Kpeglo, (2015), many different oil and gas fields from which NORM has been analysed indicates that solids found in downhole and surface structures of oil and gas production facilities excludes ^{238}U and ^{232}Th. They are not gathered together from the reservoir work that holds the oil, gas and formation water. The formation water consists of cations of calcium, barium, strontium and radium dissolved from the reservoir rock. As a result, formation water is made up of radium isotopes ^{228}Ra and ^{224}Ra from the ^{232}Th series and ^{226}Ra from the ^{238}U series. Their parents do not appear in the water produced together with the oil or gas but all three radium isotopes do. Their long lived parents ^{238}U and ^{232}Th and ^{228}Th remain in the reservoir, therefore known as 'unsupported'.

Table 4.15: Comparison of the mean activity concentration of the radionuclides in produced water from previous study (Kpeglo, 2015) and current study (Gamma Spectrometry)

Sample ID	Concentration (Bq/L)									
	^{226}Ra		^{228}Ra		^{228}Th		^{224}Ra		^{40}K	
	KPEGLO, 2015	**CURRENT**	**KPEGLO, 2015**	**CURRENT**	**KPEGLO, 2015**	**CURRENT**	**KPEGLO, 2015**	**CURRENT**	**KPEGLO, 2015**	**CURRENT**
PW1	6.7	8.6	6.6	8.3	0.82	3.4	0.82	3	6.3	12.3
PW2	7.6	8.4	6.9	8.5	1.22	3.1	1.43	3.2	8.3	12.2
PW3	6.2	8.3	6.4	8.6	0.71	3	0.69	3.1	7.7	11.8
PW4	6.6	8.7	6.6	8.8	0.81	3.2	0.78	2.8	5.9	12.8
PW5	6.8	8.5	6.7	8.2	0.92	3.1	0.92	3.3	7.3	13.2
PW6		8.8		8.9		3.7		3.5		12.1
PW7		8.3		7.8		3.4		3.2		12.2
PW8		8		8.2		3.2		3		12.3
PW9		8.4		8.5		3.3		2.9		12.5
PW10		9		8.7		3.1		2.8		12
Mean	6.78	8.5	6.64	8.45	0.896	3.25	0.928	3.08	7.1	12.34

In comparing the mean concentration of each of the radionuclides in produced water from the previous study and this research, it is evident that the mean activity concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th, ^{224}Ra and ^{40}K from this research were higher compared with the study by Kpeglo, 2015 as presented in Table 4.15.

Table 4.16: Paired T-test results for ^{226}Ra in produced water

Sample Pair	Mean	SD	Standard Error	p-value
$^{226}Ra_1$- $^{226}Ra_2$	-1.72000	0.54037	0.24166	0.002

The p-value obtained from the T-test (0.002) as shown in Table 4.16, is less than 0.05 which is statistically significant. This shows that there is a significant difference between the activity concentrations of ^{226}Ra in produced water from the previous study and this research work.

Table 4.17: Paired T-test results for ^{226}Ra in produced water

Sample Pair	Mean	SD	Standard Error	p-value
$^{228}Ra_1$- $^{228}Ra_2$	-7.55200	0.40580	0.18148	0.000

The p-value of 0.000 in Table 4.17 is less than 0.05 which is statistically significant. This shows that there is a significant difference between the activity concentrations of ^{228}Ra in produced water from the previous study and this research work.

Table 4.18: Paired T-test results for ^{228}Th in produced water

Sample Pair	Mean	SD	Standard Error	p-value
$^{228}Th_1$- $^{228}Th_2$	3.48000	0.22804	0.10198	0.000

The p-value of 0.000 in Table 4.18 is less than 0.05 which is statistically significant. This implies that there is a significant difference between the activity concentrations of ^{228}Th in produced water from the previous study and this research work.

Table 4.19: Paired T-test results for ^{224}Ra in produced water

Sample Pair	Mean	SD	Standard Error	p-value
$^{224}Ra_1$- $^{224}Ra_2$	-1.156E1	0.56279	0.25169	0.000

The p-value of 0.000 in Table 4.19 is less than 0.05. The mean difference then is statistically significant. This indicates that there is a significant difference between the activity concentrations of ^{224}Ra in produced water from the previous study and this research work.

Table 4.20: Paired T-test results for ^{40}K in produced water

Sample Pair	Mean	SD	Standard Error	p-value
$^{40}K_1$- $^{40}K_2$	4.02000	0.14676	0.37868	0.000

The p-value of 0.000 in Table 4.20 is less than 0.05 at which this test was conducted. Therefore it can be concluded that the mean difference is statistically significant. This implies that there is a significant difference between the activity concentrations of ^{40}K in produced water from the previous study and this research work.

Table 4.21: Comparison of the mean activity concentration the radionuclides in produced water from the previous study (Kpeglo, 2015) and current study (Alpha Spectrometry)

Sample ID	Concentration (mBq/L)							
	^{234}U		^{238}U		^{230}Th		^{232}Th	
	KPEGLO, 2015	**CURRENT**	**KPEGLO, 2015**	**CURRENT**	**KPEGLO, 2015**	**CURRENT**	**KPEGLO, 2015**	**CURRENT**
PW1	6.1	10.2	5.5	11.5	6.4	7.5	2.1	4.8
PW2	2.5	7	2.3	6.2	4.6	9.1	1.7	3.8
PW3	1.6	9.1	1.5	12.3	8	8.5	1.6	5.5
PW4	5.5	6.8	5	7.4	6.8	10.2	5.6	7.1
PW5	4.8	5.9	4.3	5	5.6	5.8	2.7	4.7
PW6		7		6.3		9.1		3.8
PW7		12.5		10.4		11.1		5.6
PW8		7.8		5.3		7		4.5
PW9		10.2		11.5		7.9		5.7
PW10		9		12.4		8.8		6.5
Mean	4.1	8.55	3.72	8.83	6.28	8.5	2.74	5.2

In comparing the mean concentration of each of the radionuclides determined by alpha spectrometry in produced water from the previous study and this research, it is evident that the mean activity concentrations of ^{234}U, ^{238}U, ^{230}Th and ^{232}Th from this research were higher comparatively to the study by Kpeglo, 2015 as shown in Table 4.21.

Table 4.22: Paired T-test results for ^{234}U in produced water

Sample Pair	Mean	SD	Standard Error	p-value
$^{234}U_1$- $^{234}U_2$	-3.70000	2.63439	1.17813	0.035

Table 4.22 shows a p-value of 0.035 which is less than the p-value of 0.05 at which this test was conducted. Therefore it can be concluded that the mean difference is statistically

significant. This implies that there is a significant difference between the activity concentrations of ^{234}U in produced water from the previous study and this research work.

Table 4.23: Paired T-test results for ^{238}U in produced water

Sample Pair	Mean	SD	Standard Error	p-value
$^{238}U_1$- $^{238}U_2$	-4.76000	3.89910	1.74373	0.052

The p-value obtained from this test was 0.052 which is greater than 0.05. Therefore the mean difference is not statistically significant. This implies that there is no statistical significant difference between the activity concentrations of ^{238}U in produced water from the previous study and this research work. This is presented in Table 4.23.

Table 4.24: Paired T-test results for ^{230}Th in produced water

Sample Pair	Mean	SD	Standard Error	p-value
$^{230}Th_1$- $^{230}Th_2$	-1.94000	1.90342	0.85123	0.085

The p-value obtained from this test was 0.085 as shown in Table 4.24 which is greater than 0.05. Therefore the mean difference is statistically insignificant. This implies that there is no statistical significant difference between the activity concentrations of ^{230}Th in produced water from the previous study and this research work. This can be attributed to an error made in the laboratory or during sample preparation.

Table 4.25: Paired T-test results for ^{232}Th in produced water

Sample Pair	Mean	SD	Standard Error	p-value
$^{232}Th_1$- $^{232}Th_2$	-2.44000	0.92087	0.41183	0.04

Table 4.25 shows a p-value of 0.04 less than 0.05 which is statistically significant. This implies that there is a significant difference between the activity concentrations of ^{232}Th in produced water from the previous study and this research work.

4.3 Measurement of Radon emanation fraction, Radon mass exhalation rate, Radium equivalent activity, hazard indices (Internal and External) and the annual effective dose

Radon emanation fraction (EF) is used to assess the amount of ^{222}Rn that is released from waste materials which contains naturally occurring radionuclides. It serves as a principal radiological hazard index for evaluation of ^{222}Rn. ^{222}Rn is known to be more radiologically hazardous to human health than the radionuclides of other radon isotopes. This is due to the fact that ^{222}Rn as well as its individual decay progenies such as ^{210}Pb and ^{210}Po have longer half lives compared to other radon isotopes. The evaluation of the emanation fraction (EF), in this study was limited to the daughter radionuclide of ^{226}Ra content in the waste sample (^{222}Rn).

Table 4.26: Radon emanation fraction and Radon mass exhalation rate for waste samples

Sample ID	Radon emanation fraction (EF)	Radon mass exhalation rate (Rn_{ex}) ($\mu Bq.kg^{-1}.s^{-1}$)
SL1	0.845 ± 0.245	658 ± 94
SL2	0.917 ± 0.283	655 ± 77
SL3	0.895 ± 0.220	693 ± 96
SL4	0.901 ± 0.274	732 ± 116
SL5	0.926 ± 0.295	617 ± 77
Mean	0.897	671
SD	0.032	43
Range	0.845 – 0.926	617 – 732

The mean values obtained for the radon emanation fraction (EF) and the radon mass exhalation rate (Rn_{ex}) as shown in Table 4.26 were 0.897 ± 0.263 and 671 ± 92 $\mu Bq.kg^{-1}.s^{-1}$ with each ranging from 0.845 – 0.926 and 617 – 732 respectively.

Radon release to a large extent is dependent on the physical characteristics of the medium in which the NORM radionuclides are found.

Table 4.27: Radium equivalent activity in (Ra_{eq}), external (H_{ex}) hazard index, internal (H_{in}) hazard index, External gamma absorbed dose rate and external annual effective dose calculated for Sludge samples

Sample ID	Ra_{eq} (Bq/kg)	H_{EX}	H_{IN}	$D_{\gamma r}$ (nGy/h)	$E_{\gamma.ext}$(mSv)
SL1	1085.26	2.93	4.42	480.92	1.35
SL2	1053.72	2.85	4.25	466.2	1.31
SL3	1086.03	2.93	4.42	481.3	1.35
SL4	1043.9	2.82	4.31	463.63	1.30
SL5	1054.49	2.85	4.25	466.64	1.31
Mean	1064.68	2.88	4.33	471.75	1.32
Range	1043.9-1086.03	2.82 – 2.93	4.25 – 4.42	463.63 – 481.3	1.30 – 1.35
*RRV	370	1	1	60	20

*RRV: Recommended Reference Value

Table 4.27 illustrates the hazard parameters for the sludge samples. It gives a presentation of the mean and range of the radium equivalent activity (Ra_{eq}), external (H_{EX}) and internal hazard (H_{IN}) as well as the external annual effective dose ($E_{\gamma.ext}$) and the external gamma absorbed dose rate ($D_{\gamma r}$). The mean value for Ra_{eq} was 1064.68 Bq/kg and fell in the range of 1043.9 – 1086.03 Bq/kg. H_{EX} mean was 2.88 with range from 2.82 – 2.93, H_{IN} mean was 4.33 ranging from 4.25 – 4.42. The $D_{\gamma r}$ mean was 471.75 nGy/h with a range of 463.63 – 481.3; for the $E_{\gamma.ext}$, the mean value was 1.32mSv and ranged from 1.30 – 1.35. From the values obtained for each of the parameters, it can be observed that they all exceeded the recommended reference values for safe use. The external annual effective dose which was calculated using exposure period of 2000hrs per year was below the dose limit for occupationally exposed worker which is 20mSv per year

averaged over 5years (100mSv in 5years and 50mSv in any single year. With this, the sludge samples if not managed properly, could cause a significant radiological risk.

CHAPTER FIVE

SUMMARY/CONCLUSIONS AND RECOMMENDATIONS

Overview

The concluding remarks, summary and recommendations to stakeholder institutions are presented in this chapter.

5.1 Summary

The exploration and production activities of crude oil and generation of waste in the Jubilee oilfield of Ghana has prompted the fundamental objective of this research work which was to re-assess the radiological impact (hazards and risks) to workers and the general public in the study area from exposure to naturally occurring radioactive materials (NORM), as well as to establish a trend analysis on the levels of activity concentration of natural radionuclides.

External gamma-ray exposure from natural radioactivity concentration in sludge was used in the evaluation of radiation exposure. Analytical procedures that were developed for non-destructive gamma spectrometry and alpha spectrometry after radiochemical separation was used in establishing data on the natural radionuclides activity concentration of ^{40}K, ^{238}U and ^{232}Th series for the assessment of radiation exposure.

Data on the activity concentrations of ^{40}K, ^{238}U and ^{232}Th series radionuclides in the different samples including the radiation and doses have been determined. With the application of the gamma-ray spectrometry, the activity concentrations of ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th, ^{224}Ra and ^{40}K have been enumerated as well as the activity concentrations of

^{234}U, ^{238}U, ^{230}Th and ^{232}Th in the different samples using alpha spectrometry after radiochemical separation. The average activity concentrations of each of the radionuclides (^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th and ^{40}K) established by gamma-ray spectrometry in crude oil samples were below the minimum detectable activities (MDA) of <0.45, <1.20, <0.48, <0.20 and <1.50 Bq/L respectively, while the average concentrations of ^{234}U, ^{238}U, ^{230}Th and ^{232}Th evaluated by the alpha spectrometry were 171.1 ± 2.4, 207.4 ± 42.5, 176.1 ± 45 and 67.6 ± 24.2 mBq/L respectively.

The average activity concentrations of each of the radionuclides (^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th and ^{40}K) established by gamma-ray spectrometry in sludge samples were 0.35 ± 0.05, 0.19 ± 0.04, 0.22 ± 0.5, 0.14 ± 0.03 and 0.08 ± 0.01 kBq/kg respectively, while the average concentrations of ^{234}U, ^{238}U, ^{230}Th and ^{232}Th evaluated by the alpha spectrometry were 12.18 ± 1.5, 10.4 ± 1.6, 6.6 ± 0.7 and 5.58 ± 0.7 Bq/kg respectively.

Again, each of the radionuclides (^{226}Ra, ^{228}Ra, ^{224}Ra, ^{228}Th and ^{40}K) established by gamma-ray spectrometry in produced water samples recorded average activity concentrations of 7.64 ± 0.3, 7.62 ± 0.4, 2.78 ± 0.6, 2.91 ± 0.6 and 11.11 ± 0.8 Bq/L respectively, while the average concentrations of ^{234}U, ^{238}U, ^{230}Th and ^{232}Th evaluated by the alpha spectrometry were 8.55 ± 1.7, 8.83 ± 1.6, 8.5 ± 1.4 and 5.2 ± 1.4 mBq/L respectively.

The average values obtained for radon emanation fraction (EF) and radon mass exhalation rate (Rn_{ex}) were 0.897 ± 0.263 and 671 ± 92 $\mu Bq.kg^{-1}.s^{-1}$

For radium equivalent activity (Ra_{eq}), the average value was 1064.68 Bq/Kg. External hazard index (H_{EX}) average was 2.88, while the average value for internal hazard index

(H_{IN}) was 4.33. Lastly, the corresponding average values for external absorbed gamma dose rate (Dγr) as well as the annual effective dose ($E_{\gamma.ext}$) for occupationally exposed worker were 471.75 nGy/h and 1.32mSv.

The statistical test of association that was generated using paired t-test at 95% confidence interval with a p-value <0.05 had most of the obtained p-values being less than the set p-value for the test. ^{232}Th recorded the highest p-value of 0.092.

5.2 Conclusion

From the data obtained from each of the samples analyzed, a conclusive remark can be given that, for crude oil, their activity concentrations were not significant with most found to be below detection limit. In previous years (Kpeglo, 2015), crude oil from the Jubilee oilfields recorded activity concentrations that were below Minimum Detectable Limits. This indicates that crude oil from the Jubilee oilfields is relatively clean.

Sludge also recorded activity concentration values that were below the Canadian Derived Release Limits for solids (Diffuse NORM Sources) for each of the radionuclides. ^{226}Ra however, recorded an average activity concentration that exceeded the DRLs. From the previous study in Ghana, the activities that were obtained for sludge were higher in comparison with this present study. This can be attributed to increase in the number of production wells which can serve as a dilution factor to the concentration of activities obtained as well as the different sources of the sludge sample, such as sludge from produced water storage tanks or crude oil storage tanks. With respect to the high values

obtained, it is proper that the activity concentrations in sludge are monitored regularly in order that sludge disposal is properly managed in subsequent years.

Moreover, the sludge sample recorded values which exceeded the recommended reference values of external (H_{EX}) and internal hazard (H_{IN}) indices for safe use, as well as the radium equivalent activity (Ra_{eq}).

On the other hand, produced water recorded average activity concentrations that exceeded the Canadian Aqueous Derived Release Limits (DRL) for the discharge of liquids. As a result it is essential that the established guidance levels for the discharge of radioactive effluents into water bodies are enforced. This will help in the alleviation of environmental contamination. Comparatively, the reference study of this research recorded lower values of activity concentration. This difference can be as a result of the ageing or maturity of the Jubilee oilfield from the time the previous study was conducted till the time of this research.

The average concentrations of ^{226}Ra and ^{228}Ra from the produced water were also above the aqueous Derived Release Limit (DRL) of Canada. Relatively, results from the jubilee oilfield were high in radium concentration compared to the oilfields of most countries. Gulf of Mexico is one of the oilfields reported in literature to have a higher radium concentration in produced water, as well as al Jafra, Attala and Qahar of Syria (Stephenson, 1992; Al-Masri and Suman, 2005).

The external annual effective dose which was calculated using exposure period of 2000hrs per year was 1.32mSv, which is below the ICRP recommended dose limit for an

occupationally exposed worker. ICRP recommends a dose limit of 20mSv per year averaged over 5years (100mSv in 5years and 50mSv in any single year).

Based on the results from the paired t-test, it can be concluded that almost all of the mean differences of the activity concentrations of the radionuclides between the previous study and this study were statistically significant especially Produced water, thus there is a significant difference between the mean activity concentration of the radionuclides in the previous study and the current study. This indicates that there has been a significant increase in the activity concentrations of the radionuclides from the previous research (Kpeglo, 2015) to this current research though they are within the world wide range. The marginal increase in the mean activity concentrations can be attributed to increase in exploration and production or extraction, thus more oil wells being dug; consequently large volumes of waste are being generated leading to an increase in radioactivity levels. An increase in the depth of the oil wells is also a contributing factor as the radiological properties of the reservoir rocks add up to the activity concentration of radionuclides. This gives an indication of a possible increase in radiological hazards to workers and the public in general and that it is likely it will follow in that trend in subsequent years.

5.3 Recommendations

5.3.1 Nuclear Regulatory Authority

a. To ensure that the general public, workers and the environment are protected, it is imperative that the regulatory authority plays and enforces its mandate of regulating and managing institutions, facilities or industries such as oil and gas

since the radioactivity related to petroleum waste and produced water in this study exceeded the aqueous Derived Release Limits (DRLs) guiding diffuse NORM sources recommended by Health Canada.

b. National guidelines for monitoring NORM should be established to ensure regulatory monitoring of these facilities and industries.

5.3.2 Oil and gas companies

a. Radiation protection and safety training must be organized regularly for workers who handle contaminated equipment especially during the transport, processing and disposal of waste as well as, during maintenance and decontamination of equipment.

b. The overall radiation protection programme which includes individual and workplace monitoring must be established at controlled areas to deal with the matter of radiation exposure of workers and the general public.

c. Workers who deal directly with radioactive waste such as sludge and sludge contaminated equipment are advised to use/wear workplace Personal Protective equipment to reduce internal exposure through inhalation.

5.3.3 Future Research

a. Radionuclide analysis in petroleum waste must be conducted regularly to provide information on radioactivity levels as oil production increases with time so as to inform policy makers such as the regulatory authority and operators of facilities.

b. Risk assessment to guarantee a good enough level of protection for human health and the environment in accordance with up-to-date international standards.

REFERENCES

Al-Masri, M. S., & Suman, H. (2003). NORM waste management in the oil and gas industry: The Syrian experience. Journal of Radioanalytical and Nuclear Chemistry. 256(2003): 159-162.

Alnabhani, K., Khan, F., & Yang, M. (2015). Technologically Enhanced Naturally Occurring Radioactive Materials in Oil and Gas Production: A Silent Killer, Process Safety and Environmental Protection (2015). https://doi.org/10.1016/j.psep.2015.09.014

Australian Petroleum Production & Exploration Association (APPEA) Limited (2002). Guidelines for Naturally Occurring Radioactive Materials, APPEA, Australia.

Avwiri, G. O., Esi E., Agbalagba, E. O. (2013). Gamma Spectroscopy Analysis of Produced Water from Selected Flow Stations in Delta State. Nigeria, Intenational Journal of Environmental Monitoring and Analysis. 1 (5): 16-174. doi: 10.11648/j.ijema.20130105.11.

Baird, R. O., Merrel, G. B., Rogers, V. C., Nielson, K. K. (1990). Management and Disposal Alternatives for NORM Wastes in Oil Production and Gas Plant Equipment, Rep. RAE-8837/2-2, Rogers & Associates Engineering, Salt Lake City, UT.

Bakke, T., Klungsøyr. J. Sanni, S. (2013). Environmental Impacts of Produced Water and Drilling Waste Discharges from the Norwegian Offshore Petroleum Industry. Marine Environmental Research 92(2013): 154-169.

Beretka, J. and Mathew, P. J. (1985).Natural Radioactivity of Australian Building Materials, industrial waste and by-products, Health Phys Vol. 48(1985): 87-95.

Chowshury, S., Husain, T., Veitch, B., Bose, N., Sadiq, R. (2004). Human health risk assessment of naturally occuring radioactive materials in produced water e a case study. Human and Ecological Risk Assessment 10 (6): 1155-1171.

El Afifi E.M., Awwad, N.S. (2005). Characterization of TE-NORM waste associated with oil and natural gas production in Abu-Rudeis, Egypt. Journal of Environmental Radioactivity 82(2005): 7-19.

Exploration & Production (E&P) Forum, 1987. Low specific activity scale origin treatment and disposal. Report No. 6.6/127, Old Burlington Street, London W1X 1LB, pp. 25-28.

Ghana National Petroleum Corporation (2013). Retrieved (15th March, 2018), from

http://www.gnpcghana.com/home/.

Godoy, J. M., and Crux, R. P. (2003). ^{226}Ra and ^{228}Ra in scale and sludge samples and their correlation with the chemical composition. Journal of Environmental Radioactivity 70(2003): 199-206.

Hart, A. D., Graham, B. D., Gettleson, D. A., Smith, B. W. (1995). Naturally Occuring Radioactive Materials associated with produced water discharges. SPE 29727. 12pp. In: Proceedings of the SPE/EPA Exploration & Production Environmental Conference, Houston, TX. Society of Petroleum Engineers, Inc., Richardson, TX.

Hamilton, L. D., Meinhold, A. F, Nagy J. (1991). Produced water radionuclide hazard/risk assessment - phase 1. Prepared for the American Petroleum Institute. BNL 47403. Brookhaven National Laboratory.

Health Canada (2011). Canadian Guidelines for the Management of Naturally Occurring Radioactive Materials (NORM). Prepared by the Canadian NORM Working Group of the Federal Provincial Territorial Radiation Protection Committee. ISBN: 978-1-100-23019-1, Pub.: 130465.

Heaton, B., Lambley, J., (1995). TENORM in the oil, gas and mineral mining industry. Applied Radiation and Isotopes 46(1995): 577-581.

International Atomic Energy Agency, (2014). Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards. No. General Safety Requirements Part 3, IAEA, Vienna.

International Atomic Energy Agency, (2010). Radiation Protection and the Management of Radioactive Waste in the Oil and Gas Industry, Training Course Series No. 40, IAEA, Vienna.

International Atomic Energy Agency, (2005). Naturally occuring radioactive materials (NORM IV). Proceedings of an International Conference Held in Szczyrk, Poland, 17–21 May 2004, IAEA-TECDOC 1472 (May 2004): 17–21.

International Atomic Energy Agency, (2003). Radiation Protection and the management of radiaoctive waste in the oil and gas industry, Safety Report Series No. 34, IAEA, Vienna.

International Agency for Research on Cancer (1988). Man Made Mineral Fibers and Radon, IARC Monograghs vol. 43,IARC, Lyon.

International Commission on Radiological Protection (1981). Limits on Inhalation of Radon Daughters by workers, Publication 32, Pergamon Press, Oxford.

International Commission on Radiological Protection (1993). Protection against Radon-222 at home and at work, Publication 65, Pergamon Press, Oxford.

International Commission on Radiological Protection (2007). Recommendations of the International Commission on Radiological Protection, Publication 103.

Kathren, R. L. (1998). NORM sources and their origins. Applied Radiation and Isotopes 49(1998): 149-168.

Kinsey, R. R. (1997). The NUDAT/PCNUDAT Program for Nuclear Data. Capture-Gamma-Ray Spectroscopy and Related Topics (Proc. 9th Int. Symp., Budapest).

Kpeglo, D. O. (2015). Radiation Exposure to Natural Radioactivity in Crude Oil and Petroleum Waste from Oil Fields in Ghana ; Modelling , Risk Assessment and Regulatory Control. PhD Dissertation, University of Ghana, Accra, Ghana.

Kpeglo, D. O., J. Mantero, E. O. Darko, G. Emi-Reynolds, A. Faanu, G. Manjón, I Vioque, E. H. K. Akaho, R. García-Tenorio (2016). Radiochemical Characterization of Produced water from Two Production Offshore Oilfields in Ghana. Journal of Environmental Radioactivity 152(2016): 35-45.

Kraemer T. F., Reid D. F., (1984). The occurrence and behaviour of radium in saline formation water of the U.S. Gulf Coast Region. Isotope Geoscience 2(1984): 153-174.

Kvasnicka, J. (1998)."The total Management of NORM in the Offshore Petroleum Industry" In proceedings of the APPEA conference. 8-11 March, 1998. Canberra.

Kvasnicka, J. (1996)."Radiation Protection in the Offshore Petroleum Industry". In the proceedings of the 1996 International Congress on Radiation Portection of the International Radiation Protection Assoociation", Vienna, 14-19 April, 1996. Vol.4, pp 621-623.

Lagera L., Hart A., Graham B. (1999). Radionuclides in oil and gas operational discharges and environmental samples associated with offshore oil and gas production facilities. I: Continental shelf Associates, Inc. Radionuclides, metals and hydrocarbons in oil and gas operational discharges and environmental samples associated with offshore production facilities on the Texas/Louisiana continental shelf with an environmental assessment of metals and hydrocarbons. Prepared for U.S. Department of Energy.

Lehritani M., Mantero J., Casacuberta N., Masque P., Garcia-Tenorio R. (2012). Comparison of two sequential separation methods fo U and Th determination in environmental samples by alpha-particle spectrometry. Radiochemica Acta

100(2012): 431-438.

Lysebo I., Birovliey A., Strand T. (1996). NORM in oil production-occupational doses and environmental aspects. In: Proc. of the 11th Congress of the Nordic Radiation Protection Society, 26-30 August 1996, Reykjavik, p 137.

Lysebo , I., Strand, T. (1997), "NORM in oil production in Norway" Radiological problems with Natural Radioactivity in the Non-Nuclear Industry (Proc. Int. Symp. Armsterdam,1997), KEMA, Arnhem.

Mays, C. W., Rowland, R. E., and Stehney, A. F. (1985). A Cancer Risk from the Lifetime Intake of RA and U Isotopes, Health Physics, 48(1985): 635-647.

Neff J. M.(1997). Potential for Bioaccumulation of Metals and Organic Chemicals from Produced water Discharged Offshore in the Santa Barbara Channel, California: A Review. Report to the Western Statres Petroleum Association, Santa Barbara, CA, from Batelle Ocean Sciences, Duxbury,MA, USA. 201 pp.

Nelson R. (2007). A preliminary investigation into levels of naturally occurring radioactive materials (NORM) from offshore oil and gas production. In: Abstracts of the international Produced Water Conference: Environmental Risks and Advances in Mitigation Technologies. K. Lee and J. Neff (Chairs), St. John's Newfoundland, Canada, October 17 - 18, 2007. National Energy Board of Canada, Environmental Studies Research Fund (ESRF).

NRPA (2004). Natural radioactivity in produced water from the Norwegian oil and gas industry in 2003, Norwegian Radiation Protection Authority, Straralevern Rapport 2005:2.

Odo, J. E. and Tomson, M. B. (1994). "Why Scale Forms and How to Predict it". SPE Production & Facilities, February 1994, pp 47-54.

OECD/NEA. (1979). Exposure to radiation from natural radioactivity in building materials, Report by NEA Group of Experts, Nuclear Energy Agency (Paris: OECD).

Omar M, Ali HM, Abu MP (2004). Distribution of radium in oil and gas industry wastes from Malaysia. Appl.Radiat Isot 60(2004): 779-782.

Paranhos Gazineu, M. H., De Araújo, A. A., Brandão, Y. B., Hazin, C. A., & Godoy, J. M. D. O. (2005). Radioactivity concentration in liquid and solid phases of scale and sludge generated in the petroleum industry. *Journal of Environmental Radioactivity*. https://doi.org/10.1016/j.jenvrad.2004.11.003

Petroleum Commission of Ghana (2015). Retrieved (11th February, 2018), from www.

petrocom.gov.gh/maps.html.

R øe, T, I., (1998). Produced water discharges to the North Sea: a study of bioavailability of organic produced water compounds to marine organisms. Ph.D thesis. Trondheim: Norwegian University of Science and Technology, Faculty of Chemistry and Biology.

Shawky S., Amer H., Nada A. A., Abd El-Maksoud T. M., Ibrahiem N. M. (2001). Characteristics of NORM in the oil industryfrom Eastern and Western desserts of Egypt. Applied Radiation and Isotopes 55(2001): 135-139.

Smith, K. P.,Blunt, D. L.,Williams, G. P., Tebes C. L. (1996). Radiological dose assessment related to the management of naturally occurring radioactive materials generated by the petroleum industry. Technical Report ANL/EAD-2, Argonne National Laboratory, Argonne, IL, September 1996.

Smith, K. P. (1992). An Overview of Naturally Occurring Radioactive Materials (NORM) in the Petroleum Industry, Environmental Assessment and Information sciences Division, Aegonne National Laboratory, 9700 South Sass avenue, Argonne, Illinois 60439.

Statistics solutions (2018). Retrieved (26th July, 2018), from www.statisticssolutions.com/manova-analysis-paired-sample-t-test/.

Stephenson, M. T. (1992). a survey of produced water studies In: Ray, J. P., Engelhardt, F. R. (Eds.), Produced Water TEchnological/Environmental Issues and Solutions, Plenum Press, New York, pp 10-10.

Stephenson, M. T., Supernaw, I. R. (1990). Offshore Operators Committee 44 Platform Study Radionuclide Analysis Results, Offshore Operators Committee, New Orleans, Louisiana.

Strand, T., Lysebo, I., Kristensen D., Birovljev A., (1997).Deposits of naturally occurring radioactivity in production of oil and natural gas. NRPA report 1997:1. Østerås, Norwegian Radiation Protection Authority, 1997. (In Norwegian).

Tullow Ghana Limited, (2018). Retrieved (12th March, 2018), from https://www.tullowoil.com/operations/west-africa/ghana/jubilee-field.

USEPA (1993). Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the offshore category of the Oil and Gas Extraction Point Source Category, US Environmental Protection Agency EPA-821-R-93-003. Office of Water, Washington, DC, USA.

UKOOA (1992). UK north sea oil and gas industry: environmental inputs, impacts and

issues. United Kingdom Off-hore Operations Association Ltd, Report prepared by Environmental and Resource Technology Ltd, London, UK.

Vandenhove, H., (2002). European Sites Contaminated by Residues from the Ore-extracting and Processing Industries. International Congress Series, 1225, pp 307-315.

Wanty, R. B., and Shoen, R., (1993). A Review of the Chemical Processess Affecting the Mobility of Radionuclides in Natural waters, With Applications, in Gunderson, L.C.S, and Wanty, R. B..eds., Field Studies of Radon in Rocks, Soils and Water: Boca Raton, Florida, C. K. Smoley, p. 334.

World Health Organization (1993). Indoor Air Quality: A Risk Based Approach to Health Criteria for Radon Indoors, Doc. BUR/ICP/CEH 108 (S), World Health Organization Regional Office for Europe, Copenhagen.

Zaidan, J. A. R. (2010). Natural Occurring Radioactive Materials (NORM) in the Oil and Gas Industry. Journal of Petroluem Researches and Studies, Issue No.(1).

APPENDICES

Appendix A: Paired T-Test results of the radionuclides in crude oil (Alpha Spectrometry).

```
T-TEST PAIRS= 238Th1 WITH 232Th2 (PAIRED)
  /CRITERIA=CI(.9500)
  /MISSING=ANALYSIS.
```

T-Test

[DataSet0]

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	$^{238}Th_1$	2.2820E2	5	11.07700	4.95379
	$^{232}Th_2$	1.2400E2	5	20.34699	9.09945

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	$^{238}Th_1$ & $^{232}Th_2$	5	-.448	.449

Paired Samples Test

		Paired Differences					t
					95% Confidence Interval of the Difference		
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper	
Pair 1	$^{238}Th_1$ - $^{232}Th_2$	1.0420E2	27.17904	12.15483	70.45277	137.94723	8.573

Paired Samples Test

		df	Sig. (2-tailed)
Pair 1	$^{238}Th_1$ - $^{232}Th_2$	4	.001

```
T-TEST PAIRS= 238Th1 WITH 232Th2 (PAIRED)
  /CRITERIA=CI(.9500)
  /MISSING=ANALYSIS.
```

T-Test

[DataSet0]

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	***Th1	61.8000	5	9.70135	1.65529
	***Th2	68.6000	5	8.41427	3.76298

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	***Th1 & ***Th2	5	.591	.294

Paired Samples Test

		Paired Differences					t
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference Lower	Upper	
Pair 1	***Th1 - ***Th2	-6.80000	6.90652	5.08869	-15.37558	1.77558	-2.202

Paired Samples Test

		df	Sig. (2-tailed)
Pair 1	***Th1 - ***Th2	4	.092

Appendix B: Paired T-Test results of the radionuclides in produced water (Gamma Spectrometry).

```
T-TEST
  /TESTVAL=0
  /MISSING=ANALYSIS
  /VARIABLES=226Ra1 226Ra2
  /CRITERIA=CI(.9500).
```

T-Test

[DataSet0]

One-Sample Statistics

	N	Mean	Std. Deviation	Std. Error Mean
$^{226}Ra_1$	5	6.7800	.51138	.22861
$^{226}Ra_2$	10	8.5000	.28874	.09088

One-Sample Test

	Test Value = 0					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
$^{226}Ra_1$	29.656	4	.000	6.78000	6.1444	7.4156
$^{226}Ra_2$	93.540	9	.000	8.50000	8.2949	8.7051

```
T-TEST PAIRS=226Ra1 WITH 226Ra2 (PAIRED)
  /CRITERIA=CI(.9500)
  /MISSING=ANALYSIS.
```

T-Test

[DataSet0]

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	$^{226}Ra_1$	6.7800	5	.51186	.22891
	$^{226}Ra_2$	8.5000	5	.15811	.07071

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	$^{226}Ra_1$ & $^{226}Ra_2$	5	-.031	.961

Paired Samples Test

		Paired Differences					t
					95% Confidence Interval of the Difference		
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper	
Pair 1	$^{226}Ra_1$ - $^{226}Ra_2$	-1.72000	.54037	.24166	-2.39096	-1.04904	-7.117

Paired Samples Test

		df	Sig. (2-tailed)
Pair 1	$^{226}Ra_1$ - $^{226}Ra_2$	4	.002

```
T-TEST PAIRS=^226Ra1 WITH ^226Ra2 (PAIRED)
  /CRITERIA=CI(.9500)
  /MISSING=ANALYSIS.
```

T-Test

[DataSet0]

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	$^{226}Ra_1$	6.7800	5	.51186	.22891
	$^{226}Ra_2$	8.5000	5	.15811	.07071

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	$^{226}Ra_1$ & $^{226}Ra_2$	5	-.031	.961

Paired Samples Test

		Paired Differences					t
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference Lower	Upper	
Pair 1	$^{111}Ra_1$ - $^{111}Ra_2$	-1.72000	.54037	.24169	-2.39088	-1.04912	-7.117

Paired Samples Test

		df	Sig. (2-tailed)
Pair 1	$^{111}Ra_1$ - $^{111}Ra_2$	4	.002

T-TEST PAIRS=$^{111}Ra_1$ WITH $^{111}Ra_2$ (PAIRED)
/CRITERIA=CI(.9500)
/MISSING=ANALYSIS.

T-Test

[DataSet0]

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	$^{111}Ra_1$	.9200	5	.28252	.13082
	$^{111}Ra_2$	8.4800	5	.23875	.10677

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	$^{111}Ra_1$ & $^{111}Ra_2$	5	-.168	.789

Paired Samples Test

		Paired Differences					t
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference Lower	Upper	
Pair 1	$^{111}Ra_1$ - $^{111}Ra_2$		.40680	.18148	-8.05588	-7.04814	-41.814

Paired Samples Test

		df	Sig. (2-tailed)
Pair 1	$^{232}Th_1$ - $^{232}Th_2$	4	.000

T-TEST PAIRS=$^{232}Th_1$ WITH $^{232}Th_2$ (PAIRED)
/CRITERIA=CI(.9500)
/MISSING=ANALYSIS.

T-Test

[DataSet0]

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	VAR00004	8.8400	5	.18166	.08124
	VAR00013	8.1600	5	.15166	.06782

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	$^{232}Th_1$ & $^{232}Th_2$	5	.073	.908

Paired Samples Test

		Paired Differences					t
					95% Confidence Interval of the Difference		
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper	
Pair 1	$^{232}Th_1$ - $^{232}Th_2$	6.48000	.22804	.10198	6.18688	6.76314	34.124

Paired Samples Test

		df	Sig. (2-tailed)
Pair 1	$^{232}Th_1$ - $^{232}Th_2$	4	.000

T-TEST PAIRS=$^{222}Ra_1$ WITH $^{222}Ra_2$ (PAIRED)
/CRITERIA=CI(.9500)
/MISSING=ANALYSIS.

T-Test

[DataSet0]

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	$^{222}Ra_1$	.9980	5	.19678	.08798
	$^{222}Ra_2$	12.4600	5	.54588	.24413

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	$^{222}Ra_1$ & $^{222}Ra_2$	5	.092	.883

Paired Samples Test

		Paired Differences					t
					95% Confidence Interval of the Difference		
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper	
Pair 1	$^{222}Ra_1$ - $^{222}Ra_2$	-1.158E1	.58278	.26169	-12.28278	-10.88521	-45.948

Paired Samples Test

		df	Sig. (2-tailed)
Pair 1	$^{222}Ra_1$ - $^{222}Ra_2$	4	.000

T-TEST PAIRS=$^{40}K_1$ WITH $^{40}K_2$ (PAIRED)
/CRITERIA=CI(.9500)
/MISSING=ANALYSIS.

T-Test

[DataSet0]

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	$^{40}K_1$	7.1000	5	.88995	.44272
	$^{40}K_2$	3.0800	5	.16235	.08802

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	$^{40}K_1$ & $^{40}K_2$	5	.733	.114

Paired Samples Test

		Paired Differences					t
					95% Confidence Interval of the Difference		
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper	
Pair 1	$^{40}K_1$ - $^{40}K_2$	4.02000	.84878	.37962	2.96381	5.07139	10.616

Paired Samples Test

		df	Sig. (2-tailed)
Pair 1	$^{40}K_1$ - $^{40}K_2$	4	.000

Appendix C: Paired T-Test results of the radionuclides in produced water (Alpha Spectrometry).

```
T-TEST PAIRS=234U1 WITH 234U2 (PAIRED)
  /CRITERIA=CI(.9500)
  /MISSING=ANALYSIS.
```

T-Test

```
[DataSet0]
```

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	$^{234}U_1$	4.1000	5	1.95320	.87350
	$^{234}U_2$	7.8000	5	1.78185	.79687

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	$^{234}U_1$ & $^{234}U_2$	5	.007	.991

Paired Samples Test

		Paired Differences					t
					95% Confidence Interval of the Difference		
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper	
Pair 1	$^{234}U_1$ - $^{234}U_2$	-3.70000	2.63439	1.17813	-6.97102	-.42898	-3.141

Paired Samples Test

		df	Sig. (2-tailed)
Pair 1	$^{234}U_1$ - $^{234}U_2$	4	.035

```
T-TEST PAIRS=238U1 WITH 238U2 (PAIRED)
  /CRITERIA=CI(.9500)
  /MISSING=ANALYSIS.
```

T-Test

```
[DataSet0]
```

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	$^{238}U_1$	3.7200	5	1.73839	.77743
	$^{238}U_2$	8.4800	5	3.24761	1.45238

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	$^{238}U_1$ & $^{238}U_2$	5	-.145	.816

Paired Samples Test

		Paired Differences					t
					95% Confidence Interval of the Difference		
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper	
Pair 1	$^{238}U_1$ - $^{238}U_2$	-4.76000	3.89910	1.74373	-9.60138	.08138	-2.730

Paired Samples Test

		df	Sig. (2-tailed)
Pair 1	$^{238}U_1$ - $^{238}U_2$	4	.052

```
T-TEST PAIRS=230Th1 WITH 230Th2 (PAIRED)
  /CRITERIA=CI(.9500)
  /MISSING=ANALYSIS.
```

T-Test

```
[DataSet0]
```

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	$^{230}Th_1$	6.2800	5	1.27750	.57131
	$^{230}Th_2$	8.2200	5	1.66943	.74659

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	$^{230}Th_1$ & $^{230}Th_2$	5	.187	.764

Paired Samples Test

		Paired Differences					t
					95% Confidence Interval of the Difference		
		Mean	Std. Deviation	Std. Error Mean	Lower	Upper	
Pair 1	$^{230}Th_1$ - $^{230}Th_2$	-1.94000	1.90342	.85123	-4.30341	.42341	-2.279

Paired Samples Test

		df	Sig. (2-tailed)
Pair 1	$^{230}Th_1$ - $^{230}Th_2$	4	.085

```
T-TEST PAIRS=232Th1 WITH 232Th2 (PAIRED)
  /CRITERIA=CI(.9500)
  /MISSING=ANALYSIS.
```

T-Test

```
[DataSet0]
```

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	$^{232}Th_1$	2.7400	5	1.65620	.74068
	$^{232}Th_2$	5.1800	5	1.23167	.55082

Paired Samples Correlations

		N	Correlation	Sig.
Pair 1	$^{232}Th_1$ & $^{232}Th_2$	5	.835	.078

Paired Samples Test

	Paired Differences					t
				95% Confidence Interval of the Difference		
	Mean	Std. Deviation	Std. Error Mean	Lower	Upper	
Pair 1 $^{232}Th_1$ - $^{232}Th_2$	-2.44000	.92087	.41183	-3.58341	-1.29659	-5.925

Paired Samples Test

	df	Sig. (2-tailed)
Pair 1 $^{232}Th_1$ - $^{232}Th_2$	4	.004