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Radiation Exposure to Natural Radioactivity in Crude Oil and Petroleum Waste from Oil Fields in Ghana; Modelling, Risk Assessment and Regulatory Control

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by

DAVID OKOH KPEGLO (ID: 10255978)

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MPhil (Legon), 2009

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DECLARATION

This dissertation is the result of research work undertaken by David Okoh KPEGLO in the department of Nuclear Safety and Security, university of Ghana, under the supervision of Prof. Emmanuel O. Darko (SNAS, UG-Legon, Ghana), Prof. G. Emi-reynolds (SNAS, UG-Legon, Ghana), Prof. Rafael García-Tenorio García-Balmaseda (University of Seville, Spain), and Dr. Juan Mantero Cabrera (University of Seville, Spain).

Sign: Date: 04- 03 - 2016

Kpeglo Okoh David
(Student)

Sign: Date: 04- 03 – 2016

Prof. Emmanuel O. Darko
(Principal Supervisor)

Sign: Date: 04- 03 – 2016

Prof. G. Emi-reynolds
(Co-Supervisor)

Sign: Date: 04- 03 – 2016

Prof. Rafael García-Tenorio García-Balmaseda
(Co-Supervisor)

Sign: Date: 04- 03 - 2016

Dr. Juan Mantero Cabrera
(Co-Supervisor)

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DEDICATION

This research work is dedicated to the OKOH KPEGLO Family

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ABBREVIATIONS

AECS	Atomic Energy Commission of Syria
AFPC	Al-Furat Petroleum Company
ALARA	As Low As Reasonably Achievable
API	American Petroleum Institute
APPEA	Australian Petroleum Production and Exploration Association
BSS	Basic Safety Standards
CHARM	Chemical Hazard Assessment and Risk Management
CMOS	Complementary Metal-Oxide Semiconductor
C-NLOPB	Canada-Newfound Land Offshore Petroleum Board
DJ	Diffused Junction
ENI	Ente Nazionale Idrocarburi (Italy)
EPA	Environmental Production Agency
E&P	Exploration and Production
ERA	Ecological Risk Management
ESRF	Environmental Studies Research Fund
FPSO	Floating Production Storage and Offloading
GAEC	Ghana Atomic Energy Commission
GHEITI	Ghana Extractive Industries Transparency Initiative
GPNC	Ghana National Petroleum Corporation
GSA	Ghana Standard Authority
HPGe	High Purity Germanium
HPWJ	High Pressure Water Jetting

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IAEA	International Atomic Energy Agency
IARC	International Agency for Research on Cancer
ICRP	International Commission on Radiological Protection
ICP-QMS	Inductively Coupled Plasma Quadrupole-Based Mass Spectrometry
MCA	Multi-Channel Analyzer
NORM	Naturally Occurring Radioactive Material
NRC	Nuclear Regulatory Commission
NRPA	Norwegian Radiation Protection Authority
NYSDEC	New York State Department of Environmental Conversation
OPAR	Oslo/Paris
PCB	Polychlorinated Biphenyl
ROPME	Regional Organization for Protection of the Marine Environment
RPB	Radiation Protection Board
SEM	Scanning Electron Microscopy
SSB	Silicon Surface Barrier
SSDL	Secondary Standard Dosimetry Laboratory
SOPCL	Salt pond Offshore Producing Company Limited
SWACO	Solid Waste Authority of Central Ohio
TECDOC	Technical Documentation
TGL	Tullow Ghana Limited
UKOOA	United Kingdom Offshore Operation Association
UNSCEAR	United Nation Scientific Committee on the Effects of Atomic Radiation
USEPA	United States Environmental Agency

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WEEE	Waste Electronic and Electrical Equipment
WERF	Water Environment Research Foundation
WHO	World Health Organization
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

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ABSTRACT

In this research work radiological hazards and risks to members of the public and workers from exposure to natural radioactivity as a result of crude oil production activities and waste generation from the Saltpond and Jubilee oilfields of Ghana, have been investigated via several exposure pathways using alpha spectrometry after radiochemical separation, non-destructive gamma spectrometry, Scanning Electron Microscope (SEM) and Inductively Coupled Plasma Quadrupole-Based Mass Spectrometry (ICP-QMS) and other complimentary analytical tools. Additionally, in this study a Human health risk assessment model for cancer risk associated with NORM (Naturally Occurring Radioactive Material) components in produced water was developed.

Characterization and determination of specific activities of ^{234}U, ^{238}U, ^{210}Po, ^{230}Th, ^{232}Th, ^{226}Ra, ^{210}Pb, ^{234}Th, ^{228}Ra, ^{228}Th, ^{224}Ra, and ^{40}K for several environmental and NORM waste samples in different matrices have been established. The elements Al, Ba, Ca, Cl, Cu, Fe, K, Mg, Na, P, Pb S, Si, Sr, and Zn were identified and semi qualitatively quantified by Scanning Electron Microscope for NORM waste samples.

The total annual effective dose of 0.35 $mSv.y^{-1}$ obtained for all exposure pathways for the public in this study was below the International Commission on Radiological Protection (ICRP) recommended dose limit of 1 $mSv.y^{-1}$ for members of the public, whilst the total annual effective dose of 80.86 $mSv.y^{-1}$ obtained in this study for workers clearly exceeded the ICRP recommended dose limit for an occupationally exposed worker of 20 $mSv.y^{-1}$, averaged over 5years, but not exceeding 50 $mSv.y^{-1}$ in any single year. The estimated total lifetime fatality cancer risk and the lifetime hereditary effect values were 1.3×10^{-3} and 4.9×10^{-5} for the public, and 23.2×10^{-2} and 5.7×10^{-3} for adult workers respectively. In

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conclusion, radium concentrations obtained in this study for scale, sludge and produced water from the oilfields of Ghana are of radiological importance and hence, there may be the need to put in place some measures for future contamination concerns due to their bioavailability in the media and bioaccumulation characteristics. The results from this study will assist in decision-making for future set-up of appropriate national guidelines for the management of NORM waste from the emerging oil and gas industry in Ghana.

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CHAPTER ONE

INTRODUCTION

1.1 Background

It is well known that the presence of NORM (naturally occurring radioactive material) is acknowledged as a problem in several extractive industries worldwide, a paradigmatic example being the oil and gas industry (Hamlat et al., 2001), where NORMs represent a considerable waste issue. The international community has been considering disposal options for these NORM wastes in order to make negligible the public radiological impact(Matta et al., 2002).

Radiation exposure from NORM generated by the oil and gas industry can occur from seven environmental pathways: radon inhalation, external gamma exposure, ground water ingestion, surface water ingestion, dust inhalation, food ingestion and skin beta exposure (Smith, 1992). Individuals at risk from exposure to NORM radiation from the oil industry include workers at equipment cleaning facilities, oilfield workers, workers at NORM disposal facilities, and the general public, particularly, in the coastal cummunities close to shallow water offshore oilfields and land disposal facilities.

The general population may be at risk to NORM via radon inhalation; and ingestion of groundwater, surface water and food. Improper disposal of NORM contaminated waste (scales, sludges and drilling mud) generated by the oil and gas industry may lead to soil and water contamination and to higher indoor radon levels in nearby buildings (Smith, 1992; USEPA, 1993). Ingestion of food grown in contaminated soils or seafood harvested in areas

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contaminated by produced water outfalls may also result in radiation exposure increments. A recent risk assessment for radium discharged in produced waters indicated a potential risk of exposure for an individual who ingests large amounts of seafood harvested near a produced water discharge point over a lifetime (Smith, 1992).

It is therefore, of prime importance to gather baseline radioactivity data for water sources and soil in communities along the coast of such oilfields to serve as reference data for the future . These data will be useful not only to evaluate the present radiological state of the coastal environment, but also for subsequent evaluations of the possible future environmental contamination due to activities of the extractive industry.

The presence of naturally occurring radioactive materials (NORMs) in the earth's crust is well known. The ^{238}U, ^{235}U and ^{232}Th series, as well as ^{40}K are particularly important as they contain a number of radionuclides that are encountered in oil and gas products, produced water and in all sludge and scale deposits in subsurface and/or surface production facilities. (IAEA, 2003).

Generally, the variation in the ^{226}Ra activity concentrations in NORM wastes of different origins, can be attributed to the differences in the Ra/Ba ratio in formation waters, scale and/or sludge formation processes on the exterior surfaces of the casing material and the amount of ^{226}Ra in the subsurface (White and Rood, 2001). The Ra content depends on the amount of Ra present in subsurface formation, formation water chemistry, extraction and treatment processes and the age of the waste after production. In general, the solubility of radium in water increases with the increase of saline content and at both high and low pH values. Naturally occurring radioactive material scale is produced when Ra dissolved in the

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formation water is co-precipitated with Ba, Sr, or Ca as sulphates **(**White and Rood, 1999**).** These materials form insoluble hard deposits inside the production equipment **(**Smith et al., 1999**),** while NORM sludge results from precipitation of Ra, Ba, Sr and Ca sulphates or silicates and carbonates.

In many oilfields, produced water is re-injected into the reservoirs to maintain pressure. Normally, the water injected in the wells has a different composition from the water already present in the reservoir (formation water). When the water/oil emulsion is carried to the surface during the pumping operation, precipitation of residues on the inner surfaces of piping can take place. This precipitation and the consequent scale formation is due to variations of sulphate and carbonate solubilities and is associated with pH and temperature variations, pressure changes and injection of incompatible waters **(**Smith et al., 1996**).**

Produced water, which is extracted during oil and gas production, includes formation water, injected water, small volumes of condensed water, and any chemical added down the hole or during the oil/water separation process (USEPA, 1993). Produced water is the highest volume of waste generated in association with oil and gas production operations. Despite treatment before discharge to satisfy regulatory limitations on oil content, produced water contains a certain amount of naturally occurring radioactive materials (NORM) such as ^{226}Ra and ^{228}Ra. NORM are difficult to remove from produced water, which make the assessment of their effects on human health important to the oil and gas producing industries.

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Radium-226 (^{226}Ra) is the NORM material of major interest because it is an intermediate member of the Uranium- 238 series and mostly in higher concentrations. It is water soluble, and it is classified as water- borne pollutant.

Radium is brought to the surface dissolved in the water that accompanies the hydrocarbons (produced water). Uranium and thorium, on the other hand, remain in the reservoir, as they will not be leached into passing fluids. Potassium, which is released slowly upon dissolution from the rock matrix, is also present in the water. The degree of accumulation of radioactive materials is always significant for ducts and equipment that carry produced water. For this reason, NORM concentrations are, in general, higher in scales and sludge formed in water-handling equipment **(**Smith et al., 1996**)**. Radiation levels measured after the water separation stage are, consequently, negligible or much lower than those observed in other cases, where the water is still present in the mixture. Consequently, a high water production rate, such as is characteristic of older oil fields, results in increased NORM accumulation on tubing and equipment (Gazineu and Hazin, 2008**)**.

NORM in the oil and gas industry represents a considerable waste issue and the international community has been considering disposal options (Matta et al., 2002; Hamlat et al., 2001). Estimates suggest that up to 30 % of domestic oil and gas wells in the USA may produce some elevated NORM contaminates **(**Derald and Talmage, 2002**).** In 1998, serious attention was given to health impacts from the uncontrolled release of waste containing NORM, concentrated and accumulated in tubing and surface equipment in the form of scale and sludge **(**Hamlat et al., 2001; Al-Masri and Aba, 2005**)**.

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Radiation protection considerations arise mainly from the removal of this scale and sludge during maintenance and decommissioning operations resulting in exposure to external gamma radiation and inhalation of dust, and from the subsequent disposal of such materials as waste. Individuals working close to heavily scaled pipes and vessels may also need to be subjected to radiation protection measures (IAEA, 2003; Hamlat et al., 2001). The focus on health concerns related to the enhanced naturally occurring radioactive material (NORM) associated with oil and gas production, primarily involves the generation and release of chemically inert radon (^{222}Rn), produced by the radioactive decay of radium (^{226}Ra), a member of the uranium decay series. The radiation risks associated with the handling, transport and disposal of the NORM wastes contaminated with ^{226}Ra, are primarily due to the inhalation of ^{222}Rn, and are dependent on the rate at which ^{222}Rn is transported to the atmosphere or on the diffusion and subsequent emission from the NORM waste matrix to the staff operators **(**El Afifi et al.,2004**)**. Therefore, it is necessary to underpin the radiological characteristics of the NORM wastes released from oil and gas production.

The NORM extractive industries are not being regulated for NORM in most non-developed countries. In Ghana, there are over 200 registered mining companies operating small, medium and large scale mining, but only radionuclide concentrations assessment resulting from industrial activities such as mining and mineral processing has been carried out in some few mines (Darko et al., 2010; and Faanu et al., 2013).

In addition to the mainly gold mining companies, Ghana also recently (in 2010) became an oil producing country, producing oil in commercial quantities. Currently, there are two producing oilfields located in the country, the Jubilee Deepwater offshore field and Saltpond

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shallow water offshore field, with activities which could lead to contamination of the marine environment, coastal lands and water bodies.

In this regard, a national programme to establish baseline radioactivity measurements in the environmental compartments which can be affected by extractive industries that have just started operations as well as for existing ones are vigorously being pursued by the Radiation Protection Institute of Ghana, with the purpose of gathering reference data.

In Ghana, some work have been carried out to evaluate the risks associated with NORMs in the mining industry (Darko et al., 2005), and some few workers in the mining industry are quite aware of the potential problems associated with NORMs. However, no work has been carried out to assess the potential hazards associated with NORMs in the oil fields of Ghana. To this end, this research explores the occurrence of NORM and estimates the activity concentration of radionuclides and other parameters such as the radiation hazard indices, the radium equivalent activity, the radon emanation coefficient, the absorbed dose rate and effective dose of crude oil, petroleum wastes and environmental samples from the Ghanaian Oil fields and its coastal environs. In this regard, analytical procedures for alpha and gamma spectrometric techniques which are key analytical tools for the characterization and determination of the isotopic signatures of several environmental and NORM waste samples for different matrices was developed, as alongside, complimentary chemical analytical tools. Additionally, in this study a human health risk assessment model for cancer risk associated with NORM components in produced water may be developed.

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1.2 Statement of the Problem

NORM are everywhere and humans are constantly exposed to it particularly in the Oil and Gas industry. The enhancement of these NORM poses a major challenge to public health and occupational protection concerns. NORM, therefore, requires control for purposes of radiological protection of the worker, the public or the environment when they are present in sufficient concentrations just as is the case in the oil and gas industry, hence, must be monitored regularly.

Currently, data on the radioactivity levels in oil and gas at the Jubilee oilfields at the West Cape Three Points in Ghana as well as the Saltpond offshore fileld is unavailable. This is because there have not been any radiological survey of the facilities and the surrounding areas. This situation could be of great concern to occupational protection and public health as well as environmental radiation protection particularly, as the country has started drilling oil in commercial quantities about five years ago**.**

Hence the need to carry out a detail study such as this to ascertain the levels of natural radionuclides and also to assess the risk to workers and members of the public is very necessary. It is significant to note that it is only through a comprehensive study of this nature that will ensure accurate data is gathered that will aid in realistic decisions on the controls to be enforced. Any remedial actions can then be justified based on the data from this study.

A common problem in oil production is the accumulation of scale on the interior surfaces of oil pipes. The scales are mostly composed of barium sulphate, barium carbonate, and calcium carbonate. The scale material originates from the reservoir underground formations and the bed rocks, and is carried out by the oil to the surface. In some conditions, where

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water is present, radioactive radium can be washed out of the underground rocks and brought to the surface with oil and production fluids. Depending on the formation and age of the well, removal, storage and disposal of the scale can result in serious health and environmental risks if not handled properly, both for workers and the public.

Produced water is the highest volume of waste generated in association with oil and gas production operations. Despite treatment prior to discharge to satisfy regulatory limitations which is mainly on oil content, produced water contains a certain amount of naturally occurring radioactive materials (NORM) such as ^{226}Ra and ^{228}Ra. NORMs are difficult to remove from produced water, which makes the assessment of their effects on human health important to the oil and gas producing industries. This work therefore assesses levels of potential radiological hazard associated with NORMS in crude oil and petroleum waste from the Saltpond and Jubilee Oil Fields of Ghana.

1.3 Research Objectives

Naturally occurring radionuclides of the uranium-thorium series and potassium-40 are generated from extractive industries such as mining of U-Th and other minerals, oil and gas extraction and processing, etc. The U-Th series and K-40 from terrestrial origin are considered ubiquitous and inexhaustible natural elements of the earth's crust. The progenies of the U-Th series are known to be carcinogenic when exposed in excess of certain levels, e.g. Rn-222, Po-214, Po-210, etc. The primary objective of this study is therefore to assess the effective doses for the risk associated with exposure to naturally occurring radioactive materials in the oil and gas industries in Ghana from modelling view point, and also to determine the regulatory limitations of produced water and NORM wastes discharged from the oil fields.

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The specific objectives of this research are to:

i. identify the various radionuclides associated with NORMs in crude oil and petroleum waste from the Saltpond and Jubilee Oil Fields of Ghana
ii. determine the radioactivity concentration of NORMs in crude oil and petroleum waste from the Saltpond and Jubilee oil fields.
iii. provide an estimate of the radiation hazard indices, the radium equivalent activity, the radon emanation coefficient, radon mass exhalation rate and the absorbed dose rate in air for petroleum waste samples.
iv. estimation of the occupational exposure of workers due to external radiation and inhalation.
v. assess the current state of Radiological protection of workers, the public and the surrounding environment of the Saltpond and Jubilee oil fields.
vi. develop Human health risk assessment model for cancer risk associated with NORM components in produced water.
vii. analyze and evaluate different safe waste management options in relation to the NORM wastes generated by the Oil industry in Ghana.

1.4 Significance of the study

This work is necessary since no studies have been carried out on radioactivity levels associated with NORMs in crude oil and petroleum waste from the Saltpond and Jubilee Oil Fields of Ghana. Records available so far indicate that no occupational radiological information exits associated with this activity in Ghana.

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This research has particularly been necessitated as Ghana has started drilling oil in commercial quantities from the Saltpond and Jubilee Oil Field. Hence findings from this work will help put in place appropriate control measures with respect to basic radiological protection, environmental control, and waste management systems associated with NORMs to be generated by the oil industry. In this regard, the occurrence of radiological hazards and consequences associated with NORM which may pose serious health implications to workers, the public and the environment, can be assessed and prevention and mitigation measures undertaken where appropriate.

It will also provide a basis for further detailed assessment of radiation exposures from NORMs in the Oil and Gas industry in Ghana.

The necessary awareness through this study will be created for management of these facilities so that workers are appropriately trained on basic radiation safety at work and the public radiation protective measures

This research will also serve as a useful data for Regulatory Bodies, Oil Field Operators, Oil Exploration Companies, Oil Refineries and Service Companies in the Oil and Gas industry in Ghana. This study is also important to minimize, and in some cases eliminate future problems that are associated with NORMs in the oil and gas industry in Ghana.

1.5 Scope and Limitation

The work is intended to cover measurement of the uranium series and their daughter products as well as radon at the Saltpond and Jubilee oilfields, oil and gas waste management treatment facility (Zeal Environmental Technologies) and coastal communities within Saltpond in the central and western regions of Ghana. Various experimental and

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theoretical methods and instrumentations have been applied. Previous studies carried out have focused on other areas in Ghana.

1.6 Structure of the Thesis

This Thesis discusses the radiation exposure and risk associated with crude oil and petroleum waste from Saltpond and Jubilee oilfields in Ghana. The Thesis is made up of six chapters with introductory note, review of literature, analytical procedures of alpha and gamma spectrometry, materials and methods, discussions of results and concluding remarks with recommendations.

Chapter 1 provides a general introduction to the thesis including, research objectives, problem statement, research justification and hypothesis. A brief background of the study under investigation have been presented. Chapter 2 presents a vivid report on the literature survey which reveals information and previous work done by other researchers in other countries. Radiation detection methods and analytical procedures to key analytical tools alpha and gamma spectrometry developed for measurements of radioactivity in this study are presented in chapter three.

The approach and methods used in this study to collect data and information as well as mathematical models are presented in Chapter four. Chapter five discusses the results of the study in a clear and concise manner, and summary, conclusions and recommendations are provided in Chapter six.

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CHAPTER TWO

LITERATURE REVIEW

Overview

This Chapeter reviews work done reported in a number of publications and discussions on some radiological aspects of NORMs with respect to occupational radiation protection, public health and environmental radiation protection and the need for this work.

2.1 NORM in the Oil and Gas Industry

The first reports of NORM associated with mineral oil and natural gases appeared in 1904 **(**Mclennan, 1904**)**. Later reports described the occurrence of ^{226}Ra in reservoir water from oil and gas fields **(**Kolb and Wojcik, 1985**)** and, in the 1970s and 1980s several observations prompted renewed interest (IAEA, 2003). The radiological aspects of these phenomena, the results of monitoring and analyses and the development of guidelines for radiation safety are now reported extensively (IAEA, 2003) and there are quite a number of published data.

In Ghana, some significant work has been carried out to evaluate the risks associated with NORMs in the mining industry (Darko et al., 2005) and most workers in the mining industry are aware of the potential problems associated with NORMs. However, historical antecedents have revealed that no work has been carried out to assess the potential hazards associated with NORM in the oil and gas industry in Ghana and hence there is no published data.

In the exploration and extraction processes of oil and gas, the 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

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^{210}Pb,.etc., are brought to the slurry surfaces and may contain levels of radioactivity above the surface background (El Afifi and Awwad, 2005**)**. As these materials are handled, their radioactive constituents may be separated, resulting in NORM waste. The petroleum waste (scale or sludge) are produced by two mechanisms: either incorporation or precipitation onto the production equipment such as: pipelines, storage tank, pumps etc. The waste generated in oil and gas equipment is due to the precipitation of alkaline earth metals as sulfate, carbonates and/or silicates. Nuclear spectroscopic analysis showed that the main radionuclides present in NORM waste associated with petroleum industries are ^{238}U, ^{235}U and ^{232}Th series. The mineralogical analysis by X-ray techniques (XRF and XRD) indicate the incorporation and co-precipitation of these radionuclides with the alkaline earth metals (e.g. Mg, Ca, Sr, Ba) and some quantities of lead sulphate, carbonate and/or silicate **(**Shuller et al., 1995**)**.

The volume of NORM waste generated by the petroleum industry is quite impressive. The U.S. Environmental Protection Agency (USEPA) estimates that 25,000t of NORM-contaminated scale and 225,000 t of NORM-contaminated sludge are produced annually by the American petroleum industry (USEPA, 1993).

In the European Union, the total production of natural gas and oil is 140 Mt and 0.23×10^{12} m^3, respectively, which generates an annual sludge production of 10,000 m^3 **(**Vandenhove, 2002**)**.

The dominating radionuclides present in scales and other precipitates are ^{226}Ra and ^{228}Ra, with typical concentrations ranging from 1 to 1000 kBq kg^{-1}, although concentrations as high as 15,000 kBq kg^{-1} have been reported in literature (USEPA, 1993). Values for ^{228}Ra in scales and sludge are, in general, not much less than for ^{226}Ra. Besides, reported radium

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concentrations in sludge are normally lower than in scales **(**Vandenhove, 2002; Paschoa, 1998**).**

This notwithstanding, there is quite an appreciable literature on NORMs in the oil and gas industry in many oil producing countries around the world. The following paragraphs is an overview of some works done in various oilfields, being discussed in detail some radiological aspects of NORM with respect to occupational radiation protection, public health and environmental protection.

In a work done at Syrian oilfields, 152 scale samples collected from equipment were analyzed for their radioactivity content **(**Al-Masri and Aba, 2005**)**. The average ^{226}Ra activity concentration in these samples was found to be 174 kBq kg^{-1}, while the highest concentration for this isotope was 1520 kBq kg^{-1}. For ^{228}Ra, on the other hand, the average and maximum values were 91 and 868 kBq kg^{-1}, respectively. A gradual increase in ^{226}Ra specific activity from downhole tubes to the equipment and tubing at the surface installations was also reported.

In another study, carried out in New York State, scale and sludge samples collected from the oil industry showed activity concentrations 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 **(**NYSDEC, 1999). At the same time, values 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 Brazil, values of activity concentration for scales removed from an offshore oil producing facility ranged from 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 collected from the same facility presented concentrations ranging

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from 0.36 to 367 kBq kg^{-1} for ^{226}Ra and from 0.25 to 343 kBq kg^{-1} for ^{228}Ra, respectively **(**Godoy and Crux, 2003).

A recent study that measured the ^{222}Rn emanation fraction in NORM scale wastes associated with oil and gas production in Egypt found values ranging from 0.02 to 0.087 (Rood, 2001; El Afifi et at., 2004) . Due to the difference in the particle size, the amounts of ^{222}Rn emanating from the sludge waste are generally higher than that from the scale waste. The typical ^{222}Rn emanation fraction for sludge measured by others is 0.2 (Smith et al, 1996a). In the basic case, a ^{222}Rn emanation fraction of 0.04 was used. When the ^{222}Rn emanation fraction was doubled (0.08), the resultant equivalent dose rate increased from 74 to about 150µSv.y^{-1}, while a ^{222}Rn emanation fraction of 0.02 resulted in a lower equivalent dose rate of 37µSv.y^{-1} (El Afifi et al., 2004**).**

2.2 Origin of Petroleum

There are currently two plausible scientific theories that explain the process of oil formation. The first step is the biotic or biogenic theory, which states that oil was formed hundreds of millions of years ago, following the extinction of dinosaurs (i.e. terrestrial reptiles of the Mesozoic era) and algae that inhabited the earth some 65-248 million years ago. The remaining organic matter was then buried under many layers of sediment, and was exposed to high levels of litho-spherical heat and pressure, which then transformed this preserved matter into hydrocarbons (black gold or oil). According to geologists, this process is thought to occur amid the earth‘s solid rock layers, at temperatures ranging from 80-350 degrees Celsius and pressures ranging from 0.8-2 kbar (Dyer and Graham, 2002; Dutkiewicz et al.,

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2003). The oil then migrates and remain in porous stones (such as limestone or sandstone, which have a porosity of about 20%) until it is discovered.

The second theory is known as the abiotic or abiogenic theory, which states that oil is not a fossil fuel, but that it was formed from inorganic materials deep within the earth's crust. According to this theory , hydrogen and carbon molecules found in the earth 's mantle are subject to extremely high temperatures and pressures , causing them to form hydrocarbon molecules , which then migrate upward into oil reservoirs , through deep fracture networks in the earth crust . Supporters of the abiogenic theory claim that the millions of barrels per day (1 barrel =159L) could not possibly be supplied by the limited number of pre-historic animals (algae and dinosaurs) that existed (Dutkiewicz et al., 2003).

2.3 NORMs in the Petroleum Industry

NORMs are present in components of both petroleum production facilities and natural gas production facilities. NORMs can be associated with the presence of crude oil, produced water and natural gas. Petroleum industry NORMs are mainly scale, sludge and sand (IAEA, 2003; APPEA, 2002). In gas plant components, where only natural gas and/or its fractions are present, NORM occur on internal walls in the form of thin films and/or coatings formed by the decay products of radon gas. Considering that some formation water is also present in natural gas, small quantities of NORM sludge can be present in gas plants as well. NORMs occurring in oil installations mainly contain ^{226}Ra and ^{228}Ra, the activity of which is usually in equilibrium with the activity of their decay products.

Scales in pipes and vessels are the most common NORMs in the petroleum industry. Scales are solid minerals that precipitate from produced water which has high salinity and contains

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sulphates and/or carbonates plus calcium, barium and strontium. The most common scales consist of barium sulphate ($BaSO_4$), strontium sulphate ($SrSO_4$) or calcium carbonate ($CaCO_3$). Scale-forming material may also precipitate on sand and sludge particles and debris of scale may be mixed with sludge and sand inside vessels.

Scale formation is caused by a combination of the following events (IAEA, 2003**;** APPEA, 2002**)**: Mixing of incompatible waters; pressure changes; temperature changes; impurities; additives; variation of flow rates; changes in water acidity; fluid expansion; gas evaporation; etc.

The most important scale formation processes are mixing of incompatible waters and temperature changes. Under high temperature and pressure conditions in an oil reservoir, trace concentrations of barium, strontium, calcium and radium are leached out from reservoir sand and are present in a soluble form in the formation water.

This water also contains sulphates, carbonates and other ions (APPEA, 2002). Events that may cause precipitation of scale particles have been mentioned earlier. When scale precipitates from a large volume of formation or produced water, radium is concentrated within a small amount of solid scale such that the radium concentration in scale exceeds the radium concentration in the formation or produced water by several orders of magnitude. As uranium and thorium radionuclides are substantially less soluble in the formation water than radium, NORM scale contains practically no uranium and or thorium. It can be concluded that NORMs in petroleum production facilities contain mainly ^{226}Ra, ^{228}Ra and their short-lived decay products (APPEA, 2002; E& P forum, 1987). The half-life of ^{226}Ra is 1,600 years and that of radium-228 is 5.8 years. Radon decay products are continuously generated in solid NORMs in petroleum production installations by the decay of radium. Therefore,

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scale, sludge and sand emit approximately the same amount of radiation during normal operation conditions as well as during shutdowns. As the concentration of radium and radium decay products in formation and/or produced water is usually low in comparison with scale and sludge, the water itself is not a source of external radiation exposures (APPEA, 2002; E& P forum, 1987). Nevertheless, radium in discharges of the produced waters (especially from onshore facilities) may need to be considered depending on the levels of radium and on environmental considerations. Both ^{226}Ra and ^{228}Ra decay series radionuclides are summarised in Tables 2.1 and 2.2. Radionuclides below ^{226}Ra and ^{228}Ra are generated by the radioactive decay of the original radionuclide of radium.

The main forms of NORMs in petroleum and natural gas production installations are summarized in Table 2.3

Table 2.1: 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	-

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Table 2.2: 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	-

Table 2.3: NORM in Oil and Gas production (IAEA, 2003)

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,paraffins, 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-226,Ra-228,Ra-224 and / or Pb-210	More or less saline, large volumes in oil production	Each production facility

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2.4. Radiological Characteristics of NORM

The radionuclides identified in oil and gas streams belong to the decay chains of the naturally occurring primordial radionuclides ^{238}U and ^{232}Th. These parent radionuclides have very long half-lives and are ubiquitous in the earth's crust with activity concentrations that depend on the type of rock. Radioactive decay of ^{238}U and ^{232}Th produces several series of daughter radioisotopes of different elements and of different physical characteristics with respect to their half-lives, modes of decay, and types and energies of emitted radiation (Table 2.4 and Figures 2.1 and 2.2) (IAEA, 2003). Analyses of NORM from many different oil and gas fields show that the solids found in the downhole and surface structures of oil and gas production facilities do not include ^{238}U and ^{232}Th (Jonkers et al., 1997). These elements are not mobilized from the reservoir rock that contains the oil, gas and formation water (Figures 2.1 and 2.2). The formation water contains Group II (Periodic Table) cations of calcium, strontium, barium and radium dissolved from the reservoir rock. As a consequence, formation water contains the radium isotopes ^{226}Ra from the ^{238}U series (Figure 2.1) and ^{228}Ra and ^{224}Ra from the ^{232}Th series (Figure 2.2).

All three radium isotopes, but not their parents, thus appear in the water co-produced with the oil or gas.

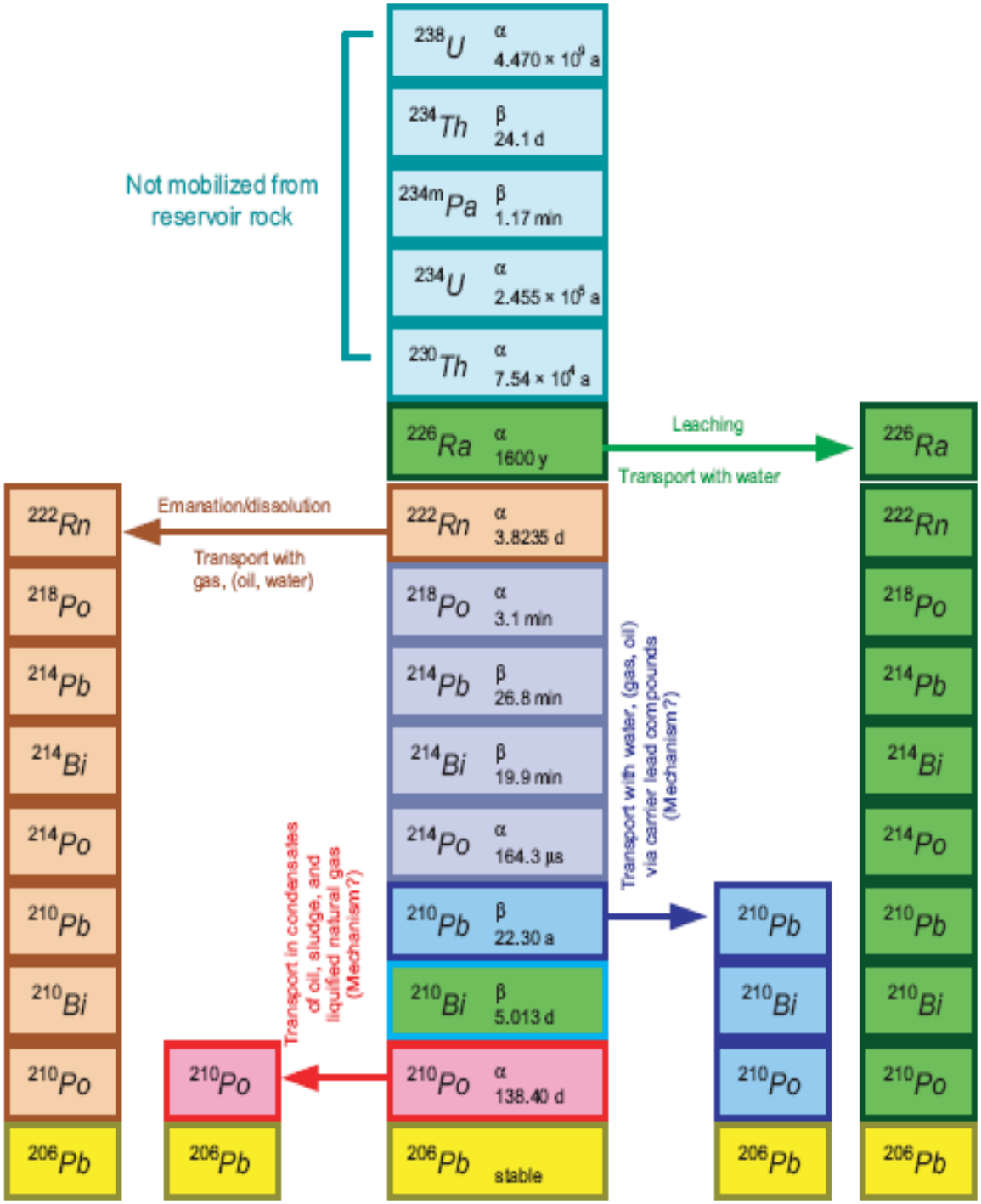

Figure 2.1 Uranium-238 decay series (IAEA, 2003)

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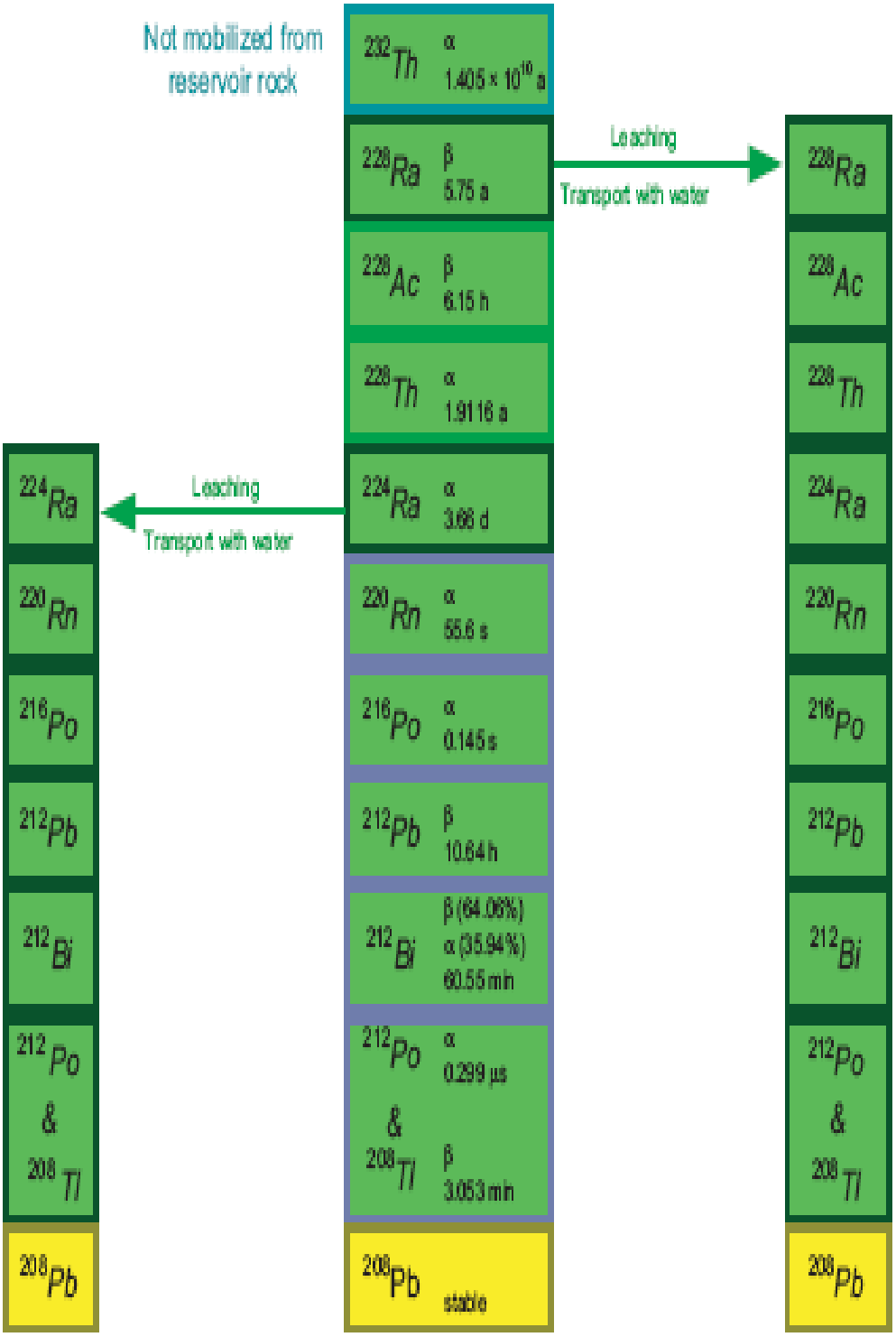

Figure 2.2 Thorium-232 decay series (IAEA, 2003)

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Table 2.4: Radioactive decay characteristics of NORMs associated with oil and gas production (IAEA, 2003)

Radionuclide	Half-life	Mode of decay	Main decay product(s)
Ra-226	1600a	Alpha	Rn-222(noble gas)
Rn-222	3.8235d	Alpha	Short live progeny
Pb-210	22.30a	Beta	Po-210(alpha emitter)
Po-210	138.40d	Alpha	Pb-206(stable)
Ra-228	5.75a	Beta	Th-228
Th-228	1.9116a	Alpha	Ra-224
Ra-224	3.66d	Alpha	Short live progeny

They are referred to 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. When the ions of the Group II elements, including radium, are present in the produced water, drops in pressure and temperature can lead to the solubility products of their mixed sulphates and carbonates being exceeded. This causes their precipitation as sulphate and carbonate scales on the inner walls of production tubulars (T), wellheads (W), valves (V), pumps (P), separators (S), water treatment vessels (H), gas treatment (G) and oil storage tanks (O) (Figure 2.3). Deposition occurs where turbulent flow, centripetal forces and nucleation sites provide the opportunities. Particles of clay or sand co-produced from the reservoir may also act as surfaces initiating scale deposition or may adsorb the cations.

If seawater, used to enhance oil recovery, mixes with the formation water, it will increase the sulphate concentration of the produced water and enhance scale deposition. Mixing may occur in the formation if 'breakthrough' occurs, which will result in scale deposits in the well completion, or the waters may be combined from different producing wells and mixed in topside plant and equipment. The mixed stream of oil, gas and water also carries the noble

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gas ^{222}Rn that is generated in the reservoir rock through decay of ^{226}Ra (IAEA, 2003; Jonkers et al., 1997).

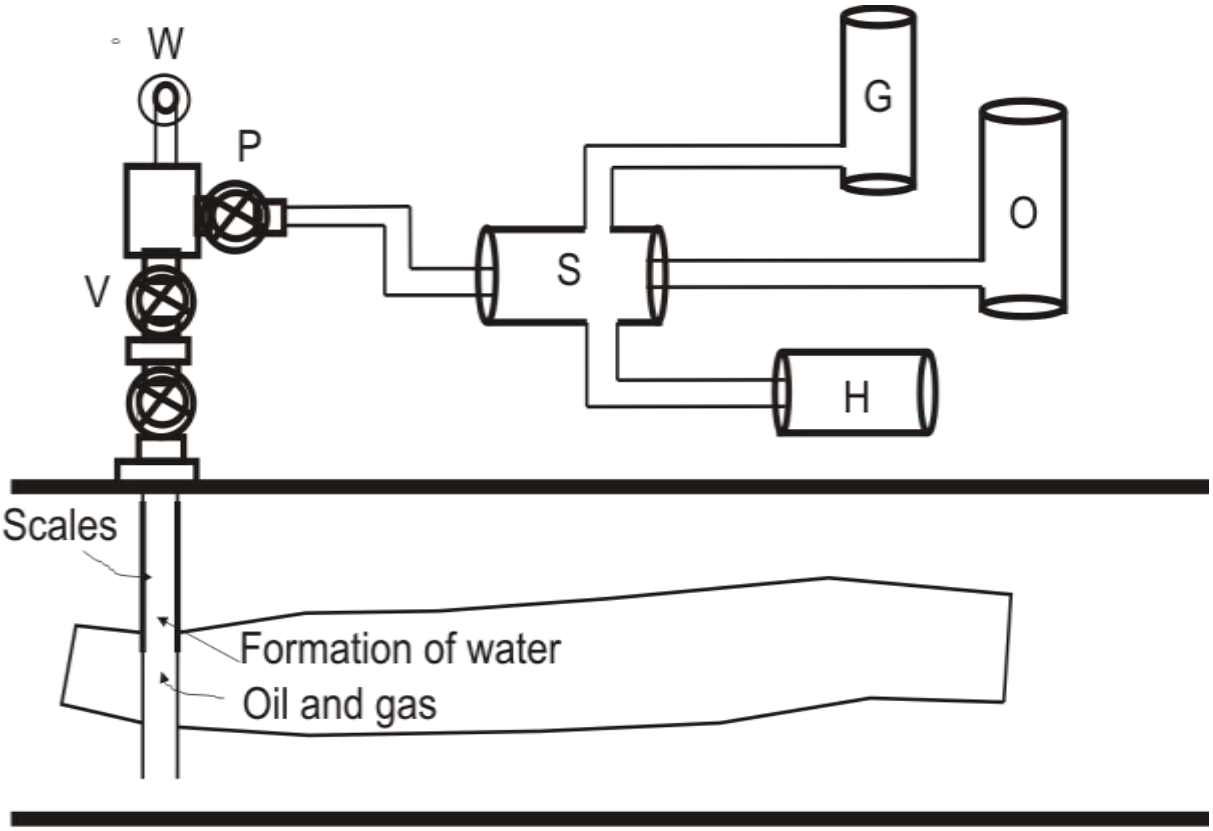

Figure 2.3 Precipitation of scales in production plant and equipment **(IAEA, 2003)**

This radioactive gas from the production zone travels with the gas–water stream and then follows, preferentially, the dry export gases (IAEA, 2003; Jonkers et al., 1997**)**. Consequently, equipment from gas treatment and transport facilities may accumulate a very thin film of ^{210}Pb formed by the decay of short lived progeny of ^{222}Rn adhering to the inner surfaces of gas lines. These ^{210}Pb deposits are also encountered in liquefied natural gas processing plants. A quite different mechanism results in the mobilization, from the reservoir rock, of stable lead that contains relatively high concentrations of the radionuclide

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^{210}Pb. This mechanism, although not well understood **(**Jonkers et al., 1997) has been observed 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.

2.5 Occurrence of NORMS in Scale, Sludge and Sand

The main types of NORMs in oil and gas installations are scale, sludge, sand and thin film deposits of radon decay products. Their occurrence depends on certain reservoir parameters and can be triggered by water flooding a reservoir **(**APPEA, 2002**).**

2.5.1 Occurrence of NORM scale

Provided the formation water contains barium, strontium or calcium as well as sulphates and carbonates, scale can build up in well tubing where a considerable pressure and temperature drop occurs between the reservoir and the crude oil in the well tubing. Scale formation in well tubing can be predicted on the basis of concentrations of cations and anions in the formation water, reservoir temperature and pressure, temperature and pressure in the well tubing etc. (APPEA, 2002; Odo and Tomson, 1994). It is important to understand that if scale forms, in the majority of cases it contains radium and its radium specific activity depends on levels of radium and thorium in reservoir sands. Generally, the specific radium activity in calcium carbonate scales is lower than the specific activity of barium sulphate scales **(**APPEA, 2002**)**. The water chemistry of several wells of a reservoir can be

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substantially different (some wells may contain elevated concentrations of barium and strontium and low concentrations of sulphates whilst the formation water of other wells may be deficient in barium and strontium but contain elevated concentrations of sulphates). This happens when a part of the reservoir is flooded by sea water, which has an elevated concentration of sulphates, to increase the production pressure. Under such circumstances an intensive scale formation occurs when the two types of incompatible water mix in a production header. Provided scale is found in the upstream sections of an oil producing facility (well tubing, production header, etc.), it is likely that NORMs would be present in the remaining parts of the facility as well. Nevertheless, their production rates differ depending on the type of the primary scale formation process and several other factors **(**APPEA, 2002**).** Scales are brittle minerals and thus scale build up in pipes and vessels frequently cracks due to temperature contractions of pipes, movement of flexible hoses, etc. Scale debris are removed from pipe surfaces and are carried with crude oil and produced water. Coarse scale debris ends up in separators and sand traps, while fines end up in slops tanks.

The most 'difficult' type of NORM from a waste management perspective is the practically insoluble barium (radium) sulphate scale that is formed in pipes and vessels. Barium sulphate scales are usually more radioactive than carbonate scales. Scale build-up in pipes and vessels may also cause production complications (clogging pipes and valves and undesirable accumulation of large quantities of NORM solids in vessels and separators) **(**Kvasnicka, 1998**)**. The specific activity of radium in NORMs from two Australian offshore petroleum production facilities has been summarised in Table 2.5 (Kvasnicka, 1992 and 1997). Because the first facility had only NORMs based on barium sulphate whilst the

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second one had a NORM mixture of barium sulphate and calcium carbonate (Kvasnicka, 1992 and 1997).The oil industry international exploration and production forum (E&P Forum, 1987) reported a wide range of radium activities in scale: northern part of the North Sea up to 3,700 Bq/g; mid North Sea up to 15,200 Bq/g; northern Europe up to 3,400 Bq/g; and southern Europe 0.37 Bq/g. In the USA, scale was reported to have a specific radium activity in excess of 100 Bq/g **(**APPEA, 2002**).** Scale build up in components of gas plants is usually minor.

Table 2.5: NORMs in two Australian offshore petroleum production facilities (Kvasnicka, 1998)

NORM Type	**Specific activities(Bq / g)**	
	Radium-226	**Radium-228**
Scale	250*	300*
	150**	240**
	21**	48**
Sludge	25*	30*
Sand	8.9*	9.6*

*Note: * The first facility had only barium sulphate based scale and NORMs.*
*** The second facility had a mixture of barium sulphate scale and calcium carbonate scale*

2.5.2 Occurrence of NORM sand

Small quantities of sand are carried in crude oil and coarse sand is trapped in sand traps located upstream from separators and in separators as well. In oil production facilities with scale build up, sand is highly contaminated with scale debris and radium content in this waste stream needs to be taken into account when disposing of such sands. In facilities with high concentrations of calcium and carbonates, a rapid precipitation of coarse calcium

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carbonate particles may occur in those facility components with a positive temperature gradient. Such crystal precipitate usually accumulates in separators and a fine fraction increases the sludge production rate. There is usually only a minor waste sand stream in natural gas plants **(**APPEA, 2002; IAEA, 2003**).**

2.5.3 Occurrence of NORM sludge

Sludge usually contains fine sand particles, corrosion particles, flakes of paint, bacteria growth and fines derived from scale. Sludge is usually accumulated in separator vessels and slops tanks of oil production facilities. The specific activity of radium in NORMs (including sludge) from two Australian offshore petroleum production facilities has been summarised in Table 2.5. In gas plants, sludge containing radium and solids accumulated in separators containing ^{210}Pb or ^{210}Po must be periodically removed **(**APPEA, 2002; IAEA, 2003**).**

2.5.4 A summary of radionuclide concentrations of NORM

A large amount of data has been collected over the years on the radionuclide concentrations in NORM, although relatively few reports have been published **(**APPEA, 2002; IAEA, 2003**)**. It would appear that the concentrations of ^{226}Ra, ^{228}Ra and ^{224}Ra in scales and sludge range from less than 0.1 Bq/g up to 15 000 Bq/g **(**APPEA, 2002**)** (Table 2.6). Generally, the activity concentrations of radium isotopes are lower in sludge than in scales. The opposite applies to ^{210}Pb, which usually has a relatively low concentration in hard scales but which may reach a concentration of more than 1000 Bq/g in lead deposits and sludge. Although 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. As a result, when scales containing ^{228}Ra grow

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older, the concentration of ^{228}Th increases to about 150% of the concentration of ^{228}Ra still present (IAEA, 2003).

Table 2.6: **Concentration of NORM in Oil, Gas and By- Products** (Jonkers et al., 1997)

Radionuclides	Crude oil (Bq / g)	Natural gas (Bq / m^3)	Produced water (Bq / L)	Hard scale (Bq / g)	Sludge (Bq / g)
U-238	0.0000001-0.01		0.0003-0.1	0.001-0.5	0.005-0.01
Ra-226	0.0001-0.04		0.002-1200	0.1-15000	0.05-800
Po-210	0-0.01	0.002-0.08		0.02-1.5	0.004-160
Pb-210		0.005-0.02	0.05-190	0.02-75	0.1-1300
Rn-222		5-200000			
Th-232	0.00003-0.002		0.0003-0.001	0.001-0.002	0.002-0.01
Ra-228			0.3-180	0.05-2800	0.5-50
Ra-224			0.5-40		

2.6 Radiation Protection Aspects of NORM

In the absence of suitable radiation protection measures, NORM in the oil and gas industry could cause external exposure during production owing to accumulations of gamma emitting radionuclides and internal exposures of workers and other persons, particularly during maintenance, the transport of waste and contaminated equipment, the decontamination of equipment, and the processing and disposal of waste (IAEA, 2003). Exposures of a similar nature may also arise during the decommissioning of oil and gas production facilities and their associated waste management facilities.

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2.6.1 Radiation exposure pathway

Radiation exposure from oil and gas NORM can occur from seven environmental pathways: radon inhalation, external gamma exposure , ground water ingestion, surface water ingestion, dust inhalation, food ingestion and skin beta exposure (Smith, 1992). Populations at risk from exposure to NORM radiation include workers at equipment cleaning facilities, oilfield workers, workers at NORM disposal facilities, and the general public. Workers at equipment cleaning facilities are considered to be at the greatest risk of exposure to NORM. Exposure pathways of concern are external gamma exposure, dust inhalation, and skin beta exposure. External exposure occurs when concentration of NORM inside equipment is high enough that gamma rays penetrate the equipment walls, and NORM contaminated scale and sludge are removed from the equipment, thereby eliminating the shielding factor provided by the equipmement walls **(**Smith, 1992**)**. Dust inhalation is possible when dry cleaning processes are used without adequate controls. Direct contact with contaminated scale and sludge can result in skin beta exposures.

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. The general population may be at risk to NORM via radon inhalation, groundwater ingestion, surface water ingestion, and food ingestion. Improper disposal of NORM contaminated scale and sludge may lead to soil and water contamination and to higher indoor radon levels in nearby buildings **(**Smith, 1992; USEPA, 1993**)**. Ingestion of food grown in contaminated soils or seafood harvested in areas

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contaminated by produce water outfalls may result in radiation exposure. A recent risk assessment for radium discharged in produced waters indicated a potential risk of exposure exists for an individual who ingests large amounts of seafood harvested near a produced water discharge point over a lifetime **(**Smith, 1992**)**.

2.6.2. External exposure

The deposition of contaminated scales and sludge in pipes and vessels may produce significant dose rates inside and outside these components (Table 2.7). Short lived progeny of the radium isotopes, in particular ^{226}Ra, emit gamma radiation capable of penetrating the walls of these components, and the high energy photon emitted by ^{208}Tl (one of the progeny of ^{228}Th) can contribute significantly to the dose rate on outside surfaces when scale has been accumulating over a period of several months.

Table 2.7: **External Gamma Radiation Dose Rates observed in some Oil Production and Processing Facilities (IAEA, 2003)**

Location	Dose rate (μSv / h)
Down hole tubing, safety valves(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 dose rates depend on the amount and activity concentrations of the radionuclides present inside and the shielding provided by pipe or vessel walls. Maximum dose rates are usually in the range of up to a few microsieverts per hour. In exceptional cases, dose rates measured directly on the outside surfaces of production equipment have reached several

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hundred microsieverts per hour **(**Jonkers et al., 1997; Van Weers, 1997**)**, which is about 1000 times greater than normal background values due to cosmic radiation and terrestrial radiation. The buildup of radium scales can be monitored without opening plant or equipment (Plate 2.1). Where scales are present, opening the system for maintenance or for other purposes will increase dose rates. External exposure can be restricted only by maximizing the distance from, and minimizing duration of exposure to, the components involved. In practice, restrictions on access and occupancy time are found to be effective in limiting annual doses to low values. Deposits consisting almost exclusively of ^{210}Pb cannot be assessed by measurements outside closed plant and equipment. Neither the low energy gamma emissions of ^{210}Pb nor the beta particles emitted penetrate the steel walls. Therefore, ^{210}Pb does not contribute significantly to external dose and its presence can be assessed only when components are opened.

Plate 2.1: ***Monitoring the outside of plant and equipment using a dose rate meter (courtesy: National Radiological Protection Board, UK)***

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2.6.3. Internal exposure

Internal exposure to NORM may result from the ingestion or inhalation of radionuclides. This may occur while working on or in open plant and equipment, handling waste materials and surface contaminated objects, and during the cleaning of contaminated equipment. Ingestion can also occur if precautions are not taken prior to eating, drinking, smoking, etc. Effective precautions are needed during the aforementioned operations to contain the radioactive contamination and prevent its transfer to areas where other persons might also be exposed. The non-radioactive characteristics of scales and sludge also demand conventional safety measures, and therefore the risk of ingesting NORM is likely to be very low indeed. However, cleaning contaminated surfaces during repair, replacement, refurbishment or other work may generate airborne radioactive material, particularly if dry abrasive techniques are used. The exposure from inhalation could become significant if effective personal protective equipment (including respiratory protection) and/or engineered controls are not used.

The potential committed dose from inhalation depends on both the physical and chemical characteristics of NORM. It is important to consider the radionuclide composition and activity concentrations, the activity aerodynamic size distribution of the particles (quantified by the activity median aerodynamic diameter, or AMAD), and the chemical forms of the elements and the corresponding lung absorption types. The BSS (IAEA, 1996) quotes the following lung absorption types for the elements of interest 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)

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(d) Bismuth (nitrate): fast (F)

(all unspecified compounds): medium (M)

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

(oxides, hydroxides): slow (S).

The effective dose per unit intake (Table 2.8) of dust particles of 5 μm AMAD (the default size distribution for normal work situations) and 1 μm AMAD (a size distribution that may be more appropriate for work situations such as those involving the use of high temperature cutting torches) are also reported (IAEA, 1996 and 2003).

Table 2.8: **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	$2.26x10^{-6}$	$3.8x10^{-5}$	$3.2x10^{-6}$
Pb-210	$1.1x10^{-6}$	$4.5x10^{-6}$	$8.9x10^{-7}$
Po-210	$2.2x10^{-6}$	$2.8x10^{-6}$	$3.0x10^{-6}$
Ra-228	$1.7x10^{-6}$	$1.2x10^{-5}$	$2.6x10^{-6}$
Th-228	$3.2x10^{-6}$	$3.2x10^{-5}$	$3.9x10^{-5}$
Ra-224	$2.4x10^{-6}$	$2.8x10^{-6}$	$2.9x10^{-6}$

For each case, values are quoted for the slowest lung absorption type listed in the BSS (S for thorium, M for radium, polonium and bismuth, and F for lead — as noted above) (IAEA, 1996). In addition, values for 5 μm AMAD calculated by Silk (IAEA, 2003) are quoted, based on a more conservative assumption that all radionuclides are of lung absorption type S. The inhalation of particles of 5 μm AMAD incorporating ^{226}Ra (with its complete decay

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chain in equilibrium), ^{228}Ra, and ^{224}Ra (with its complete decay chain in equilibrium), each at a concentration of 10 Bq/g, would deliver a committed effective dose per unit intake of about 0.1–1 mSv/g, the exact value depending on the extent of ingrowth of ^{228}Th from ^{228}Ra and the lung absorption types assumed. For 1 μm AMAD particles, the committed effective dose per unit intake would be about 25–30% higher (based on the slowest lung absorption types) (IAEA, 1996).

2.6.4. Decontamination of plant and equipment

The removal of NORM-containing scales and sludges from plant and equipment, whether for production and safety reasons or during decommissioning, needs to be carried out with adequate radiation protection measures and other relevant safety, waste management and environmental aspects. In addition to the obvious industrial and fire hazards, the presence of other contaminants such as hydrogen sulphide, mercury and hydrocarbons (including benzene) may necessitate the introduction of supplementary safety measures. On-site decontamination is the method preferred by operators when the accumulation of scales and sludges interferes with the rate and safety of oil and gas production, especially when the components cannot be reasonably removed and replaced or when they need no other treatment before continued use (IAEA, 2003). The work may be carried out by the operator's workers but is usually contracted out to service companies. It will necessitate arrangements, such as the construction of temporary habitats, being made to contain any spillage of hazardous material and to prevent the spread of contamination from the area designated for the decontamination work. Decontamination work has to be performed off the site where (IAEA, 2003):

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a) On-site decontamination cannot be performed effectively and or in a radiologically safe manner;

(b) The plant or equipment has to be refurbished by specialists prior to reinstallation;

(c) The plant or equipment needs to be decontaminated to allow clearance from regulatory control for purposes of reuse, recycling or disposal as normal waste.

Service companies hired to perform decontamination work need to be made fully aware of the potential hazards and the rationale behind the necessary precautions, and may need to be supervised by a qualified person. The service companies may be able to provide specific facilities and equipment for the safe conduct of the decontamination operations, for example a converted freight container on the site (Plate 2.2) or a designated area dedicated to the task (Plate 2.3). Personal protective measures will comprise protective clothing and, in the case of handling dry scale, respiratory protection as well. The regulatory body needs to set down conditions for the (IAEA, 2003):

(a) Protection of workers, the public and the environment;

(b) Safe disposal of solid wastes;

(c) Discharge of contaminated water;

(d) Conditional or unconditional release of the decontaminated components.

2.6.5. Practical radiation protection measures

The requirements for radiation protection and safety established in the BSS (IAEA, 1996) apply to NORM associated with installations in the oil and gas industry. The common goal in all situations 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 practical measures that need to be taken in order to reach these goals differ

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principally for the two types of radiation exposure: through external radiation and internal contamination (IAEA, 2003).

Plate 2.2: ***Workers wearing personal protective equipment decontaminating a valve inside an on-site facility (courtesy: National Radiological Protection Board, UK).***

Plate 2.3: ***Barrier designating a controlled area to restrict access to NORM-contaminated equipment stored outside a decontamination facility (courtesy: National Radiological Protection Board, UK).***

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2.6.5.1. Measures against external exposure

The presence of NORM in installations is unlikely to cause external exposures approaching or exceeding annual dose limits for workers. External dose rates from NORM encountered in practice are usually so low that protective measures are not needed. In exceptional cases where there are significant but localized dose rates, the following basic rules can be applied to minimize any external exposure and its contribution to total dose (IAEA, 2003):

(a) Minimizing the duration of any necessary external exposure;

(b) Ensuring that optimum distances be maintained between any accumulation of NORM (installation part) and potentially exposed people;

(c) Maintaining shielding material between the NORM and potentially exposed people.

The first two measures, in practice, involve the designation of supervised or controlled areas to which access is limited or excluded. The use of shielding material is an effective means of reducing dose rates around radiation sources but it is not likely that it can be added to shield a bulk accumulation of NORM. However, the principle may be applied by ensuring that NORM remains enclosed within (and behind) the thick steel wall(s) of plant or equipment such as a vessel for as long as feasible while preparations are made for the disposal of the material. If large amounts of NORM waste of high specific activity are stored, some form of localized shielding with lower activity wastes or materials may be required to reduce gamma dose rates on the exterior of the waste storage facility to acceptably low levels (IAEA, 2003).

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2.6.5.2. Measures against internal exposure

In the absence of suitable control measures, internal exposure may result from the ingestion or inhalation of NORM while working with uncontained material or as a consequence of the uncontrolled dispersal of radioactive contamination. The risk of ingesting or inhaling any radioactive contamination present is minimized by complying the following basic rules whereby workers (IAEA, 2003):

(a) Use protective clothing in the correct manner to reduce the risk of transferring contamination

(b) Refrain from smoking, drinking, eating, chewing (e.g. gum), applying cosmetics (including medical or barrier creams, etc.), licking labels, or any other actions that increase the risk of transferring radioactive materials to the face during work;

(c) Use suitable respiratory protective equipment as appropriate to prevent inhalation of any likely airborne radioactive contamination;

(d) Apply, where practicable, only those work methods that keep NORM contamination wet or that confine it to prevent airborne contamination;

(e) Implement good housekeeping practices to prevent the spread of NORM contamination;

(f) Observe industrial hygiene rules such as careful washing of protective clothing and hands after finishing the work.

2.7 Oil and Gas Companies in Ghana and Waste Transfer

Currently there are seven oil and gas companies as at 2013 holding concessions or blocks in the Jubilee field of Ghana in addition to the Saltpond offshore producing company limited (SOPCL) operator of Saltpond field. Some of these are; Tullow Ghana Limited (TGL),

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Kosmos Energy, Hess, Chevron, Vanco, and ENI-Exploration. Out of these companies, it is only TGL and SOPCL that are into oil and gas production at present and the rest of them are into exploration activities. Tullow Ghana limited (TGL) is an oil and gas exploration and production company duly registered with the Ghana National Petroleum Corporation and the Petroleum Commission of Ghana. Tullow is the designated operator of the Jubilee field offshore the west coast of Ghana. The offshore oil and gas production facility (FPSO Kwame Nkrumah) has been in operation in the field since June 2010. Wastes that are generated from the offshore exploration and production activities are transferred to private local waste management companies e.g. Zeal Environmental Technology Limited and MI SWACO for safe management.

2.7.1 The waste transfer

2.7.1.1 Associated waste

This waste that includes used batteries, fluorescent tubes, used computers, oily rags, oily waste water, general garbage, plastic and metallic chemical drums, used filters etc. are produced at the Jubilee field. These wastes are segregated and packed into sacks, enclosed containers, bilge water holding tanks and boxes depending on the properties of the waste and then transported to the harbour by a vessel. From the harbour the wastes are transported to the treatment facility in garbage trucks. Oily waste water/bilge water generated by vessels (ships) or as a result of cleaning of tanks for supply vessels are transferred to the Zeal facility by oil tanker from Takoradi harbour. The Plate 2.4 below shows a tanker siphoning bilge water/sludge from a vessel at Takoradi to the port reception facility at Zeal Environmental Technology Limited.

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Plate 2.4: ***Tanker siphoning bilge water/ oily waste water from a vessel (courtesy: Zeal Environmental Technology Limited, Ghana)***

2.7.1.2 Drilling waste

The drilling fluids and cuttings are produced on the rigs. The fluids are then separated from the cuttings by a solid control system. The fluids may be recirculated downhole for reuse living the cuttings behind. The cuttings are conditioned offshore and disposed in deep seas through caisson. The fluids that may fall short of some properties are transported by vessels from the Jubilee field using a complete system of cuttings and storage equipment (cutting boxes and skips, catch tanks, slider tanks, free flow positive pressure cuttings transfer system, vacuum transfer system, screw conveyor (Auger) and Brandt Transfer System) to Takoradi harbour. The catch tanks containing the fluid are further transported from the harbour to a company (MI Swaco) responsible for supply and reconditioning of the fluid (mud) for reuse. The residues of the mud placed in skips are finally transported to Zeal in dustbin cars for final treatment and disposal in the landfill.

2.7.1.3 Produced water

The produced water is discharged off board after reinjection along with sea water for reservoir pressure maintenance, or injection into suitable offshore disposal well.

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In Ghana at present, the produced water is discharged offboard. This management option is used taking into consideration our climatic conditions that favour activity of oil eating bacterial such *Alcanivorax* on any possible oil contaminants within the water. In this study the, the untreated oily waste water, treated output and produced water are going to be investigated for their radiological significance.

2.7.2 Oil and Gas Waste Management Systems in Ghana

2.7.2.1 Associated waste management

Bilge water/oily waste water are treated in the country by companies that have been approved by EPA and other relevant bodies. Zeal Environmental Technology Limited, TOR and Tilbury Environmental group are some of the companies that handle these wastes. Various oily waste separators are used to separate the oil from the water. The recovered oil is recycled or reuse e.g. residual fuel is used to mix the waste oil to increase its calorific value in other to be used as fuel to fire boilers in textile industries in the country. The water is then discharged into the marine environment if its parameters meet the effluent discharge standard set by EPA and other regulatory bodies.

Also all modern vessels have onboard oily waste separators according to Marpol 73/78 (1973/1978) Convention. Therefore vessels also treat the bilge water (Plate 2.5) before discharging off board.

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Plate 2. 5: ***Oily waste water separator on a vessel (courtesy: Zeal Environmental Technology Limited, Ghana)***

General garbage generated on vessels that berth at our shores is either sent to landfill onshore for disposal or incinerated onboard. Hazardous waste such as used oil, oily rags and PCB containing materials are not incinerated onboard. Recyclable waste e.g. metals, plastics, glass, wood etc are sent to the various recycling companies for proper management.

At Zeal where most of the TGL wastes are managed, the wastes are first segregated for easy and appropriate management option e.g. metals are separated from plastics, acids batteries are drained and the acid is neutralized with a base. The resulting solution is then added to the oily waste water for treatment. Waste electronic and electrical equipment (WEEE) are either refurbished or dismantled into various components for recycling. Plastics containers are cut with shredders and metallic drums are also crushed with crushers and recycled.

The oily rags, oil filter, plastics, wood contaminated with oil etc. are incinerated onshore at Zeal. The resulting ash is stored in tightly closed containers awaiting proper disposal option.

Left over chemicals from the oil and gas companies are either reused or sent to the source for the right management applications.

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2.7.2.2 Drilling waste management

The drilling cuttings generated offshore are discharged into the deep seas after offshore treatment. This option depends on certain factors such as the depth (beyond 500 m) of the water (sea), the climatic conditions, and the drilling fluid used during the drilling process. In some countries where their drilling and production activities take place in shallow waters as well as the activity of bacteria on the oil associated with the cuttings would be low due to very low temperatures, the cuttings are buried onshore in a lined cuttings pits.

The Oil/Water/Synthesis based mud is solidified by addition of lime. The resulting mortar is used by Zeal Environmental Technology Limited to mould blocks as a management practice.

2.7.2.3 Produced water management

The produced water is discharged offboard after offshore treatment. In countries where the offshore treatment is absent or cannot meet the stated bench mark, the water is treated onshore. Table 2.9 below shows the waste type, the company and the management options available.

It is evident from the overview of oil and gas waste management system currently available in Ghana as presented in this section and summarized in Figure 2.4 and Table 2.9 that currently the oil and gas waste management system as in place excludes major NORM related issues and a such the approved oil waste management companies may not have capacity to handle potential NORM waste such as Scale, sludge and produce water. The preceding sections present an overview of waste management systems and disposal methods for NORM waste that could serve as a guide for management of NORM waste from the oil and gas industry in Ghana

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Table 2.9: Type of waste, technology, the companies involve and the treatment option available

Type of waste	Technology	Company	Treatment/disposal options
Oily wastewater/bilge water, tank slops	API oily waste separator API oily waste separator BOWTS	Zeal Env.tal Technology LTD. Tema Oil Refinary. Tilbury Environmental Group	Discharged into the sea
Drilling cuttings, OBM,WBM, SOBM	Solidification with lime	Zeal Env.tal Technology LTD. Tema Oil Refinary.	Block, landfill Landfill Landfill
Ash (oily rags, oil filters, papers, wood)	Incineration	Zeal Env.tal Technology LTD.	Storage
Batteries (lead acid, dry cells)	-	Zeal Env.tal Technology LTD.	Acid content is neutralized and manage as oily waste, Storage.
Plastics	Shredding	Zeal Env.tal Technology LTD.	Reuse, recycle
Waste electronic and electrical equipment (WEEE)	Manual segregation	Zeal Env.tal Technology LTD.	Reuse, recycle, storage
Chemicals/chemical containers.	Incineration	Zeal Env.tal Technology LTD.	Neutralization of the chemical and recycling of the containers.
General garbage	Incineration	Zeal Env.tal Technology LTD.	Landfill

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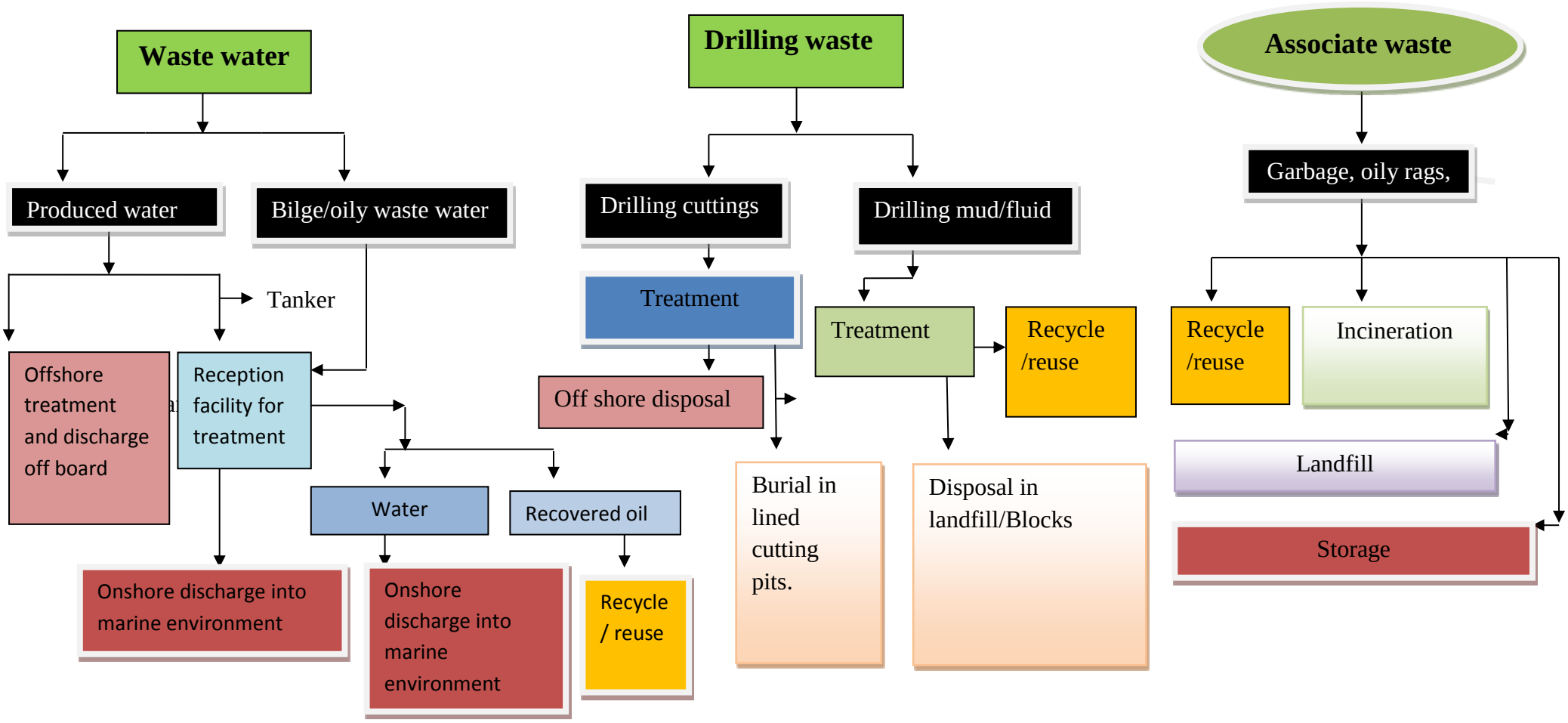

Figure 2.4: A Summary flow chart showing wastes and management processes currently being used by oil waste management companies in Ghana

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2.8 Waste Management Considerations with respect to NORMs

Solid and liquid wastes are generated in significant quantities during the operating lives of oil and gas facilities. Additional quantities of other (mostly solid) wastes may be produced during decontamination activities and during the decommissioning and rehabilitation of the production facility and associated waste management and treatment facilities. These wastes contain naturally occurring radionuclides. Depending on the activity concentrations, they may have radiological impacts on workers, as well as on members of the public who may be exposed if the wastes are dispersed into the environment. These radiological impacts are in addition to any impact resulting from the chemical composition of the wastes. Various types of NORM waste are generated during oil and gas industry operations, including (IAEA, 2003):

(a) Produced water,

(b) Sludges and scales,

(c) Contaminated items,

(d) Wastes arising from waste treatment activities,

(e) Wastes arising from decommissioning activities.

The radionuclide activity concentrations in produced water are low, but the volumes are large. The radionuclide activity concentrations in solid wastes vary from low to high, but the volumes are always relatively small. The long half-lives of the radionuclides have important implications for the management of solid wastes because of the long time periods for which control may be necessary. The fact that most of the wastes are depleted in the parent

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uranium and or thorium radionuclides also needs to be taken into consideration (IAEA, 2003).

2.8.1 Wastes from the decontamination of plant and equipment

Decontamination of plant and equipment gives rise to different waste streams depending on the type of contaminating material and the decontamination method applied. For instance, in-situ descaling produces water containing the chemicals applied as well as the matrix and the radionuclides of the scale. Mechanical decontamination by dry methods will produce the dry scale as waste. Dry waste also arises from filter systems used to remove radioactive aerosols from venting systems**.** Dry abrasive decontamination without the use of filters is to be avoided, as airborne dispersal of the contaminant may give rise to an additional waste stream that is difficult to control. The types of waste stream generated by decontamination processes are summarized below (IAEA, 2003):

(a) sludges removed from pipes, vessels and tanks;

(b) solid scale suspended in water;

(c) liquids containing dissolved scale and chemicals used for chemical decontamination;

(d) solid scale recovered from wet or dry abrasive decontamination processes;

(e) waste water resulting from removal of scale by sedimentation and or filtration of water used for wet abrasive methods, in particular high pressure water jetting (HPWJ);

(f) filters used to remove airborne particulates generated by dry abrasive decontamination methods;

(g) slag from melting facilities;

(h) flue dust and off-gas (containing the more volatile naturally occurring radionuclides) from melting facilities.

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In practice, these waste streams contain not only naturally occurring radionuclides but other constituents as well. These other constituents include the compounds from chemical mixes used for decontamination, solid or liquid organic residues from oil and gas purification and heavy metals. In particular, mercury, lead and zinc are encountered frequently in combination with NORM from oil and gas production. In practice, these other components in waste streams from decontamination will demand adoption of additional safety measures and may impose constraints on disposal options. Also, the volatility of the heavy metals mentioned above will limit the practicability of melting as a decontamination option (IAEA, 2003).

2.8.2 Waste management strategy and programmes

Radioactive waste management comprises managerial, administrative and technical steps associated with the safe handling and management of radioactive waste, from generation to release from further regulatory control or to its acceptance at a storage or disposal facility (IAEA, 2003). It is important that the radioactive waste management strategy forms an integral part of the overall waste management strategy for the operation — non-radiological waste aspects such as chemical toxicity also need to be considered, since these will influence the selection of the optimal waste management options for the radioactive waste streams. For sludges in particular, the constraints on waste disposal or processing options imposed by non-radioactive contaminants will in many cases be greater than those imposed by radioactive components. In view of the range of NORM waste types that can be generated in the industry at different times and the possibility of changes occurring in the ways in which they are generated and managed, particular attention needs to be given to the

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radiation protection issues which may arise in their management and regulatory control. Because of the nature of the industry, and the fact that the volumes and/or activity concentrations are relatively small, there is often limited knowledge among the staff about the radiation protection aspects of waste management. While the safety principles (IAEA, 1995) are the same for managing any amount of radioactive waste regardless of its origin, there may be significant differences in the practical focus of waste management programmes. Good operating practice will focus on ways in which the amount of radioactive waste can be minimized (IAEA, 2003).

2.8.3 Risk assessment

A waste management risk assessment is a quantitative process that considers all the relevant radiological and non-radiological issues associated with developing a waste management strategy. The overall aim is to ensure that human health and the environment are afforded an acceptable level of protection in line with current international standards (IAEA, 1995, 1999, and 2004). Prior to any detailed risk assessment, there should be an overall assessment of waste management options that will not be based only on radiological criteria. At the detailed risk assessment stage, the following radiological considerations are addressed in a quantitative manner (IAEA, 1995, 1999, 2003 and 2004):

(a) Identification and characterization of radioactive waste source terms;

(b) Occupational and public exposures associated with the various waste management steps from waste generation through to disposal;

(c) Long term radiological impact of the disposal method on humans and on the environment;

(d) All phases of the operation from construction to decommissioning;

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(e) Optimal design of waste management facilities;

(f) All significant scenarios and pathways by which workers, the public and the environment may be subject to radiological (and non-radiological) hazards.

The results of the assessment are then compared with criteria specified by the regulatory body. These criteria normally include annual dose limits for workers exposed during operations and for members of the public exposed to radioactive discharges during operation and after closure. The regulatory body may specify, in addition, derived levels and limits related to activity concentration and surface contamination. These derived values are usually situation specific and may relate to materials, items or areas that qualify for clearance from regulatory control (IAEA, 2003).

2.8.4 Regulatory approach

It is important that the regulatory body achieve a consistent regulatory approach for protection against the hazards associated with NORM wastes in line with international waste management principles (IAEA, 1995) and the BSS (IAEA, 1996). Regulatory bodies unfamiliar with control over radioactive wastes in the oil and gas industry need to develop a technical and administrative framework in order to address appropriately the radiation protection and waste management issues specific to that industry. Regulatory frameworks for the control of radioactive wastes generated in the oil and gas industry are under development in several IAEA Member States. For example, the management of NORM residues from industrial processes (including the oil and gas industry) by Member States of the European Union is now subject to the requirements of Article 40 of the Council Directive 96/29/ Euratom of 13 May 1996 (CEC, 1996). Implementation of this is in various

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stages of progress and involves the identification of work activities that may give rise to significant exposure of workers or of members of the public and, for those identified industries, the development of national radiation protection regulations in accordance with some or all of the relevant Articles of the Directive. It is important however to state that OVER REGULATION should be avoided and considerations of economic and social factors should be taken into account in the development of such regulations.

2.8.5 Characteristics of NORM wastes in the oil and gas industry

Waste characterization and classification are important elements at all stages of waste management, from waste generation to disposal. Their uses and applications include (IAEA, 2003):

(a) Identification of hazards;

(b) Planning and design of waste management facilities;

(c) Selection of the most appropriate waste management option;

(d) Selection of the most appropriate processing, treatment, packaging, storage and/or disposal methods.

It is important that records be compiled and retained for an appropriate period of time.

2.8.5. 1 Produced water

Produced water volumes vary considerably between installations and over the lifetime of a field, with a typical range of 2,400–4,0 000 m^3/d for oil producing facilities and 1.5–30 m^3/d for gas production (E& P forum, 1994). Produced water may contain ^{226}Ra, ^{228}Ra, ^{224}Ra and ^{210}Pb in concentrations of up to a few hundred becquerels per litre but is virtually free of ^{228}Th. Mean concentrations of 4.1 Bq/L of ^{226}Ra and 2.1 Bq/L of ^{228}Ra were recorded from a recent survey of Norwegian offshore oil production installations **(**Lysebo and Strand,

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1997**)** but concentrations at individual facilities may well reach levels 50 times higher. Ratios between the concentrations of the radionuclides mentioned vary considerably. As a consequence, the dominant radionuclide may be ^{226}Ra or ^{228}Ra or ^{210}Pb. Produced water contains formation water from the reservoir and or (with gas production) condensed water. If injection of seawater is used to maintain reservoir pressure in oil production it might break through to production wells and appear in the produced water. Produced water contains also dissolved hydrocarbons such as monocyclic aromatics and dispersed oil. The concentration of dissolved species, in particular Cl– and Na+, can be very high when brine from the reservoir is co-produced. Other constituents comprise organic chemicals introduced into the production system by the operator for production or for technical reasons such as scale and corrosion inhibition.

A wide range of inorganic compounds, in widely differing concentrations, occurs in produced water. Cation concentrations can be very high when brine is co-produced. They comprise not only the elements of low potential toxicity: Na, K, Ca, Ba, Sr and Mg, but also the more toxic elements Pb, Zn, Cd and Hg. The health implications of the last two (Cd and Hg) are the focus of particular attention by regulatory bodies and international conventions (IAEA, 2003).

2.8.5.2 Solid wastes

Solid NORM wastes include sludge, mud, sand and hard porous deposits and scales from the decontamination of tubulars and different types of topside equipment. The activity concentrations of ^{226}Ra, ^{228}Ra, ^{224}Ra and their decay products in deposits and sludge may vary over a wide range, from less than 1 Bq/g to more than 1000 Bq/g **(**Kolb and Wojcik, 1985**)**. For comparison, the average concentration of radionuclides in the ^{238}U decay series

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(including ^{226}Ra) in soils is about 0.03 Bq/g **(**UNSCEAR, 2000**)**. A production facility may generate quantities of scales and sludge ranging from less than 1 t/a to more than 10 t/a, depending on its size and other characteristics (API, 1996). The deposition of hard sulphate and carbonate scales in gas production tubulars, valves, pumps and transport pipes is sometimes accompanied by the trapping of elemental mercury mobilized from the reservoir rock. Deposits of ^{210}Pb have very high concentrations of stable lead mobilized from the reservoir rock. They appear as metallic lead and as sulphides, oxides and hydroxides. Sludges removed from oil and gas production facilities contain not only sand, silt and clay from the reservoir but also non-radioactive hazardous substances. Therefore, their waste characteristics are not limited to the radioactive constituents. In all sludges in which ^{210}Pb is the dominant radionuclide the stable lead concentration is also high. Sludges also contain (IAEA, 2003):

(a) Non-volatile hydrocarbons, including waxes;

(b) Polycyclic aromatic hydrocarbons, xylene, toluene and benzene;

(c) Varying and sometimes high concentrations of the heavy metals Pb, Zn and Hg.

In sludges from certain gas fields in Western Europe, mercury concentrations of more than 3% (dry weight) are not uncommon.

2.8.6 NORM Disposal Methods

Various disposal methods for liquid and solid NORM wastes are described in this section. The use of these methods by the oil and gas industry is not necessarily an indication that such methods constitute international best practice. Regulatory review, inspection, oversight and control over these disposal activities and methods have been generally lacking in the past. The issue of NORM waste management — and particularly disposal — has been

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identified in recent years as an area of radiation protection and safety that needs to be formally addressed by national regulatory bodies wherever oil and gas production facilities are operating. The process of selecting and developing a disposal method for NORM wastes forms an essential part of the formal radioactive waste management programme for a production facility, although the process is generally not conducted at the level of individual production facilities but at company level or at the level of associations of companies. In addition, it is important to commence selection of the optimal waste disposal method at an early stage of the project.

In developing a waste management strategy the overall aims are to:

(a) Maximize the reduction of risks to humans and to the environment associated with a particular disposal method in a cost effective manner;

(b) Comply with occupational and public dose limits and minimize doses in accordance with the ALARA principle;

(c) Comply with all relevant national and international laws and treaties;

(d) Comply with all national regulatory requirements.

Disposal methods for NORM wastes fall into four main categories:

(1) Dilution and dispersal of the waste into the environment, e.g. liquid or gaseous discharges;

(2) Concentration and containment of the waste at authorized waste disposal facilities;

(3) Processing of the waste with other chemical waste by incineration or other methods;

(4) Disposal of the waste by returning it back to the initial source of the material (reinjection into the reservoir).

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NORM wastes meeting the clearance criteria (IAEA, 1996 and 2003) specified by the regulatory body may be disposed of as normal (non-radioactive) waste.

2.8.6.1 Regulatory review and approval

The disposal of NORM radioactive wastes originating from the oil and gas industry will require the approval of the regulatory body with regard to:

(a) The acceptability and long term safety of the proposed disposal method;

(b) The risk assessments submitted by the owner/operator to demonstrate that the disposal method meets all relevant national and international legal and regulatory requirements.

2.8.6.2 Safety implications of waste disposal methods

Disposal methods are discussed in Sections 2.8.6.5 and 2.8.6.6 of this thesis. Where appropriate, key safety issues and waste management concerns are also listed, since the adoption of a method without the appropriate risk assessment and regulatory approval can lead to significant environmental impacts and associated remediation costs — particular examples include the disposal of produced water in seepage ponds (Section 2.8.6.5.3) and the shallow land burial of scales and sludges (Section 2.8.6.6.m4). Ultimately, the acceptability of a particular disposal method for a specific type of NORM waste has to be decided on the basis of a site specific risk assessment. Since the characteristics of particular types of NORM waste (i.e. solid or liquid) arising from different facilities are not necessarily uniform, it cannot be assumed that the disposal methods described are suitable for general application, i.e. at any location. Waste characteristics such as the radionuclides present, their activity concentrations, and the physical and chemical forms and half-life of the dominant radionuclide can have a major impact on the suitability of a particular disposal

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method. Site specific factors such as geology, climate, and groundwater and surface water characteristics will also influence strongly the local suitability of a particular disposal method. Only by considering all the relevant factors in the risk assessment can a considered decision be made regarding the optimal local disposal option.

2.8.6.3 Significant non-radiological aspects

The selected disposal method, in addition to meeting the fundamental principles of radioactive waste management (IAEA, 1995), also has to take account of the environmental impact of the significant non-radiological hazards associated with the wastes — this applies in particular to sludges that contain hydrocarbons and heavy metals. Discussion of these non-radiological hazards lies outside the scope of this study, but they may constitute a dominant aspect in the selection of a disposal method.

2.8.6.4 Storage of solid radioactive wastes

There may be a need to accumulate and store solid NORM wastes (such as scales) and contaminated objects (such as pipes) prior to taking further steps leading to disposal. The regulatory body has the responsibility for authorizing facilities for storage of radioactive waste, including storage of contaminated objects. A well-designed storage facility will:

(a) have clear markings to identify its purpose,

(b) contain the waste material adequately,

(c) provide suitable warnings,

(d) restrict access.

The regulatory body will normally require the waste to be encapsulated or otherwise isolated to an approved standard and the dose rate on the outside of the storage facility to be

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kept within values acceptable to the regulatory body. The regulatory body will probably also impose specific requirements for record keeping of the stored waste.

2.8.6.5 Examples of disposal methods for produced water

The large volumes of produced water preclude storage and treatment as a practicable disposal method. The impracticability of treatment applies to both radioactive and non-radioactive contaminants, although some form of treatment is usually needed to meet the requirements set by regulatory bodies with respect to non-radioactive contaminants such as dissolved and dispersed hydrocarbons. Methods that have been used to dispose of produced water include:

(a) reinjection into the reservoir

(b) discharge into marine waters and

(c) discharge into seepage ponds.

2.8.6.5.1 Reinjection into the reservoir

Reinjection into the reservoir from which the water originated is a common practice at many onshore and offshore production facilities, although there are technical constraints such as the potential for breakthrough into production wells. No added radiological risks would seem to be associated with this disposal method as long as the radioactive material carried by the produced water is returned in the same or lower concentration to the formations from which it was derived (the confirmation of which might entail taking some measurements). Should this not be the case, it is important that any regulatory decision on this method of disposal be supported by an appropriate risk assessment.

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2.8.6.5.2 Discharge into marine waters

Many production installations on the continental shelf discharge their produced water into estuaries and the sea. Regulatory requirements with respect to the discharge of NORM in this way differ between countries; in some cases there are no requirements at all and in others authorizations are required if activity concentrations exceed the discharge criteria set by the regulatory bodies. Some discharges may be subject to international maritime conventions such as the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, 1972 (the London Convention) and the Convention for the Protection of the Marine Environment of the North-East Atlantic, 1992 (the OSPAR Convention). Various reports that address the fate of radionuclides and the radiological risks associated with discharges of NORM containing produced waters pertain to discharges in coastal and offshore areas of the Gulf of Mexico and are based partly on monitoring results (Mulino and Rayle, 1993; Meinhold and Hamilton, 1993; Meinhold et al., 1995a &1995b; Hamilton et al., 1993). Risk assessments of discharges from platforms on the Dutch continental shelf are based on modelling of dispersion and exposure pathways (Heling, 1997). These risk assessments show that the calculated level of risk to humans is strongly dependent on local conditions (estuary, coastal or open sea) and on the degree of conservatism applied in the dispersion and exposure pathway modelling. It is important that risk assessments such as these are carried out and used as the basis for regulatory requirements with respect to this method of disposal. This work is going to provide the necessary data that will be needed for risk assessment based on modelling from discharge from the Ghanaian oil platforms.

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2.8.6.5.3 Discharge into seepage ponds

At several onshore oil field locations, the produced water is discharged to form artificial lagoons, ponds or seepage pits (Plate 2.6). Subsequently, the released waters drain to ground leaving radioactive deposits associated with the soil that eventually require remedial action in accordance with radiation protection principles (AECS, 1998; IAEA, 1998; Al-Masri, 1998) (Plate 2.6). It has been estimated that 30 000 contaminated waste pits and bottom sediment sites exist in coastal Louisiana, United States of America (Pardue, 1998). A key factor in determining the acceptability of this method is the radiological impact of the contaminated water on local surface water and groundwater and the potential accumulation of radionuclides in local biota. The degree of impact depends on several factors, including:

(a) the radionuclide activity levels in the produced water,

(b) the proportion of the activity contained in the deposited salts,

(c) the degree of dilution into local surface water and groundwater,

(d) the volumes produced.

Plate 2.6: ***Lagoons of produced water and remediation of contaminated land after drying the lagoon (courtesy: Atomic Energy Commission of Syria).***

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Risk assessments incorporating mathematical modelling can be used to estimate the local contamination and the resulting doses received by the critical group. The regulatory body will then have to make a decision regarding the acceptability of the disposal method.

This method can be considered as a form of waste treatment (concentrate and contain) in that the dissolved radionuclides are converted into solid deposits. The solid waste materials, including soil contaminated by the downward migration of radionuclides, will have to be collected, packaged and disposed of in a manner similar to those specified for scales and sludges (Section 2.8.6.6), or transported in bulk to a burial site that will isolate the waste more effectively than the original seepage pond area. The land areas require remediation and radiation surveys of residual contamination to be undertaken in order to obtain clearance from the regulatory body for future unrestricted use of the land. The regulatory body needs to specify the clearance levels to which the land must be decontaminated.

In considering this disposal method, the following aspects need to be addressed:

(a) selection of a suitable site;

(b) controls to prevent public access to the area;

(c) risk assessments to determine the human and environmental impacts, including long term implications, arising from contamination of soil, groundwater and surface water;

(d) possible need for occupational risk assessments and radiation protection programmes for certain activities or areas, to control exposures and limit the spread of contamination into public areas;

(e) quality assurance (QA) and record keeping programmes such as those for waste inventories;

(f) transport costs and compliance with transport regulations;

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(g) cleanup and remediation costs;

(h) disposal of the solid residues as radioactive wastes.

2.8.6.6 Examples of disposal methods for scales and sludges

NORM scales and sludges have a wide range of radionuclide activity levels and half-lives. These are produced in varying quantities during the life of an oil or gas facility. Various disposal methods are practised on a routine basis. Other methods have been evaluated by practical application and yet others have been assessed on a theoretical basis only. Some disposal methods are subject to international maritime conventions such as the London Convention and the OSPAR Convention. A brief summary with a few selected references is presented below.

2.8.6.6.1 Discharge into marine waters

The discharge of solid NORM wastes from offshore platforms is an allowed practice on the continental shelf of the United Kingdom and Norway (Van Weers, 1997; Strand and Lysebo, 1998). Limits are set on residual hydrocarbons and particle diameter. As regards the UK, operators are required to obtain authorization for these discharges and to keep records. Intentional discharge of solid NORM wastes with produced water is not allowed on the Dutch continental shelf. This method of disposal can result in the buildup of localized concentrations of scales around offshore rigs over a period of years, and the following aspects need to be addressed:

(a) need for risk assessments to determine the human and environmental impacts;

(b) possible need for occupational risk assessments and radiation protection programmes for certain activities or areas, to control exposures and limit the spread of contamination into public areas;

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(c) need for QA and record keeping programmes such as waste inventories.

2.8.6.6.2 Injection by hydraulic fracturing

Methods of disposal that employ hydraulic fracturing have been developed and used for offshore generated solid NORM wastes in the Gulf of Mexico (Fletcher et al., 1995;Young et al., 1995). Hydraulic fracturing is also considered in the generic radiological dose assessments carried out for various NORM disposal options (Smith et al., 1996) and for a Class II well (Class II injection wells are a specific category of injection well used by the oil and gas industry to dispose of salt water produced in conjunction with oil or gas, to inject fluids to enhance oil recovery, or to store hydrocarbon liquids) (Smith et al., 1997). In considering this disposal method, the following aspects need to be addressed:

(a) Site selection in relation to the long term stability of the surrounding geological structures and the required depth of emplacement;

(b) possible need for encapsulation/stabilization (e.g. in concrete) of the solid wastes;

(c) need for risk assessments to determine the human and environmental impacts;

(d) possible need for occupational risk assessments and radiation protection programmes for certain activities or areas, to control exposures and limit the spread of contamination to public areas;

(e) need for QA and record keeping programmes such as those for waste inventories.

2.8.6.6.3 Disposal in abandoned wells

Disposal in abandoned wells involves the emplacement of NORM solids, whether encapsulated or not, between plugs in the casings of abandoned wells. The method has been the subject of radiological dose assessments (Smith et al., 1996) and has been described as a preferred option for onshore disposal of scales and mercury-containing sludges (IAEA, 2003). In considering this disposal method, the following aspects need to be addressed:

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(a) Site selection with respect to the long term stability of the surrounding geological structures and the required depth of emplacement — this should be viewed in relation to the half-life of the longest lived radionuclide ^{226}Ra (1600 years only). It should also be borne in mind that long term stability of an abandoned and plugged well will be required in any case to eliminate the risk of a blow-out.

(b) Possible need for encapsulation and the associated costs.

(c) Need for risk assessments to determine the human and environmental impacts, including long term implications, arising from groundwater contamination.

(d) Possible need for occupational risk assessments and radiation protection programmes for certain activities or areas, to control exposures and limit the spread of contamination into public areas.

(e) Need for QA and record keeping programmes such as those for waste inventories. Proof of long term performance of the isolation of the waste is likely to be more difficult to provide in the case of non-radioactive constituents (which do not disappear by decay) than in the case of radioactive constituents. The Dutch Government requires 'proof of retrievability' for sludges disposed of in abandoned wells.

2.8.6.6.4 Surface disposal

Shallow land burial is discussed as one of the NORM waste disposal options in a study made by the American Petroleum Institute (Baird et al., 1990) and is described as being practised on a limited scale in Texas (Landress,1997) and in three other states in the USA (Veil and Smith, 1999; Wilson, 1994). Remediation problems caused by earthen pit disposal of scale and sludge appear to be considerable (Hadley, 1997). The presence of non-radioactive contaminants is one of the more important factors to be considered, and makes

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this method of disposal an unlikely option for sludges. Smith et al. (Smith et al., 1999) discuss the radiological assessment of NORM waste disposal in non-hazardous waste landfills. Operational guidance on possible shallow ground disposal methods is available in Ref. (IAEA, 1985). The following aspects need to be addressed:

(a) Selection of a suitable site requiring minimum depth of emplacement. It is particularly important that a suitable site be selected for such a waste management facility. The site selection process should focus on taking maximum advantage of desirable characteristics with regard to minimizing the impact of wastes and ensuring the long term stability of the facility. The various options and the final decision will be subject to economic, technical and practical constraints. Factors that need to be considered in the site selection process include:

(i) anticipated duration of the facility, i.e. temporary or final;

(ii) climate and meteorology;

(iii) hydrology and flooding;

(iv) geography;

(v) geology, geochemistry and geomorphology;

(vi) seismicity;

(vii) mineralogy;

(viii) demography and land use;

(ix) biota;

(x) amenability to decommissioning and the permanent disposal of wastes.

(b) institutional control issues.

(c) long term stability of the facility.

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(d) deed for risk assessments to determine the human and environmental impacts, including long term implications, arising from groundwater contamination

(e) possible need for occupational risk assessments and radiation protection programmes for certain activities or areas, to control exposures and limit the spread of contamination into public areas.

(f) need for QA and record keeping programmes such as those for waste inventories.

(g) transport costs and compliance with transport regulations (IAEA, 2000).

2.8.6.6.5 Land dispersal

Land dispersal (also known as 'landspreading' or 'landfarming'), with or without dilution, has been described as "a long standing waste disposal method that has been available to the petroleum industry" (Smith et al., 1998), but its acceptability for the disposal of sludges is doubtful because of the presence of heavy metals and toxic hydrocarbons. The study cited addresses potential radiation doses to workers and the public, as well as addressing regulatory aspects. The following aspects need to be addressed:

(a) Need for risk assessments to determine the human and environmental impacts, including long term implications, arising from groundwater contamination;

(b) Possible need for occupational risk assessments and radiation protection programmes for certain activities or areas, to control exposures and limit the spread of contamination into public areas;

(c) Need for QA and record keeping programmes such as those for waste inventories;

(d) Transport costs and compliance with transport regulations (IAEA, 2000).

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2.8.6.6.6 Deep underground disposal

Deep underground disposal is a well-studied method for disposal of high and intermediate level radioactive wastes from the nuclear fuel cycle. Disposal in salt caverns has been described as a potential method for NORM waste from the oil and gas industry (Tomasco, and Veil, 1999). Other possibilities include deep disposal in nearby disused metal mines. The practical potential of these methods depends strongly on the availability of suitable non-operating mines close to the oil and gas production regions. Transport costs could have a significant impact on the practicability of this option as suitable sites may be located far away from the oil and gas production areas.

The following aspects would need to be addressed in considering this disposal method:

(a) costs of setting up, operating and maintaining such a repository in comparison with the costs associated with other disposal methods;

(b) repository location in relation to the oil and gas producing areas;

(c) selection of a suitable site requiring minimum depth of emplacement;

(d) waste treatment, handling and packaging;

(e) institutional control issues;

(f) long term stability of the facility;

(g) transport costs and compliance with transport regulations (IAEA, 2000);

(h) need for risk assessments to determine the impacts on the public and on the environment;

(i) possible need for occupational risk assessments and radiation protection programmes for certain activities or areas, to control exposures and limit the spread of contamination into public areas;

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(j) need for QA and record keeping programmes such as waste inventories.

2.8.6.6.7 Recycling by melting

The recycling, by melting, of scrap metal contaminated with NORM can be regarded as a potential disposal method as well as a decontamination method. The NORM contamination is mostly concentrated and contained in the slag (Van Weers, 1997), with low residual activity being diluted and dispersed throughout the product or steel billet. However, volatile radionuclides (^{210}Pb and ^{210}Po) become concentrated in the off-gas dust and fume and may constitute an exposure or waste management issue. A recycling plant dedicated to NORM-contaminated scrap is operated in Germany (Hamm, 1998) and represents one option in the approach to recycling by melting. A preferred option would seem to be the melting of contaminated scrap with larger quantities of uncontaminated scrap, which — together with added iron and other inputs — results in a throughput of NORM-contaminated scrap that is small compared with the throughput of uncontaminated materials (Wymer et al., 1999). The addition of uncontaminated scrap, together with iron and other inputs, results in sufficient dilution of the contaminated scrap to ensure that the activity concentrations of natural radionuclides in the slag and in the emissions to the atmosphere are not enhanced significantly. The most significant radiological aspect is likely to be the occupational exposure associated with segmentation of the scrap by cutting or shearing to satisfy the size limitations imposed by the melting operation.

The feasibility of this method of disposal and the associated economic, regulatory and policy issues are discussed in Winters and Smith, 1999. The radiological aspects are presented in more detail in Wymer et al., 1999 and Smith et al., 1996.

Issues that need to be addressed include:

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(a) The possible need for dilution of the contaminated scrap metal with uncontaminated scrap metal to achieve clearance of the steel billets from regulatory control. This will depend on contamination levels; the regulatory body will have to specify appropriate clearance levels for the radionuclides of concern.

(b) The partitioning behaviour of the main radioactive elements associated with different NORM types; Th (from the decay of ^{228}Ra) and Ra partition to the slag, while Po and Pb are emitted with, or recovered from, the off-gas.

(c) The safe disposal of the contaminated slag and other wastes such as flue dust.

(d) Need for risk assessments to determine the human and environmental impacts and possible need for radiation protection programmes for certain activities or areas, and to control exposures and limit the spread of contamination into public areas.

(e) Need for QA and record keeping programmes such as those for waste inventories and activity levels in the slag and product. The recycling of radioactively contaminated scrap metal has been increasingly restricted in recent times because of the potential legal liabilities of metal dealers and scrap merchants (Lubenau and Yusko, 1998). Consequently, almost all large metal dealers and scrap steel smelting operations have installed portal gamma radiation monitors at their premises for the purposes of identifying and rejecting consignments of scrap metals contaminated with radioactive materials, sealed radiation sources and NORM. Consignments tend to be rejected, perhaps unnecessarily, even when it is proven that the portal monitor alarm has been triggered only by NORM.

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2.9 Health Effects of NORMs

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, 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.

In lung dosimetry models, in which deposition sites of radioactive material and locations of target cells are taken into account, the risk per unit of inhaled radioactive material is considered to be much greater for radioactive material in the unattached state than for radioactive material in the attached state (NRC, 1991). While it is the radon progeny rather than radon gas itself that presents the greater risk, the word 'radon' is also used generally as a convenient shorthand for both the gas and its progeny. Radon has been recognized as a radiation hazard causing excess lung cancer among underground miners (ICRP, 1981). Consequently 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 **(**Kathren, 1998**)**, increasing attention has been paid to exposure to radon and its associated health risks in the oil and gas industry.

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2.9.1 Potential effects of NORMs on the receiving environment

There are no radiation protection dose limits for fauna or flora. The current principle of environmental radiation protection for flora and fauna is based on the ICRP recommendation (ICRP, 1991). The ICRP postulated that if man is protected by certain radiological standards then biota are also protected. This implies that, provided public exposures to radiation caused by NORM discharges or by the NORM waste disposal are less than the 1 mSv/y public limit, then the radiation doses received by biota would also be acceptable. This concept of environmental radiation protection is applicable to the petroleum industry NORMs because levels of radioactivity in petroleum industry NORMs are low, as are potential operational NORM discharge rates **(**APPEA, 2002**)**:

(1) Petroleum industry NORMs are Low Specific Activity (LSA) radioactive materials and their generation rate is low. Due to this fact, radiation exposures and the radiological impact on marine life due to discharges of small volumes of NORMs are likely to be negligible.

(2) Produced water discharges from onshore oil and gas facilities may elevate radionuclide content in creek and river sediments and may be a cause of potential contamination of drinking water.

(3) The radiological impact due to discharges of NORMs (offshore as well as onshore discharges) should be estimated for a critical group of the public considering site specific conditions.

NORMs released to the environment can give rise to human radiation doses through a variety of pathways and the potentially highest radiation exposures are estimated (considering all major exposure pathways) to be received by the "critical group of the

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public" **(**APPEA, 2002**)**. The critical group should be identified or defined for every oil or gas production facility that releases NORMs to the environment.

The potential for bioaccumulation should be considered in assessing the likely dose to the critical group. In terms of offshore disposal to the sea, the discharge of LSA scale would result in only a marginal increase in radium in sand on the seabed due to dilution and dispersion **(**APPEA, 2002**)**. This would result in a low incremental radium concentration in bottom feeding marine fauna and subsequently in a negligible public radiation dose. The low risk through bioaccumulation is illustrated by considering the following example: The public dose limit of 1 mSv would be received after ingestion of the activity of ^{226}Ra and ^{228}Ra of 3,600 Bq and 1,500 Bq respectively (IAEA, 1996b). As the combined ^{226}Ra and ^{228}Ra activity concentration in barium sulfate scale is about 550 Bq/g, some 4.2 g of scale would have to be ingested to receive the dose of 1 mSv. Even if it was assumed that the radium concentration in the flesh of bottom feeding fish is the same as those living close to a nuclear reactor (about 2 Bq/kg), an individual would have to consume about a tonne of fish in a year to receive the dose of 1 mSv. This is a highly conservative assessment where the radium concentration in river sediment and water near to a nuclear reactor is far higher than would be found near an oil or gas facility in the sea. It is recommended that provided the maximum personal annual radiation exposure is of the order of 10 - 100 μSv, the associated radiation health risk is trivial and the practice could be exempted from regulatory control **(**APPEA, 2002**)**. This risk- based exemption concept also considers that since average annual natural background radiation exposures are about 2,000 μSv, a few percent increase in the annual radiation exposure can be regarded as trivial.

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2.9.2 Personal exposures due to NORM radiation in petroleum production

Natural radionuclides in NORMs emit alpha, beta and gamma radiation and thus NORMs can be a source of both external and internal radiation exposure. During routine operations, workers are exposed to external gamma radiation. The external gamma radiation passes through the steel walls of pipes and vessels and the dose rate at the surface of oil production pipes and vessels could be in order of tens of microSievert per hour. During shutdowns and maintenance periods, workers may also be exposed to inhaled radon gas and NORM dust and to external gamma radiation. The external gamma radiation dose rate inside separators is higher than at external walls because external gamma radiation inside the separator is not shielded by its steel walls (Kvasnicka, 1996). Considering that the specific activity of radium in barium (radium) sulphate scale can be in excess of 500 Bq/g (Kvasnicka, 1996), only a hundred milligrams of inhaled scale dust could cause a radiation dose in excess of the annual public dose limit of 1 mSv. Even though only a small fraction of radon gas is released from scale (Kvasnicka, 1996)**,** the radon gas concentrations in non-ventilated vessels with scale, sludge or sand could cause elevated radiation exposures. Potential inhalation of NORM dust and radon gas makes the management of radiation exposures of workers during shutdowns different from the management of radiation exposures during routine operations.

2.9.3 Human health risk assessment for NORMs in produced water

The human health risk assessment models are widely used in the decision-making process for industrial release of waste to soil, water or air. The complex nature of real life information used for risk assessment has guided the researchers to develop new approaches for better representation of human health risk. The risk assessment models consider

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parameters that are generally prone to uncertainty because of simplification and imprecise nature of the available information (Ferson, 1996). Uncertainty can be divided into two categories: (i) type A uncertainty, induced from natural variability, which cannot be reduced and (ii) type B uncertainty that resulted from lack of proper knowledge or partial ignorance of information (Roucher et al., 2002). Many techniques including probabilistic approach, mathematical and numerical modelling, interval analysis, convex modelling, fuzzy set theory, possibility theory and evidence theory are available to characterize the uncertainties in the natural processes (Chen and Hwang, 1992; Klir and Yuan, 1995; Ben-Haim and Elishakoff, 1990; Langley, 2000; Rao and Berke, 1997; Bae et al., 2003). There is no single method that offers comprehensive solutions to all the types of uncertainties (Zimmermann, 2001). Each approach has its own set of advantages and disadvantages (Zimmermann, 2001).

The most widely used approach to characterize uncertainty in risk assessment studies is Monte Carlo (MC) simulation (USEPA, 1996a). The Monte Carlo methods need (i) information on statistical dependencies among the variables; (ii) distributions of input parameters; and (iii) information on model structure to evaluate any environmental scenario. In MC simulation, the low probability parameter values have fewer chances to be randomly selected; thus a portion of possibility might be ignored (Ferson, 1996; Guyonnet et al., 1999). Moreover, Monte Carlo methods provide a single line for exceedance risk based on regulatory limit or target value, while the exceedance risk is not a single line, rather a range showing the lower and upper bounds (Ferson, 1996). The insufficient or imprecisely informative data cannot be analysed with the MC calculation (Lee, 1996; Chowdhury et al., 2004).

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The environmental problems like risk assessment from produced water discharges is associated with several parameters that are naturally variable and difficult to characterize by available statistical approaches (Chowdhury et al., 2004). Evaluation of parameter values in such cases is not precise.

Four different radioisotopes of radium (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) exist in nature. The half-lives of ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra are 11.4 days, 3.7 days, 1600 years and 5.75 years, respectively (USEPA, 1999b). Due to their short half-lives, ^{223}Ra and ^{224}Ra do not play significant role in risk assessment. Two isotopes of radium, ^{226}Ra and ^{228}Ra are of most concern as they are leachable and mobile because of their high solubility in water (Vegueria et al., 2002) and they may bioaccumulate in marine organisms (Hamilton et al., 1992). Radionuclides can accumulate in the soft tissue and bones of marine species (Mulino and Rayle 1993). The concentration factor, which is defined as the ratio of concentration in an organ or organism to the concentration in the media, varies depending on type of fish and organ such as flesh, skin or bone of fish (Meinhold and Hamilton 1993). A study on marine species showed the concentration factors of ^{226}Ra and ^{228}Ra in bone is higher than that of muscle for Sole, Ray, Sardine, Mackerel, Oil fish, Oyster, Clam, Green mussel and Snail (Iyengar 1984; Iyengar et al. 1980; Neff 2002). Radium is chemically similar to calcium and concentrates in bones, shells and exoskeletons (Meinhold and Hamilton 1993). Studies on three fish species suggest that radium is mostly accumulated in bones and least in flesh (Meinhold and Hamilton 1993). Concentration factors of radium content based on the whole organism overestimate the level of radium in the edible portion (Iyengar 1984). A minimum of 40% of the total radium in a fish is accumulated in bones and approximately 6% in edible

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flesh (Neff 2002). Several species of lake fish also bioaccumulate radium to higher concentrations in bone than in the muscles (Neff 2002).

The distribution of radium in the edible and non-edible part of a fish was not taken into account for human health risk assessment in some previous studies and thus those previous studies have predicted relatively high risks. Meinhold et al. (1996) employed Monte Carlo simulations for assessing human health risks from radium and lead in produced water, but radium distribution in different organs (bones, flesh, exoskeleton and shell) of a fish.

2.9.3.1 Physical Transport of Produced Water

To assess the impacts of the produced water constituents when they are discharged to the sea, it is necessary to consider the fate and transport mechanisms of each components and how they vary with time. The fates of these chemicals are determined by dilution, volatilization, chemical reaction, adsorption and biodegradation. The transport mechanisms and pathways for the individual chemicals are different.

After it is discharged, the plume of produced water will descend or ascend depending on its relative density to the ambient sea water, and it will bend in the direction of the ambient current until it encounters the seafloor or reaches the water surface. During the near-field phase, the plume will usually be trapped at a neutrally buoyant level before it encounters the seafloor or reaches the water surface. This phase ends within minutes and within a few meters from the discharge.

After the near-field phase, the plume reaches the produced water and seawater boundary and it spreads as a thin layer. In this phase, mixing is dominated by buoyant spreading and oceanic turbulent diffusion mechanisms. Both of these mechanisms could be important over

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a distance from the discharge point, but as the plume travels downstream, the buoyancy effect decreases and the turbulent effect increases.

2.9.3.2 Fate of Chemicals in Produced Water

After discharge to the seawater, produced water salinities are likely to change rapidly toward that of the ambient water. Smith et al. (1996b) showed that 100- fold dilution occurs within 10 m of the discharge, which reaches to 1000-fold within 103 m of the discharge.

The metals of produced water are diluted rapidly in the receiving environment upon discharge. Barium will precipitate as barium sulphate in the presence of a high natural concentration of sulphate in sea water. Iron, Manganese and Aluminium in produced water can generate inorganic metal oxide precipitates at 20-50 mg/L concentrations on release into aerobic seawater which may flocculate (a process where a solute comes out of solution in the form of floc or flakes) to form aggregates which may facilitate the rapid transport of toxic produced water constituents to the benthic environments. Elevated concentrations of co-precipitating metals and residual hydrocarbons may occur within the surface micro-layer due to the attachment of precipitates to buoyant oil droplets. Arsenic from produced water dilutes very rapidly in the receiving water environment.

The NORM of produced water is rapidly co-precipitated with barium sulphate. Small amounts of radium may accumulate in sediments near produced water discharges to shallow, poorly-mixed coastal waters.

2.9.3.3 Ecological Risk Assessment

The term of ecological risk assessment (ERA) is typically defined as ‘a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors’ (US EPA,1998b). The purpose of ERA is to contribute to the protection and management of the environment through scientifically

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credible evaluation of the ecological effects of man-made activities such as disposal of wastes from offshore oil production (Mukhtasor, 2001). In the last two decades, interest in ecological risk assessment has increased significantly and guidelines for the assessment have been made available from regulatory agencies.

Risk assessment is conducted to translate scientific data into meaningful information about the risk of human activities to the site-specific environment. The ERA framework by the US EPA allows risk managers to make informed environmental decisions (US EPA, 1998b). Different management options for produced water were evaluated in many studies in order make the decision support system more user friendly (Lawrence et al., 1993; Evans, 2001). For the assessment of risk there are several established methods provided by different organizations. The National Research Council of the National Academy of Sciences (NRC-NAS) (1992) model, US EPA model (1998b), Council of Ministers of the Environment (CCME) model (1996) and Water Environment Research Foundation (WERF) model are prominent of these. Figure 2.5 shows details of these models. The NRC-NAS model was first published in 1983 to identify the risk and quantify the degree of risk to individuals and population as a whole (NRC, 1992). US EPA provides a comprehensive model for ERA (US EPA, 1998b). There are four basis steps in this model, which are i) Problem formulation. ii) Analysis, iii) Risk characterization, and iv) Risk management and communication. Problem formulation combines a) assessment endpoints, b) conceptual models and c) analysis plans. The risk assessment process includes the use of measurement, testing and mathematical modelling to quantify the relationship between the initiating event and possible adverse effects (Suter, 1993). The ERA method is used to interpret dose-

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response data into a risk assessment by application of the response information to local site-specific pathways and biota.

There are three phases to the ERA process. The first phase is problem formulation.

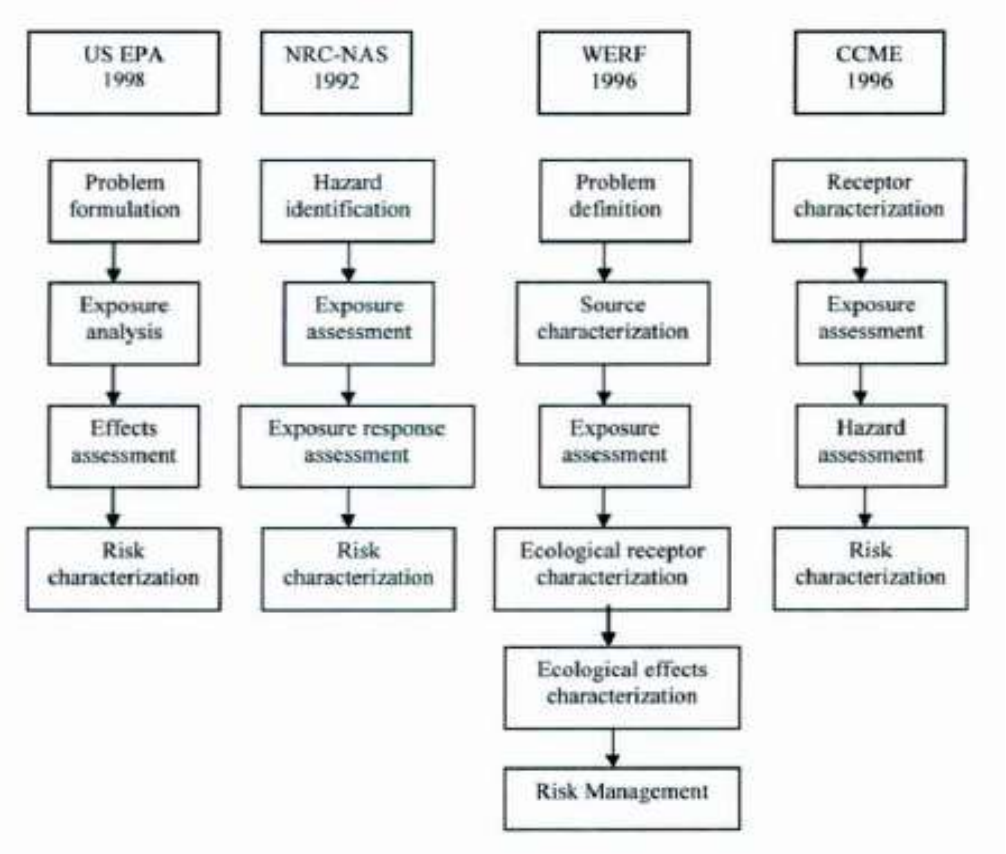

Figure 2.5: Ecological Risk Assessment Frameworks (US EPA, 1998b; NRC-NAS, 1992; WERF, 1996; CCME, 1996)

Problem formulation is used to evaluate a preliminary hypothesis about the possible ecological effects from human activities. The second phase of the assessment is the analysis phase that considers the two primary components of risk assessment (i.e. exposure and effects). The third component of the ERA process is the characterization of the ecological response and the quantitative estimation of risk. Numerous studies on ecological risk

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assessment have been carried out to assess the ecological risk from produced water (Brendehaug et al., 1992; Stagg et al., 1996; Booman and Foyn, 1996; Neff 2002, Neff et al., 2006). Considerable research has also been conducted in characterizing ecological risks from produced water contaminants (Ray and Engelhardt. 1992; Reed et al., 1996; Neff et al., 2006). Addressing the ecological impact, several regulatory agencies set different discharge criteria for the oil content of produced water in different regions (C-NOPB, US EPA, MMS, OSPAR).

When calculating human health risk from fish, fish ingestion rate is an important factor. The US EPA suggested fish intake rate is accepted and used commonly for human health risk estimation. The US EPA suggested considering the concentration only in the edible part of the fish and shellfish. The US EPA 95th percentile value of fish intake is 132 g/day (US EPA, 1991). The upper 95th percentile fish ingestion rate of 170 g/day recommended for Native American subsistence populations by US EPA (1996a). For human health risk assessment US EPA (1999a) used the 99th percentile fish consumption rate of I77g/day. This fish ingestion rate may be highly variable depending on the region. Also the US EPA recommended value is a generic one rather than the marine fishes only. In Ghana there are no such fish ingestion rate data available in the literature.

2.9.3.4 Human Health Risk Assessment

A human health risk assessment for a pollutant describes its discharge, transport and fate in the environment, and the resulting human exposure. Human health risks are then calculated using data and models that relate exposures to health effects (Meinhold et al., 1996). With the growing concern of ecological risk from produced water, concerns are growing for human health risk from the produced water pollution.

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Produced water discharges from offshore platforms may pose a human health risk through seafood ingestion. Certain types of contaminants discharged from offshore operations may be accumulated in the fish tissues and thereby pose a risk to human health (US EPA, 2000). Meinhold et al. (1996) predicted elevated risk from radium ingestion in fish for produced water discharges in the Open Bay, Louisiana. The estimated lifetime cancer risks were found to be less than 10^{-5} for consumption of fishes caught near shallow water platforms and less than $3x10^{-7}$ for consumption of fishes caught near deep water platforms. Meinhold and Hamilton (1993) and Chowdhury et al., (2004) calculated the risk associated from naturally occurring radioactive materials of produced water.

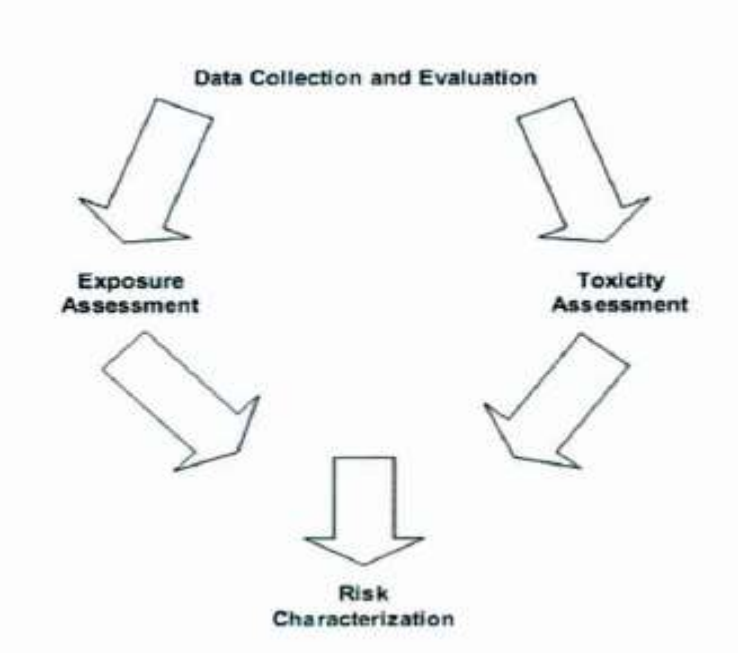

Figure 2.6: Human Health Risk Assessment Frameworks (US EPA, 1999a)

As discussed in the previous sections, though ERA has several different models; for human health risk estimation, a general approach is usually adopted as shown in the Figure 2.6 (US

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EPA, 1999a). The exposure is the most complex step for human health risk assessment, as direct field data are not readily available. For quantitative human health risk assessment Health Canada suggested the following steps (Kathryn et al., 2004):

- Collection of contaminated samples
- Data collection and statistical analysis
- Modelling by using the data characterization of the contaminated sites and receptors
- And, risk characterization

By incorporating the US EPA framework and these steps, any risk assessment model can be developed for human health risk.

Human health risk assessment estimates rely on parameters such as environmental concentrations, body weight, absorption by the body, exposure scenario and several other parameters, and each of these parameters can differ from one site to another. Two measures are commonly used to describe the probability that harm will result from exposure to a risk agent: i) individual lifetime cancer risk-the estimated increase in probability that an individual will experience a specific adverse health effect as a result of exposure to a risk agent over a lifetime; and ii) population risk-the estimated number of deaths in the exposed population (Meinhold et al., 1993). The results of a risk assessment are used by risk managers to determine the need for regulation or remediation, and to set discharge limits.

2.9.3.5 Dilution model for contaminants in fish

The concentrations of pollutants in the fish tissue need to be known in order to assess the risk. From laboratory analysis of produced water the concentrations of pollutants at the discharge point, C_o are characterised and determined. The dilution of the pollutant then can be estimated by applying the dilution model available for produced water. By using the US

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EPA (2000) recommendation, the contaminants concentrations in fish tissue can then be calculated.

After the discharge of the produced water into the ocean it mixes with the ambient water and become diluted. The discharge velocity is much higher than the ambient seawater velocity and the point of discharge is located at sufficient depth below the water surface to enhance dilution (Mukhtasor, 2001).

As stated by Furulolt (1996), the typical initial dilution in the North Sea is 1000 fold within 50 to 100 m of the discharge. To estimate the concentrations of the produced water contaminants and chemicals, hydrodynamic modelling is important and there are various models available to estimate the dilution for produced water (Mukhtasor 2001; Niu 2008). A simple dilution model can be described as (Ray and Engelhardt, 1992).

$$Dilution = \frac{V \times D \times W}{Q_e} \qquad (2.1)$$

Where;

V= Ambient flow velocity

D= Water depth

w= Width of zone of dilution

Q_e= effluent flow

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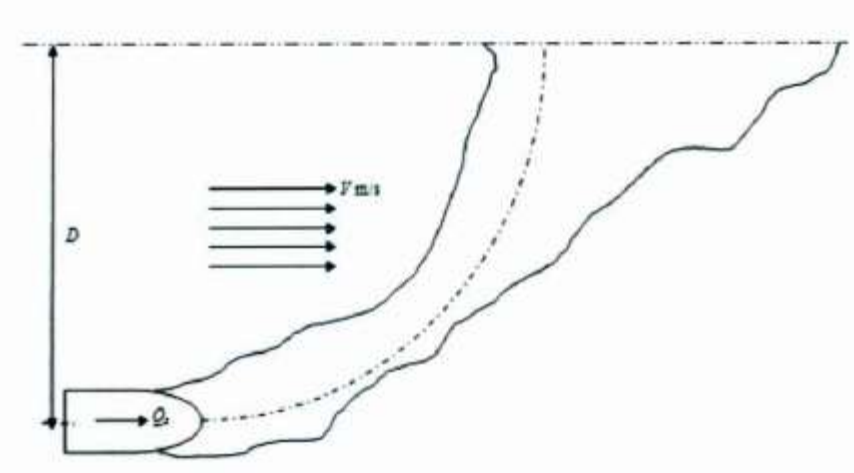

Figure 2.7: Horizontal flow profile for the Equation (2.1) dilution model.

Ambient flow velocity depends on weather conditions and the depth of water. In the Gulf of Mexico the surface currents vary from 0 to 30 cm/s with bottom currents of 3 cm/s (Ray and Engelhardt, 1992). Generally for offshore oil and gas platforms the ambient flow varies from 0.03 to 0.3 m/s (Somerville et al., 1987).

Depth of water is also another variable parameter and is considered to be shallow water depth for offshore platforms (US EPA, 1991). It can vary from 2.5 m to 150 m depending on the locations and type of the platforms (Meinhold et al., 1996; Brandsma and Smith, 1996). For zone of dilution the usual selection range varies from 100 to 500m (Ray and Engelhardt, 1992). The effluent discharge rate ranges from 3.68×10^{-6} to 0.276 m^3/s (US EPA, 1993). Another study shows the average discharge varies from 3.3 3.31×10^{-4} to 0.289 m^3/s (Walk, Haydel & Associates, 1984).

However with complex seawater conditions several other dilution models are proposed to incorporate the real time situations. The dilution models by Lee and Cheung (1991), Lee and Neville-Jones (1987), Proni et al. (1994), Huang et al. (1998) and Mukhtasor (2001) are some of the common dilution models for produced water discharges. The Chemical

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Hazard Assessment and Risk Management (CHARM) model was also developed to evaluate the potential environmental risks posed by chemicals used offshore (Stagg et al.. 1996).

Within the scope of this study, the dilution model by Rye et al. (1996) was used which is quoted as below:

$$\frac{C_o}{C_f} = \frac{V}{Q}\sqrt{96K_z\frac{r^3}{u}} \qquad 2.2$$

where;

C_o=Concentration of pollutant at the discharge point (Bq/l),

C_f= Exposure concentration for fish (Bq/l),

V= Horizontal diffusion velocity (m/s),

K_z=Vertical diffusion coefficient (m^2/s).

Q = Effluent discharge rate (m^3/s),

r = Horizontal length of consideration (m).

u = ambient current velocity (m/s).

The current speed was assumed to follow a log-normal distribution of (-3.29, 0.96) (Mukhtasor, 2001). For these conditions, the *V and* K_z values were assumed to be 0.013 m/s

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and 0.01 m^2/s respectively (Rye et al., 1996). The influence zone was assumed here as the minimum initial near field dilution model of 100 m from the point of discharge (Mukhtasor, 2001). For conservative analysis the effluent discharge rate was considered to be 0.104 m^3/s as discussed earlier above. The discharge of produced water from the Saltpond oil field is presently about 3120 L/day, but within the economic period of production, the platform may discharge significant amount of produced water; which may be up to 12-fold than that of the amount of oil produced (USEPA, 1993). The highest known oil production from the Saltpond field is 4800 barrels per day.

2.9.7 Regulatory Limitations of Produced Water Discharge

The regulatory limitations of oil content with discharged produced water are different for different regions. The regulations for the North Sea, the Baltic Ocean and the northeast Atlantic Ocean are the result of a treaty organization, the OSPAR Commission. In USA, the US EPA is overlooking the regulations for offshore produced water discharges. In Atlantic Canada, the Canada-Newfoundland Offshore Petroleum Board (C-NLOPB) is the regulatory body for the discharge limits. OSPAR regulations set limits on oil discharged, but they give emphasis on controlling the total amount going into a particular water body not the individual pollutant concentrations (Orszulik, 2007). The US EPA limits oil in produced water as an indicator of toxic pollutants but not for the potential harm caused by the oil itself (Orszulik, 2007).

The Arabian Gulf Countries (Bahrain, Iran, Iraq, Kuwait, Oman, Qatar, Saudi Arabia, and United Arab Emirates) have developed the Regional Organization for Protection of the Marine Environment (ROPME), similar to OSPAR but included a couple of regulations

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from the US EPA regulations. A Summary of the main regulatory limits is presented in Table 2.10

Table 2.10: Summary of Produced Water Discharge Regulations (OSPAR, 2007; US EPA, 2003; C-NLOPB, 2008)

Organisations/ Regions	Regulation (oil in water limit)
OSPAR (North East Atlantic)	30 mg/L
USEPA	29 mg/L daily average, 42 mg/L monthly average
Canada	60 mg/L daily average ; 40 mg/L monthly average
HELCOM (Baltic Sea)	15mg/L; up to 40mg/L
Kuwait convention (Red Sea region)	40mg/L; 100mg/L maximum
Barcelona convention (Mediterranean)	40mg/L; 100mg/L maximum
Ghana EPA	29 mg/L daily average, 42 mg/L monthly average

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CHAPTER THREE

RADIATION DETECTION METHODS

Overview

This chapter is devoted to the methodology applied in the detection of gamma and alpha particles and to the analytical procedures developed for measurements of radioactivity in this study.

3.1 Background

The backbone of studying environmental radioactivity, radioecology and radiation protection issues is radiation detection and radioactivity analysis. The radiation detectors are one of the main components of radiation detection and measurement system, which include the detector, the signal processing unit, and the output display device, such as a counter or spectrometer. Radiation detectors basically depend on the interaction of incident radiation with the detector material, which produces a detectable output signal. For each type of radiation, there is one or more suitable type of detector or detection system; each has advantages and disadvantages. Some of the instruments include: gas filled detectors (ionisation chamber counters, proportional counters and Geiger-Muller counters); scintillation counters; and solid state detectors (semiconductor detectors). The basic requirement of the instruments is that, the radiation interacts with the detector provoking a response, and if it is a spectrometer in such a manner that the magnitude of the instrument's response is proportional to the energy of the radiation.

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3.2 Detection of Gamma Radiation

3.2.1 Interaction of Gamma Radiation with Matter

There are three main mechanisms with which gamma-rays interact with matter. The energy of the radiation affects which type of interaction it undergoes with more probability. The interactions and their energy dependence are:

- Photoelectric effect, dominant at low energies,
- Compton scattering, more probable at moderate energies,
- Pair production which occurs only at and above 1.022 MeV increasing in probability above this photon energy.

Figure 3.1 depicts the dependence of each of the three mechanisms on photon energy and material atomic number.

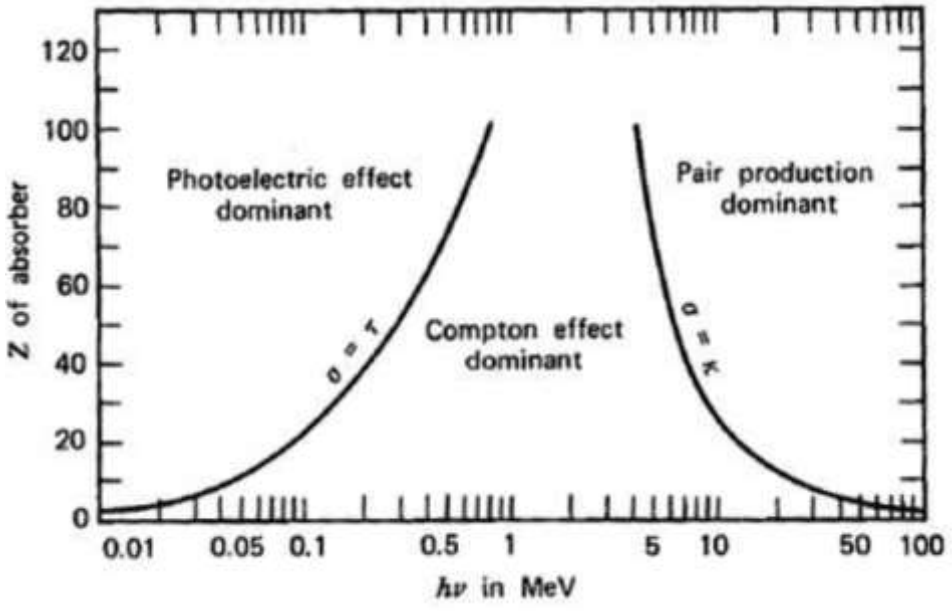

Figure 3.1: Interaction mechanisms of X and gamma-rays with matter as a function of photon energy and atomic number (Knoll, 2000)

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3.2.1.1 Photoelectric Absorption

In this interaction, the photon interacts with the atom and its energy is completely transferred to one of the tightly bound electrons, which is ejected from the atom. This freed electron, called a photoelectron, will have kinetic energy (E_{pe}) equal to

$$E_{pe}=h\nu - \phi \qquad 3.1$$

where h is the Planck constant, ν is the photon frequency, and ϕ is the electron binding energy. Generally, the photoelectric effect is dominant for low energy photons interacting in high atomic number (Z) materials.

3.2.1.2 Compton Scattering

Compton scattering is an elastic scattering between a gamma photon and an electron. The electron, called the recoil electron, gains part of the photon energy and the photon is scattered with the rest of its energy in an angle θ, see Figure 3.2 The scattered photon energy ($h\nu`$) is given by

$$h\nu' = \frac{h\nu}{1+\frac{h\nu}{m_0c^2}(1-\cos\theta)} \qquad 3.2$$

Where m_0c^2 is the rest mass energy of the recoil electron (=0.511 MeV).

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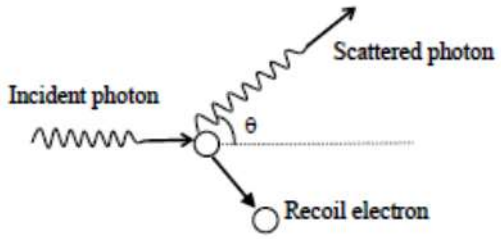

Figure 3.2: Compton scattered gamma photon

3.2.1.3 Pair Production

Pair production occurs when a gamma photon interacts with the Coulomb field of a nucleus. The photon disappears and its energy (E) is converted to an electron positron pair, Figure 3.3. The gamma photon must possess energy higher than 1022 keV, which is the combined rest mass of the electron and the positron ($=2m_oc^2$).

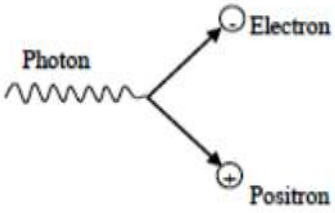

Figure 3.3: Pair production process

Excess energy over the pair rest mass appears as kinetic energy of the pair:

$$E = 2m_o C^2 + E_{e-} + E_{e+} \qquad 3.3$$

where E_{e-} is the kinetic energy of the electron and E_{e+} is the kinetic energy of the positron. Pair production is more probable for higher gamma energies, and it dominates the total interaction probability for photon energies above 5 MeV, see Figure 3.1.

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3.2.2 Gamma Spectroscopy and HPGe Detectors

3.2.2.1 Gamma Spectroscopy

Gamma (γ) spectroscopy using HPGe detectors is very widely used to obtain good estimation of natural and artificial radionuclide concentrations, or activities, in any sample. γ –ray measurement techniques are the backbone of radionuclide concentration estimation in environmental samples because most radionuclides emit γ –rays, the high penetration of γ –rays permits comparatively simple source preparation, and γ –ray spectrometry gives good selectivity in discriminating among radionuclides. The most important detection media for γ –ray spectrometry are inorganic scintillators such as Nal(Tl), CsI(Na), and CaI_2(Eu), and semiconductors such as HPGe. The most often used γ –ray detectors are NaI (T1) and HPGe. The probability of the various types of interactions depends upon the dimensions and the nature of the detecting medium and upon the energy of the incident photon. The total intrinsic detection efficiency is dependent upon the geometric arrangement. The photopeak/total ratio (or photo fraction) is relatively independent of geometry for a given detector. The selection of γ –ray spectrometer is based on its photopeak counting efficiency, energy resolution, and cost. To evaluate the activity of a gamma emitter, the detector's photo peak efficiency must be determined accurately. The photopeak efficiency depends on many factors, including photon energy, detector characteristics and measured sample geometry (Knoll, 2000). The estimation of the detector photopeak efficiency requires the use of calibration standard sources of the same composition, density, geometry geometry and, if it is possible, same radionuclide content as the measured samples. γ –ray spectrometry based on an HPGe detector is preferred for the determination of radionuclides in environmental samples because of the higher resolving power (energy resolution = full

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width at half maximum [FWHM]) of the HPGe detector than that of the NaI (Tl) detector; high-energy resolution is essential for analysis of the complex γ –spectra. Nal (Tl) scintillation is preferred when high-energy resolution is not essential. The energy resolution of NaI (Tl) crystal (3 in. by 3 in.) is about 6% for the photopeak of ^{137}Cs at 661.6 keV (i.e., it is about 40 keV) and about 60 keV for the photopeak of ^{60}Co at 1332 keV, while the energy resolution of HPGe detectors is about 1.9 keV for the photopeak of ^{60}Co at 1332 keV. The main advantages of Nal (Tl) are that they can be obtained in larger sizes, they have a high efficiency, and they cost less that semiconductor detectors. The disadvantages of HPGe detectors are their lower efficiency than that of NaI (Tl) and the necessity to cool them to liquid nitrogen temperature.

3.2.2.2 HPGe Detectors

Germanium semiconductor material of high purity can be manufactured in large size crystals, which are suitable for the spectrometry of high energy gamma photons. Detectors using such material are referred to as 'Hyper Pure Germanium' (HPGe) detectors. Figure 3.4 shows several contact configuration of such detectors. HPGe detectors are operated at liquid nitrogen temperature of -196^{o}C to reduce the thermally induced leakage currents. Such detectors have very good energy resolution compared to other gamma detectors such as NaI or Si detectors, allowing for the differentiation between close gamma lines. Germanium has a relatively high atomic number, compared to silicon, which require smaller crystal volume to completely attenuate gamma photons and deposit their energy within the detector crystal.

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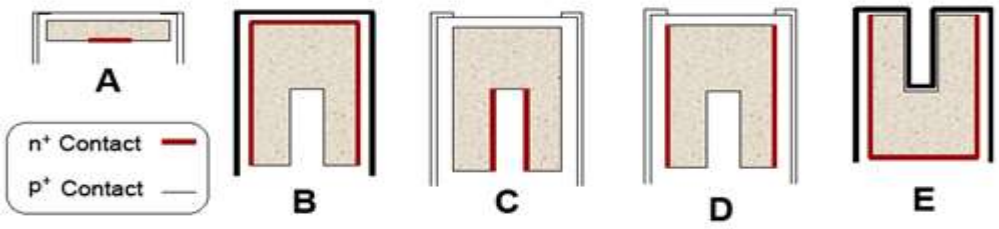

Figure 3.4: Different constructions of Ge detectors; (A) plane, (B) coaxial, (C) ReGe, (D) XtRa and (E) well detector (Hurtado et al., 2007)

Gamma measurements in this thesis were performed using an e**Xt**ended **Ra**nge Germanium coaxial detector (XtRa) of 37.1% relative efficiency. It has a 10 centimetres passive shielding of ancient lead and an active shielding made with an organic scintillation detector (named as Veto BC-418 in Figure 3.5) that works in anti-coincident mode with the Ge detector resulting in very low background level (Hurtado et al., 2007). All the associated electronic chain is shown in Figure 3.5.

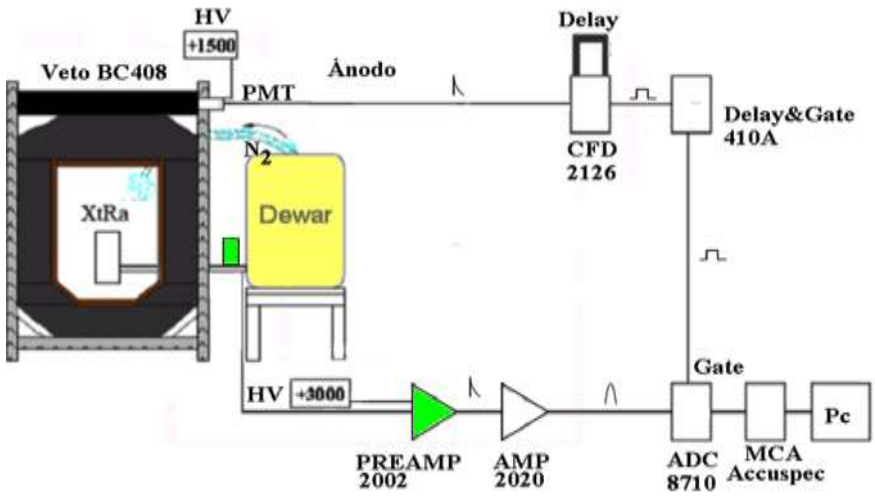

Figure 3.5: Electronic system, detector and shielding from the gamma detector used in this work (Hurtado et al., 2007)

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Table 3.1: Characteristics of the XtRa system used in this study (Mantero, 2013)

Relative eficciency	37,1 %
FWHM (122 keV from ^{57}Co)	0,97 keV
FWHM en (1332 keV from ^{60}Co)	1,79 keV
Ge cristal volumen	160 cm^3
Energy range*	10 keV to 10 MeV
Polarization Voltage	+3000 V

(*) Energy calibration used within this detector was from 30 kev to 3 Mev

3.2.3 Software for gamma spectra analysis: Genie 2000

The spectra analysis program Genie 2000, collects information provided by the multichannel analyzer (MCA in Figure 3.5) and displays the information in a data file- which in our case corresponds to 8192 channels -that store the number of events recorded in each one of them being sorted in order of increasing energy. This is the software (figure 3.6) developed by Canberra and that normally accompanies their manufacturer detectors.

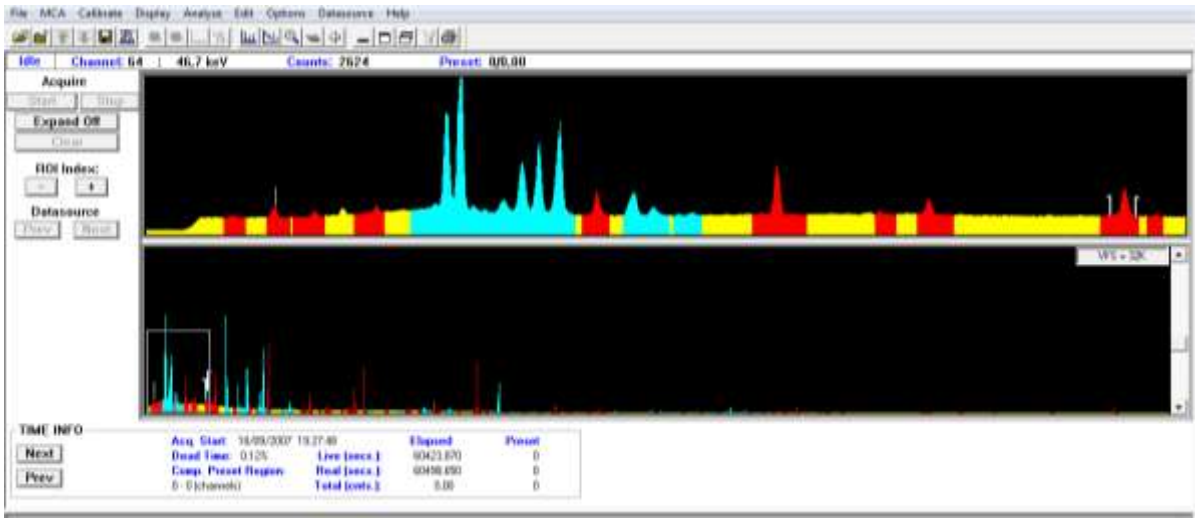

Figure 3.6: Genie 2000 screenshot with singlets (red) and multiplets (blue) photopeaks groups (Genie 2000, 2004)

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Many parameters must be taken into account (Genie 2000, 2004) to make a correct analysis of a spectrum. While Genie2000 software has a set of algorithms to generate the final activity concentration results, in this thesis, we used this software just to get the net areas of each photopeak that interests us. The identified photopeaks are adjusted to a gaussian curve approaching its low energy tail by exponential functions.

Once we have the net areas, different spreadsheets in Excel were implemented to finally get the activity concentration of each sample.

3.2.4 Calibration of the gamma spectrometry system

Prior to the measurements, the detector and measuring assembly were calibrated for energy and efficiency to enable both qualitative and quantitative analysis of the samples to be performed.

3.2.4.1 Energy calibration

One of the essential requirements in nuclear spectroscopy measurement is the ability to identify the photo peaks present in a spectrum produced by the detector system (IAEA, 1989). This is achieved by carrying out energy calibration of the detection system.

The calibration was carried out by a set of standard point sources with well-defined energies within the energy range of interest from 46.5keV to 2000 keV. The channel number that corresponds to the centroid of each full energy event on the MCA was recorded and plotted to obtain a linear curve with second order polynomial. The linear curve obtained from the data points is an indication that the system is operating properly (IAEA, 1989). The system was checked each day of operation for the stability of the slope and intercept by

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measurement and plot of at least two different gamma energies. The standard was counted on the gamma detector until the count rate of total absorption could be calculated with a statistical uncertainty of <5% at a confidence level of 95%.

Once energy calibration is performed, the next step in the sequence of spectrum analysis would be the calibration in resolution. The resolution is defined by the parameter FWHM (width at half height of the photopeak), and assuming that photopeak fits a Gaussian, the value will take this parameter FWHM = 2.35σ being assigned the standard deviation σ from software to the Gaussian distribution.

The resolution of Ge detectors usually comes originally specified because it provides information about the spacing capability photopeaks presenting a particular system. Generally nominal resolutions often used are: ^{55}Fe (5.9 keV), ^{57}Co (122 keV) and ^{60}Co (1333 keV) to cover various energy intervals.

Table 3.2: Results in the energy-resolution calibration process of XtRa gamma detector (Mantero, 2013)

Point source	Energy (keV)	Channel	FHWM (keV)
^{133}Ba	53.161 *1*	83.80 ± 0.09	0.94± 0.01
^{133}Ba	80.997 *1*	167.15 ± 0.04	0.97± 0.04
^{133}Ba	276.398 *2*	752.38 ± 0.06	1.16± 0.01
^{133}Ba	302.853 *1*	831.57 ± 0.04	1.18± 0.01
^{133}Ba	356.017 *2*	990.71 ± 0.03	1.219± 0.003
^{133}Ba	383.851 *3*	1074.15 ± 0.05	1.16± 0.03
^{137}Cs (^{137m}Ba)	661.657 *3*	1905.93 ± 0.,03	1.43± 0.01
^{60}Co	1173.237 *4*	3437.78 ± 0.,03	1.74± 0.01
^{60}Co	1332.501 *5*	3914.72 ± 0.03	1.82± 0.01

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3.2.4.2 Photopeak efficiency calibration

The photopeak efficiency of the detector refers to the ratio of the actual events registered by the detector in each photopeak to the total number of events with a defined energy emitted by the source of radiation. An accurate photopeak efficiency calibration of the system is necessary to quantify radionuclides present in the sample. It is essential that all settings and adjustment of the detector system be carried out prior to determining the efficiencies and this should be maintained until a new calibration is undertaken (IAEA, 1989)

In general, the efficiency of detection decreases logarithmically as a function of energy and it is geometric dependent. Appropriate radionuclides must be selected for use as standards in efficiency calibration. It is recommended to have a number of calibration points approximately between 60 keV and 2000 keV (IAEA, 1989).

The mixed radionuclides standard used for the energy calibration was also used for the photopeak efficiency calibration. The standard was counted on the detector until the count rate of total absorption could be calculated with a statistical uncertainty of <5% at a confidence level of 95%. The net counts for each of the full energy events in the spectrum was determined and their corresponding energies used in the determination of the efficiencies. The expression used to determine the efficiencies is given as follows (Darko et al., 2007).

$$\eta(E) = \frac{N_T - N_B}{\mathrm{P}_E \mathrm{A}_{STD} \mathrm{T}_{STD}} \qquad (3.4)$$

Where;

P_E is gamma emission probability for energy (E),

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η (E) is the photopeak efficiency of the detector,

N_T is the total counts under a photopeak

N_B is the background count

A_{STD} is the activity (Bq) of the radionuclide in the calibration standard at the time of calibration,

T_{STD} is the counting time of the standard.

3.2.4.2.1 Efficiency calibration for Marinelli beaker geometry

Liquid samples were measured in Marinelli beakers. For that reason, a water standard was prepared in the same geometry containing the nuclides shown in Table 3.3.

Table 3.3: Radionuclides used in liquid samples efficiency calibration (Mantero, 2013)

Radionuclide	$T_{1/2}$ (years)	Energy (keV)	P_E (%)
^{57}Co	0.74	122.0614 *4*	85.60 *17*
		136.4743 *5*	10.68 *8*
^{113}Sn	0.32	255.05 *3*	1.82 *6*
		391.690 *15*	64
^{88} Y	0.29	898.042 *3*	93.7 *3*
		1836.063 *12*	99.2 *3*
^{60} Co	5.27	1173.237 *4*	99.9736 *7*
		1332.501 *5*	99.9856 *4*
^{210}Pb	22.3	46.539 *1*	4.25 *4*
^{241}Am	432.2	59.5412 *2*	35.9 *4*
^{109}Cd	1.27	88.04 *5*	3.61 *10*
^{139}Ce	0.38	165.864 *6*	80 *4*
^{85}Sr	0.18	514.0067 *19*	96
^{137}Cs	30.7	661.657 *3*	85.1 *2*

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The efficiency values corresponding to these energies are fitting in Log-Log scale as seen in Figure 3.7 where several order polynomial fit were tested in order to get the best fitting function in this set of experimental points. In equation (3.5) E_0=1 KeV.

$$\ln\eta = \sum_{i=0}^{n} a_i \left[\ln\left(\frac{E}{E_0} \right) \right]^i \qquad (3.5)$$

After trying with order 3, 4, 5, 6 polynomial fitting, it was decided that a 5th order polynomial was the best option. From 6th order or higher polynomials produce better statistics in the fitting but start making "unrealistic" fluctuations in medium-high energy range for having a more accurate fitting, for that reason, a 5th order was the best option used in this work.

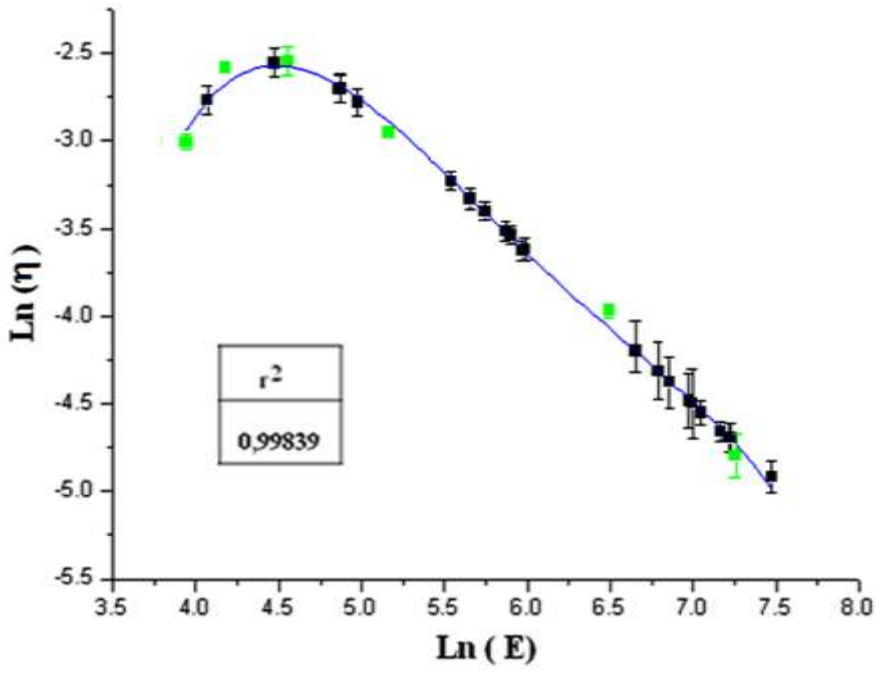

Figure 3.7: Efficiency calibration curve for liquid samples in 1 L Marinelli geometry

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The fitting parameters in this geometry are shown in Table 3.4 containing also statistics as r-square (r^2) and reduced chi-square (χ^2). The first statistics tends to one while the second is minimized, checking the quality in the fitting.

Table 3.4: Fitting parameters and statistics from Ln(η)-Ln(E) fitting process

Fitting parameters	Statistics
a_0 = -179.44636	
a_1 = 141.20605	r^2 = 0.9984
a_2 = -43.64382	
a_3 = 6.5241	
a_4 = -0.47167	χ_r^2 =0,0011
a_5 = 0.01308	

3.2.4.2.2 Efficiency calibration for Petri dish geometry

Another geometry used in this thesis was the Petri dish where solid samples were stored in cylindrical geometries with 12 mm height. Considering the interest of this study in natural radionuclides from ^{238}U and ^{232}Th series, natural radionuclides reference material were chosen for this task.

IAEA reference materials IAEA-RGU-1(U-ore) and IAEA-RGTh-1 (Th-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 into same petri dish containers as that of solid matrix samples for the efficiency calibration of the gamma system. The results for both reference materials in Petri dish are shown in Table 3.5

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Table 3.5: Experimental efficiency values (η (E), with uncertainty (σ) in % for Petri dish geometry in IAEA_U ore (left) and IAEA Th ore (right) (Mantero, 2013)

		Standard IAEA_U ore	
Emission	E(keV)	η (E)	σ
210Pb	46.5	5.04	0.08
227Th	50.13	5.21	0.31
234Th	63.3	4.78	0.50
230Th	67.7	5.85	0.38
235U	205.3	4.87	0.24
227Th	235.9	3.84	0.29
214Pb	295.2	2.58	0.03
214Pb	351.9	2.26	0.03
214Bi	609.3	1.32	0.02
234Pa	1001	1.27	0.10
214Bi	1120.3	0.81	0.01
214Bi	1238.1	0.80	0.02
214Bi	1764.5	0.62	0.01
214Bi	2204.2	0.50	0.01

		Standard IAEA_Th ore	
Emission	E(keV)	η (E)	σ
232Th	63.8	5.89	0.48
212Pb-1	238.6	3.84	0.11
228Ac-3	338.3	2.83	0.09
208Tl-1	583.2	1.61	0.06
212Bi-1	727.3	1.59	0.05
208Tl-2	860.6	1.28	0.05
228Ac-1	911.2	1.24	0.04
228Ac-2	968.9	1.19	0.04
208Tl-3	2614.5	0.47	0.01

3.2.5 Background measurements in the XtRa gamma detector

When working with natural radionuclides, it is usual to find natural emitters in the background gamma measurements, so the first step to perform is a detail description of the background belonging to one detection system. In this case, this XtRa detector was setup for having lower background levels compared to normal setting-up of HpGe gamma detectors. Figure 3.8 illustrate the background level achieved with the XtRa system (in yellow color) compared with another gamma detector (ReGe, in green color) also available in the laboratory of University of Seville.

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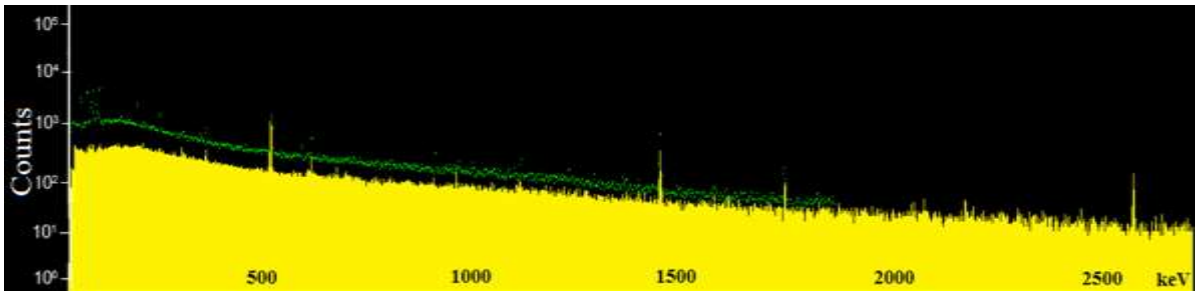

Figure 3.8: Comparison of background spectra measured in Rege detector (green dots) and Xtra detector (yellow area) after measuring the same time (254000 s) in both systems (Hurtado, 2004)

.

The background photopeaks located at both systems are listed below (Figure 3.9). The conclusion is quite clear, the XtRa detector has a much lower background than that of the ReGe and hence the XtRa was a better choice for gamma measurements in this thesis.

Peak Analysis From Channel: 30
Peak Analysis To Channel: 8192

	Peak No.	ROI start	ROI end	Peak centroid	Energy (keV)	FWHM (keV)	Net Peak Area	Net Area Uncert.	Continuum Counts
F	1	130-	146	137.98	46.24	1.58	3.12E+003	81.03	4.69E+003
F	2	197-	216	206.03	63.02	1.65	4.79E+003	93.42	6.40E+003
M	3	233-	268	244.68	72.54	2.10	2.81E+003	117.03	8.02E+003
m	4	233-	268	253.88	74.81	2.11	6.32E+003	122.59	1.06E+004
M	5	282-	309	292.76	84.39	1.75	2.43E+003	81.46	7.34E+003
m	6	282-	309	303.74	87.10	1.75	7.35E+002	68.28	7.03E+003
F	7	312-	340	325.53	92.47	1.73	6.62E+003	102.43	9.46E+003
F	8	527-	542	533.36	143.71	1.54	5.88E+002	69.44	5.14E+003
F	9	692-	713	704.51	185.90	1.73	2.74E+003	285.56	6.34E+003
F	10	909-	942	918.33	238.60	1.77	1.74E+003	68.37	7.28E+003
F	11	1140-	1161	1149.64	295.63	1.34	2.61E+002	200.46	3.63E+003
F	12	1314-	1330	1322.70	338.29	1.54	2.84E+002	115.86	2.50E+003
F	13	1370-	1390	1379.05	352.18	1.59	6.57E+002	49.27	2.77E+003
F	14	2006-	2047	2024.82	511.37	2.88	4.10E+003	238.67	3.38E+003
F	15	2302-	2325	2317.34	583.48	1.98	4.51E+002	129.25	1.54E+003
F	16	2415-	2438	2423.46	609.64	2.06	6.99E+002	40.74	1.60E+003
F	17	2896-	2913	2902.90	727.83	1.30	1.14E+002	27.78	9.09E+002
F	18	3639-	3660	3648.35	911.59	1.93	4.14E+002	96.93	8.03E+002
F	19	3875-	3893	3883.66	969.60	2.15	2.16E+002	26.66	6.03E+002
F	20	4002-	4023	4013.01	1001.48	1.74	2.04E+002	166.98	7.18E+002
F	21	4486-	4509	4497.08	1120.81	1.97	2.02E+002	95.63	6.75E+002
F	22	5856-	5892	5875.45	1460.60	2.44	1.87E+003	115.44	5.50E+002
F	23	6403-	6422	6412.57	1593.01	1.72	6.98E+001	58.87	2.05E+002
F	24	7093-	7118	7104.74	1764.04	2.42	3.49E+002	22.17	2.35E+002

M = First peak in a multiplet region
m = Other peak in a multiplet region
F = Fitted singlet

Errors quoted at 1.000 sigma

Peak Analysis From Channel: 30
Peak Analysis To Channel: 8192

	Peak No.	ROI start	ROI end	Peak centroid	Energy (keV)	FWHM (keV)	Net Peak Area	Net Area Uncert.	Continuum Counts
F	1	117-	128	123.05	66.70	1.26	1.71E+002	35.49	1.32E+003
F	2	511-	522	518.33	198.64	0.90	1.38E+002	30.71	1.36E+003
F	3	632-	644	639.77	239.18	0.76	1.06E+002	26.83	1.36E+003
F	4	969-	983	978.34	352.19	1.31	1.64E+002	29.04	9.62E+002
F	5	1436-	1472	1454.61	511.17	2.80	3.00E+003	63.69	1.67E+003
F	6	1742-	1756	1749.21	609.51	1.38	1.07E+002	24.58	6.85E+002
F	7	4291-	4310	4299.56	1460.80	1.74	5.37E+002	24.82	2.19E+002
F	8	5200-	5218	5209.49	1764.54	1.81	1.44E+002	56.32	1.16E+002
F	9	6521-	6535	6527.13	2204.36	1.41	4.35E+001	8.30	8.71E+001
F	10	7748-	7770	7758.68	2615.05	2.02	2.77E+002	14.21	6.90E+001

M = First peak in a multiplet region
m = Other peak in a multiplet region
F = Fitted singlet

Errors quoted at 1.000 sigma

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Figure 3.9: List of the peaks found in the background of the Rege detector (left) and Xtra (right) detector (Hurtado, 2004).

3.2.6 Determination of Minimum Detectable Activity in gamma spectrometry

Minimum detectable activity (MDA) is defined as the smallest quantity of radioactivity that could be measured under specified conditions. The MDA is an important concept in low level counting particularly in environmental level systems where the count rate of a sample is almost the same as the count rate of the background. Under these conditions, the background is counted with a blank, such as sample holder, and everything else that may be counted with an actual sample. The minimum detectable activities (MDA) were calculated from the background spectrum for gamma measurements according to equation (3.6) (Hartwell, 1975)

$$\text{MDA}=\frac{\left(2.71+4.65\sqrt{N_{TB}\left(\frac{t_T}{t_B}\right)+N_C}\right)}{t_T.I.\varepsilon} \qquad (3.6)$$

Where;

N_{TB} is the background count for the region of interest of each radionuclide

t_T is the sample measurement time

t_B is the background counting time,

N_C is the integral

I is the gamma emission probability (gamma yield) of each radionuclide,

ε is the photopeak efficiency for the measured gamma ray energy.

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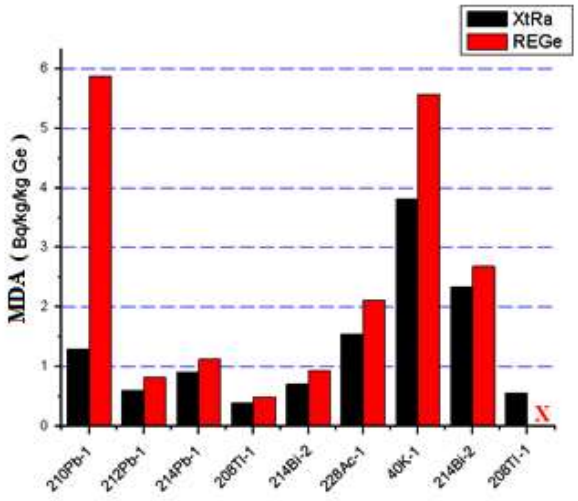
With ~ 200000s as normal measuring time in environmental samples, and after applying equation (3.5) to both background and environmental soil sample measurements, levels of MDA were calculated in two gamma systems ReGe and XtRa detector. Figure 3.10 shows these levels in Bq (Table) and in Bq/ kg of sample per kg of Ge crystal (graphic) where, one more time, we found that XtRa system is the best option for gamma measurements.



MDA	E(KeV)	XtRa (Bq)	REGe (Bq)
210Pb-1	46,5	0,55	2,03
212Pb-1	238,6	0,26	0,28
214Pb-1	351,9	0,38	0,39
208Tl-2	583,2	0,17	0,17
214Bi-1	609,3	0,30	0,32
228Ac-1	911,2	0,66	0,73
40K-1	1460,8	1,62	1,92
214Bi-2	1764,5	0,99	0,93
208Tl-1	2614,5	0,24	–

Figure 3.10: MDA in natural gamma emissions within two gamma systems available in the laboratory of University of Seville (Mantero, 2013)

3.3 Detection of Alpha Radiation

3.3.1 Interaction of alpha particles with Matter

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In general, the interaction of a charged particle with matter will be characterized either by its loss of energy or by its deflection in relation with its incident direction. These effects are mainly the result of the following two processes of electromagnetic nature:

a) Inelastic collisions with the atomic electrons of the medium

b) Elastic dispersion from the nucleus.

In relation with the first process, it is possible to indicate that cross-sections in the order of $\sigma \sim 10^{-17}$-10^{-16} cm^2 are found to transfer energy to the atom that finish either excited or ionized. In both cases, the amount of energy transferred in each interaction of this type is very small in comparison with the total kinetic energy of the particle, but the condensed matter is so dense, that an enormous number of collisions per unit length occur, loosing considerable amounts of energy. In fact, the typical distance that an alpha particle can cross in matter is of order of 10^{-5} m while for the gamma radiation is of the order of 10^{-1} m [Knoll, 2000]. As an example, Figure 3.11 shows the different simulations generated by the program SRIM (**S**topping and **R**ange of **I**ons in **M**atter) for 5.000 alpha particles. In Figure 3.11, the x axis represent the length reached by alpha particles of 1, 4, 8 y 15 MeV in air under normal conditions of pressure and temperature.

As a brief description, we can say that SRIM is a software program devoted to the calculation of ranges of ions in matter with a well -defined reputation in the nuclear physics field since the first versions from 1985 (Ziegler et al, 1985). This software package is revised approximately every six years, with the latest version being 2013. SRIM is software of open diffusion that can be uploaded at WWW.SRIM.Org, with more than 700 scientific citations per year (Ziegler et al, 2010).

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From similar simulations to the shown ones in Figure 3.11, it is possible to conclude that in the energetic range from 3 to 6 MeV (where it is possible to find the energies of the alpha emissions for all the alpha emitters which appear in this work), the α particles reach between 13 and 36 mm in air (6 mm per MeV of the particle)

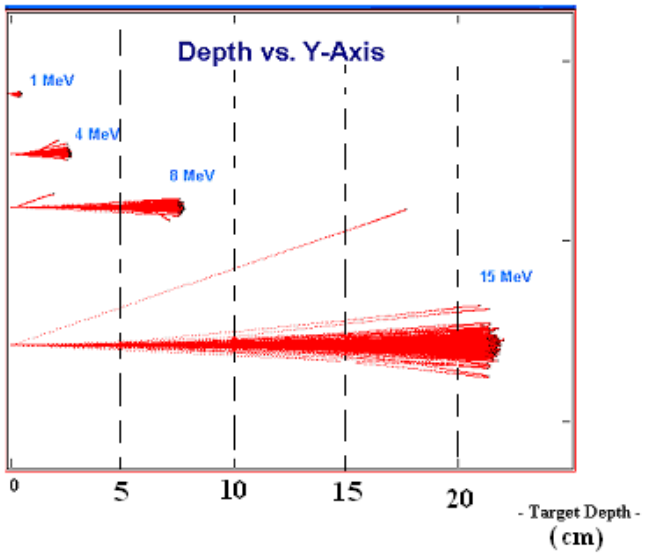

Figure 3.11: Simulation of the range reached by alpha particles of different energies in air (T=20°C, P=760 Torr, relative humidity 50%) performed with the code SRIM 2013 (Mantero, 2013)

3.3.2 Alpha spectroscopy and silicon detectors

Alpha – spectroscopy is a very sensitive, nuclide specific method for the determination and identification of alpha emitting isotopes in low level activity (MDA= 0.1 – 1 mBq). The quantification of possible internal exposure by inhalation and ingestion is an important requirement in radiation protection, knowing that the alpha particles have a high health hazards if they were incorporated to the human body. The measurements therefore should

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yield not only the quantity (activity) of the radionuclides but the identification of them as well.

Many naturally occurring radionuclides, particularly members of the uranium, thorium, and actinium decay series, and the transuranic elements are mainly α-emitters. There is a clear difference between α-particles and other kinds of radiation with a high linear energy transfer and high energy range typically between 4 and 9 MeV. The counting background of the counter may be either due to the α-particle active materials in their construction material or due to contamination. The background count rates, counting efficiencies, and MDA values for different α-particle counting techniques are given in Table 3.6. To increase the sensitivity of the α-particle counting system one can use a detector with a large active area or concentrate the α-particle active material in a source sample. The thickness of the α-source affects the quality of α-particle counting and spectrometry methods. Gross-α counting can be performed using a gas-filled detector or liquid scintillation counter. For high α-particle spectrometry, a very thin source sample preparation is essential to reduce the self-absorption of the α-particles in the source itself. Source sample counts in a vacuum chamber can reduce the absorption of α particle in the air between the sample and the detector.

Table 3.6: The background count rate, counting efficiency, and MDA values for different α-particle measurement techniques

measurement techniques	Background (cpm)	Counting efficiency (%)	MDA(Bq/l) in 100min
Gas flow proportional counting	0.05-0.5	35	2.1
Liquid scintillation counting with PSA	0.1-1.0	95	0.5
α-spectrometry	0.003-0.01	25	0.4

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The main advantage of **α** spectrometry is its high sensitivity due to the high-yield **α** decay process, low background, and elimination of other possible interferences by chemical separation. Also it is applicable to a wide range of radionuclides and environmental samples the main disadvantage is the lengthy chemical separation and source preparation procedure

3.3.2.2 Alpha Series of Passivated Implanted Planar Silicon (PIPS) Detector

Silicon charged particle detectors produced by diffused-junction or surface barrier technology have served the scientific and industrial community for several decades to perform alpha-particle spectrometry. Current applications however, demand detectors having lower noise, better resolution, higher efficiency, greater reliability, more ruggedness and higher stability than those older technologies can produce. Canberra's Passivated Implanted Planar Silicon (PIPS) detector brings all these advantages to the field of charged particle detectors.

CANBERRA's Alpha Series of Passivated Implanted Planar Silicon (PIPS) Detector, based on 3 μ CMOS technology, is the most advanced products in semi-conductor technology for alpha spectrometry counting. The super thin window allows for optimal resolution at the close distances needed for high efficiency alpha counting, but there is still a limit. The best alpha detectors available today can only resolve (distinguish between) peaks ~17 keV apart, under ideal counting conditions and with a commercially prepared source.

The performance of the (PIPS) detector surpasses that of traditional silicon surface barrier (SSB) type detectors and diffused junction (DJ) type devices. The PIPS detector has a number of advantages over the older technologies for room temperature detection of alpha particles.

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The electrical contacts on a PIPS detector are ion-implanted to form precise thin and abrupt junctions for good alpha resolution. The entrance window of a PIPS detector is stable and rugged and standard detectors are bakeable to 100 °C. The leakage current, a major contributor to detector noise is typically 0.1 to 0.001 that of SSB and DJ type detectors. The Model A450-18 AM is by far the most popular model detector for standard alpha spectroscopy.

The A Series PIPS Detectors (Figure 3.12) are optimized for Alpha particle detection or Alpha Spectroscopy applications which require high resolution, high sensitivity and low background. High resolution is achieved by maintaining a uniformly thin entrance window over the detector surface and by reducing leakage current and noise. Alpha resolution of ~ 17 keV (FWHM) is routinely achieved for a 450 mm^2 active area detector. High sensitivity is enhanced by the thin window and ensured by a minimum depletion depth of 140 microns which will absorb Alpha particles of up to 15 MeV thus covering the complete range of all Alpha emitting radionuclides. Absolute efficiency of up to 40% can be achieved. Low background is achieved through the use of carefully selected packaging materials and through clean manufacturing and testing procedures. Backgrounds of less than 0.05 cts/hr cm^2 are routinely achieved. The A series PIPS find applications in widely different scientific disciplines such as: Radiochemical analysis, Environmental studies and surveys, Health physics, Survey of nuclear sites, Geological and geomorphological studies (such as U-Th dating etc. (Canberra, 2013)

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Figure 3.12: CANBERRA's A- series PIPS detectors (Mantero, 2013)

3.3.3 Alpha Analyst system and its calibration

The alpha-spectrometric system used in this work is an 8- chamber Alpha analyst system (Canberra) (Figure 3.13). In our laboratory, each chamber was equipped with a PIPS detector and devoted to the exclusive measurement of one element in order to avoid cross contamination. The measurements were carried out at a source to detector distance of 0.5cm. The accumulation and analysis of Alpha spectra was done using Genie 2000 software with measurement time of 200,000s.

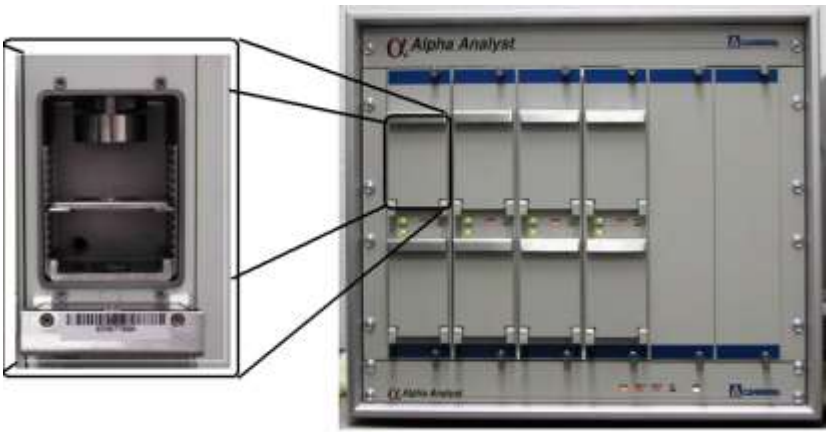

Figure 3.13: Eight (8) - chamber Alpha analyst system (Mantero, 2013)

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3.3.3.1 Energy calibration

The energetic interval to be covered in our measurements is between 4 and 6 MeV. In order to perform the energy-channel calibration in this energy interval for each chamber, a dissolution containing ^{239}Pu, ^{242}Pu and ^{243}Amwas electrodeposited in a stainless steel circular planchet with a diameter of 25 mm.

Once different parameters of the measurement system are optimized (Vioque, 2002) (examples are the polarization voltage of the detectors and the vacuum grade of the chambers) the energy calibration for each chamber was performed optimizing the amplification gain. The results obtained in the energy calibration of one of the 8 chambers is shown in Table 3.7

In principle, a linear fitting describes perfectly the energy response of the alpha spectrometers in our laboratory (García Tenorio, 1983), and even changing the distance between the source and the detectors, the maximum alpha peaks do not suffer any movement in channels (Martinez Aguirre, 1990).

Table 3.7: Sources used for the energy calibration of the alpha spectrometers and channels found for the alpha peaks in one of the eight chambers of the Alpha Analyst system. The energies and their associated uncertainties have been extracted from (Chu et al., 1999)

Radionuclide	E (keV)	Intensity of alpha emission (%)	Channel
^{239}Pu	5105.5 *8* 5144.3 *8* 5156.59 *14*	11.5 *8* 15.1 *8* 73.3 *8*	501 507 509
^{242}Pu	4856.2 *12* 4900.5 *12*	22.4 *20* 77.5 *30*	465 471
^{243}Am	5233.3 *10* 5275.3 *10*	11.0 *4* 87.4 *4*	521 526

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If the energy calibration (obtained as was indicated in the previous paragraphs) is used in analysis of U spectra, it is necessary to extrapolate out of the fitted zone (as it can be observed in Figure 3.14). For that reason, when U spectra have been analyzed, a process of self-calibration has been applied, taking as starting point the initial calibration performed with Pu and Am.

In our alpha spectrometers we work with 1024 channels instead of 8192 channels used in gamma-ray spectrometry. We can reduce the number of channels because the alpha spectra show little interferences (the background is extremely low and the elements are isolated chemically). In addition, and for the commented reasons, the energy calibrations do not need to be as exhaustive as performed in gamma-ray spectrometry.

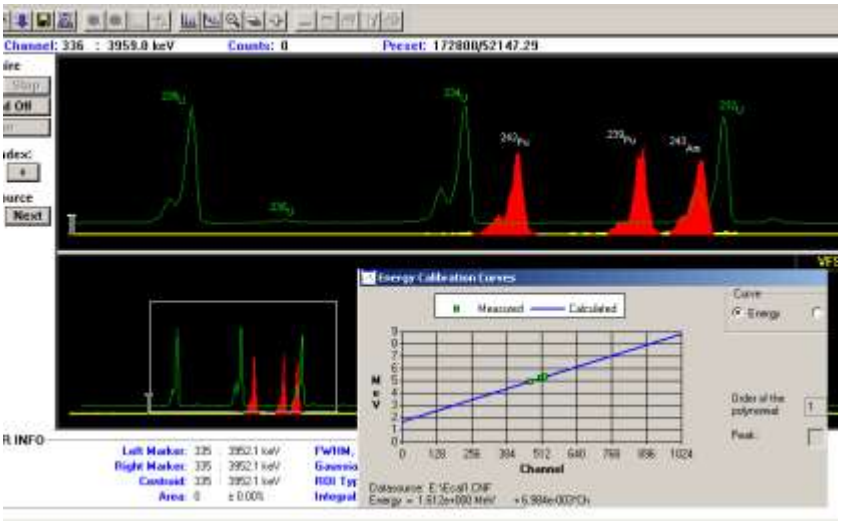

Figure 3.14: Spectrum obtained in the energy-channel calibration with peaks used marked in red and green showing the alpha-peaks corresponding to the different U isotopes (Vioque, 2002)

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Once the energy-channel calibration has been performed, it is possible to identify the different radionuclides which are present in the analyzed samples. In order to quantify their activities, another calibration which is needed is the efficiency calibration (ε_α).

3.3.3.2 Efficiency calibration

The physics associated to the interaction of radiation with matter for alpha particles follows different mechanisms from that of gamma rays. In fact, for alpha spectrometry the intrinsic detection efficiency (ratio between the responses given by the detection system and the number of alpha particles hitting it) does not present dependence with the energy in the energy interval of interest in this work. In the detector interaction all the particles arriving, loose all their energies, and for that reason the intrinsic detection efficiency can be assumed to be 100%.

However, for the determination of the counting efficiency there are other factors that should be taken into account. These factors are:

a) Geometric factors, although if the measurements are performed always under the same conditions, we will have a constant influence of this factor for each detector.
b) Self-absorption factors in the measurement sources, which in the case of electrodeposited sources can be considered negligible.
c) Absorption factor between the measurement source and the detector. This factor can be considered negligible if enough vacuum is done in the detection chambers.

The indicated considerations simplify enormously the work to be performed for the calculation of the counting detection efficiency in alpha-particle spectrometry with PIPS detectors because only a dependence with the geometry source-detector is expected.

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The counting efficiency calibration has been performed with a source of ^{241}Am (α_1 = 5.378 MeV and α_2 = 5.477 MeV) that contains a certified activity of 274.5 ± 1.0 Bq. Measurements were performed at different distances of source-detector. The obtained results are shown in the Figure 3.15

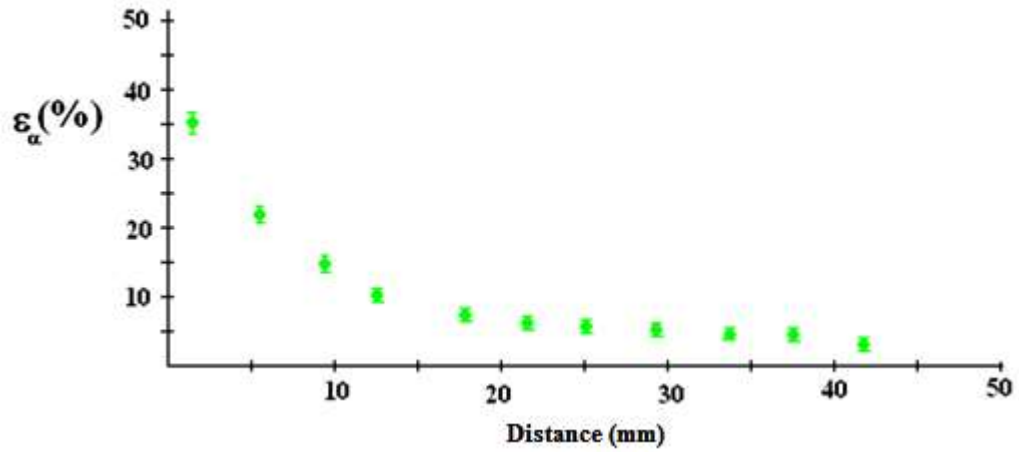

Figure 3.15: Experimental variation of the counting efficiency with the distance source-detector (Vioque, 2000).

With basis in the results shown in the Figure 3.15, it could seem convenient to place the source as near as possible to the detector in order to obtain the maximum counting efficiency. However, it is necessary to also consider the influence of the distance (source-detector) in the resolution of the alpha peaks because at shorter source-detector distances there is increase in the solid angle and possible partial losses of energy by the alpha particles emitted by the source. These alpha particles can cross longer distances in the detector windows. In addition, the quite short distances between the source and the detector leads to an increase in the contamination risk of the detector notably due to the possible implantation of back-scattered nucleus. The selected source-detector distance is then simply a

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compromise, being fixed at 5.5 mm, the second position (shelf) of all the chambers (see Figure 3.15)

Using the commented ^{241}Am calibration source, the counting efficiency for the eight chambers at a source-detector distance has been determined. The obtained results are compiled in Table 3.8.

Table 3.8: Experimental results determined for the counting efficiencies in the eight chambers at a source-detector distance of 5.5 mm (Mantero, 2013)

Chamber	*1A*	*1B*	*2A*	*2B*	*3A*	*3B*	*4A*	*4B*
ε_α(%)	18.3±1.1	23.0±1.3	20.8±1.2	21.9±1.2	21.2±1.2	23.4±1.3	19.4±1.2	22.2±1.3

If the geometric factor is calculated (fixed by the sample-detector solid angle) as a function of three parameters (radius of the source, radius of the detector and source-detector distance) (García-León et al 1984), it can be concluded that the counting efficiencies obtained experimentally are in agreement with the fraction of solid angle substended by the sample in relation to the detector. In this way, it is confirmed that the intrinsic efficiency is practically 100% and the negligible influence of the self-absorption effects in the source and the absorption effects in the trajectories between sources and detector. Nevertheless, the detector in chamber 1A have a counting efficiency that is 15% lower than the calculated geometric factor indicating that this detector is not so much efficient as the other ones.

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3.3.4 Calculation of Minimum Detectable Activity in alpha spectrometry

For Alpha measurements the MDA was calculated as (Hartwell, 1975)

$$\text{MDA}= \frac{1}{I.\varepsilon.C_1.t_T}\left(2.71 + 3.29\sqrt{N_B + \frac{N_B.t_B}{t_T}}\right) \quad (3.7)$$

Where;

N_B is the background count for the region of interest of each radionuclide

t_T is the sample measurement time

t_B is the background counting time,

C_1 is the Radiochemical yield calculated for tracer

I is the Intensity of alpha emission of each radionuclide,

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

The MDA in our system has been determined. Some results are shown in Table 3.9, being necessary to remark that in this case the MDA are in general three orders of magnitude lower than the obtained ones by gamma ray spectrometry, mostly due to the very low background values of our alpha spectrometric system.

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Table 3.9: MDA values in some alpha chambers (Mantero, 2013)

Chamber	Radionuclide	t_B (s)	t_T (s)	ε	$MDA_{hartwell}$ (mBq)
1A	^{238}U	148841	167953	0.18	0.97
	^{235}U	148841	167953	0.18	0.97
	^{234}U	148841	167953	0.18	1.52
1B	^{238}U	453759	865952	0.23	0.27
	^{235}U	453759	865952	0.23	0.23
	^{234}U	453759	865952	0.23	0.29
3A	^{232}Th	148624	525051	0.21	0. 25
	^{230}Th	148624	525051	0.21	0.42
3B	^{232}Th	334421	400000	0.23	0.49
	^{230}Th	334421	400000	0.23	0.67
4A	^{210}Po	444545	605253	0.19	0.41
4B	^{210}Po	348016	384747	0.22	0.36

From this table it is possible to obtain some interesting conclusions:

- For measurement times shorter than 200000s (Chamber 1A) is recorded an MDA value lower than 1 mBq. For measurement times higher by a factor 2 or 3 (Chamber 1B), the MDA values decreased in the same proportion.
- It is possible to observe the existence of a small contamination in the ^{234}U window of chamber 1A.
- There is also in general more background in the ^{230}Th window than in the ^{232}Th window.

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CHAPTER FOUR

MATERIALS AND METHODS

Overview

In this Chapter, a description of the study area, sampling, sample preparation and measurement procedures are presented. Mathematical formalisms for the calculation of the activity concentration, the radiation hazard indices, the radium equivalent activity, the radon emanation coefficient, radon mass exhalation rate, the absorbed dose rate and effective dose are also described together with the practical information of the Human Health Risk Assessment Model used.

4.1 Description of Study Area

4.1.1 Saltpond Oilfield and surrounding coastal towns

The study area includes the Saltpond oilfield and four communities within and around Saltpond. Saltpond is a town along the coast in the vicinity of a shallow water offshore oilfield in the Mfantseman District of the central region in Ghana. The oilfield (Figure 4.1) is located about 12 kilometres off the coast of Saltpond in the northern-central area of the Takoradi Arch and approximately 100 km west of Accra, in a water depth of 85 feet (25.9 m) and extends over an area of 5 square kilometres. Saltpond, (5° 12' 0 N, 1° 4' 0 W), is a populated town that covers an area of 10 km^2 and has an approximate population of 20,000 inhabitants (GNPC, 2013). The four coastal communities considered for this study are Ankaful, Nankesedo, Kormantse and Abandze all of which lie about 1.5km apart. In Figure 4.2, a map of the study area, including the location of the coastal communities is shown.

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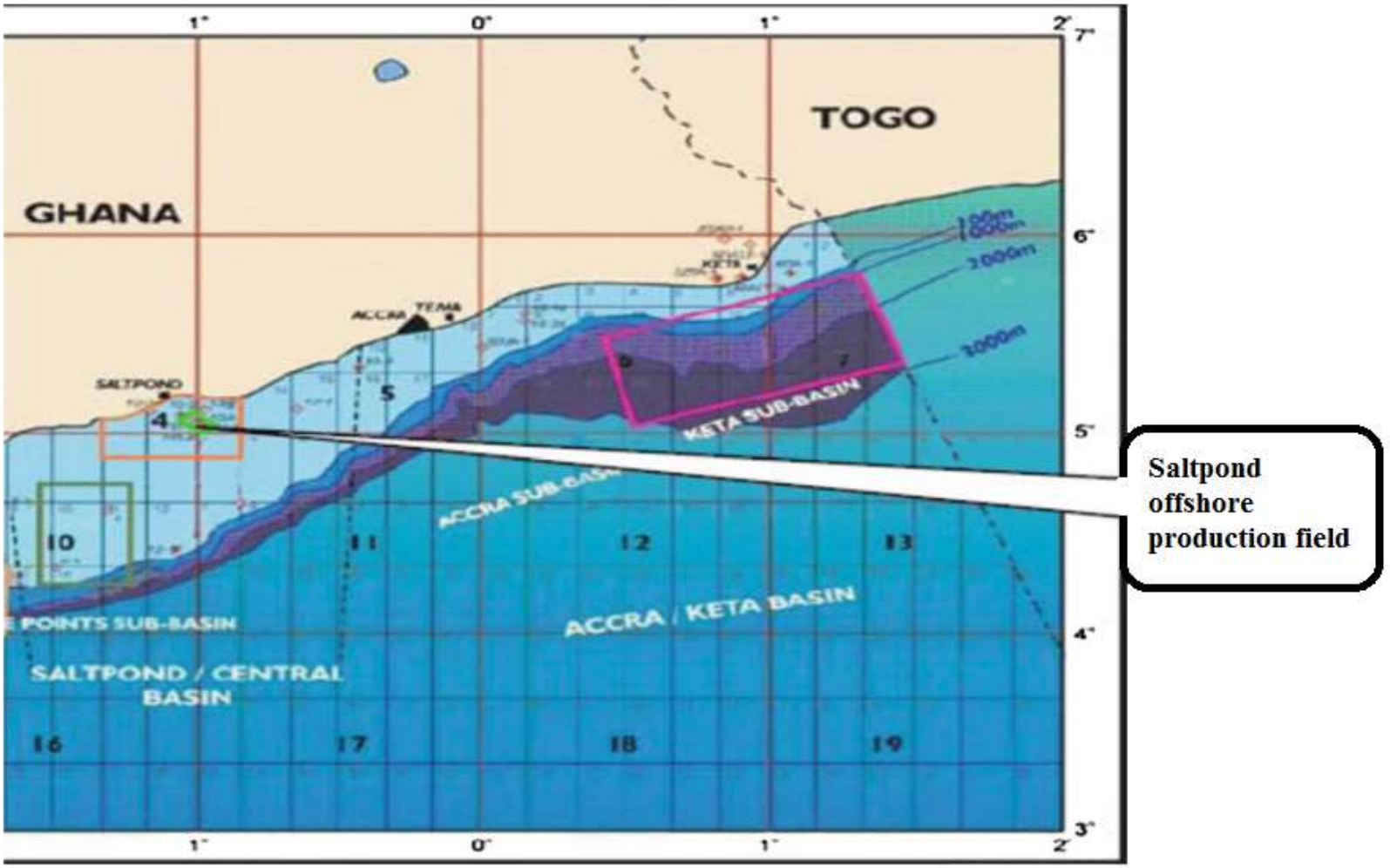

Figure 4.1: Saltpond offshore oil production field (GNPC, 2013)

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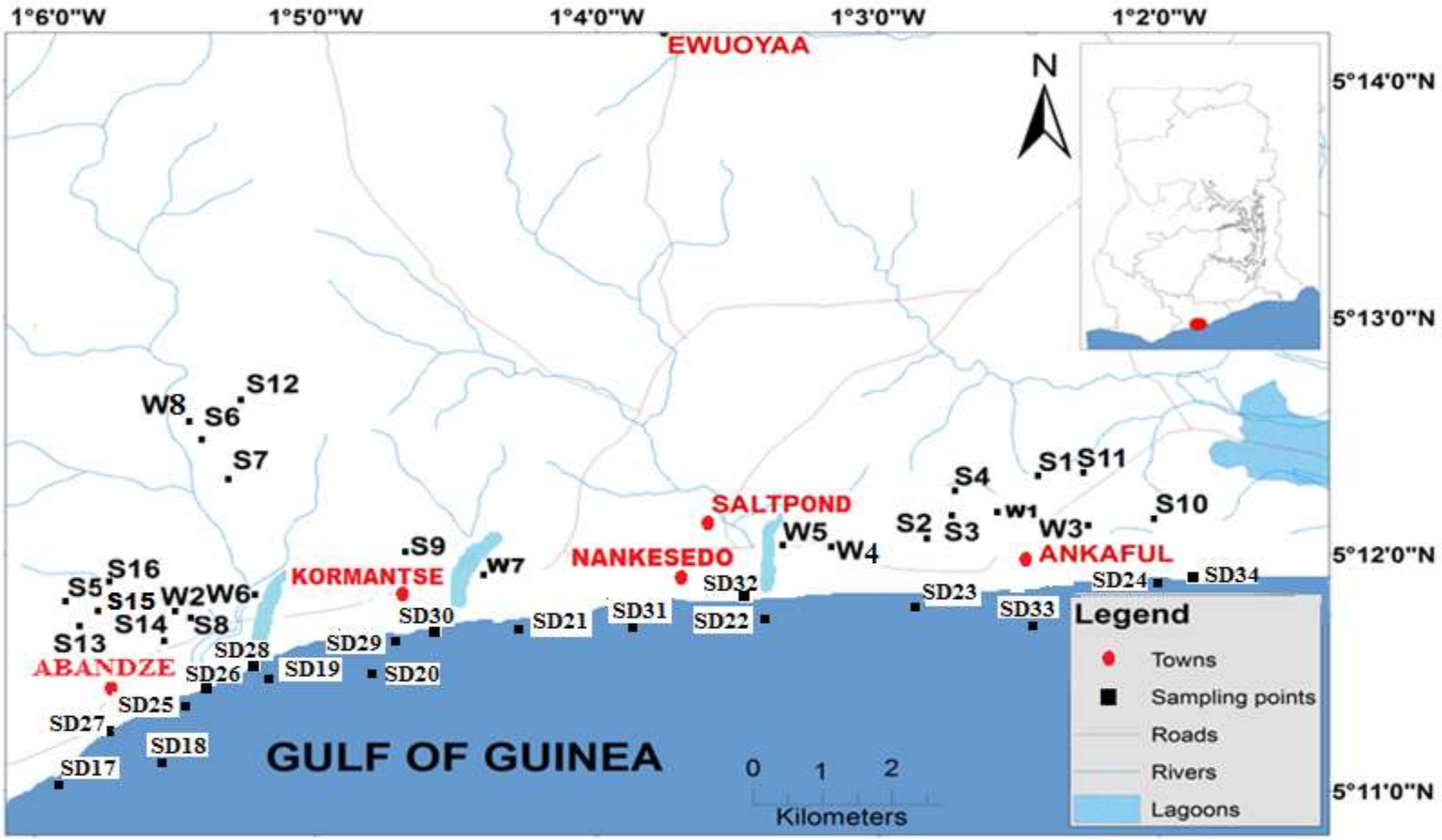

Figure 4.2: Map showing the study area and the location of the sampling points (S =soil, W=water, SD =sediment) using ACK GIS

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4.1.1.1 Geology of Saltpond oilfield

The Saltpond Basin is a Paleozoic wrench modified pull-apart basin centrally located between the Tano-Cape Three Points and Accra-Keta basins. It covers an area of approximately 12,294 sq. km. Sediments in the basin were deposited in non-marine to coastal marine environments. The basin has been stratigraphically divided into formations namely Elmina Sandstone, Takoradi Sandstone, Takoradi Shales, Efia Nkwanta Beds and Sekondi Sandstone. The structure of the basin is characterized by multiple faulting, which has resulted in a complex set of horsts and grabens. The only known and proven petroleum system in the Saltpond Basin is the Lower Paleozoic Petroleum System. This system has Devonian source rocks and Devonian to Carboniferous reservoirs. The reservoirs are sandstones of the Takoradi Sandstone Formation. Trapping is both structural (fault-bounded blocks) and stratigraphic (sandstones interfingering into shales) with sealing provided by the Takoradi Shale Formation (MoF, 2014).

4.1.1.2 Relief, Geology, Meteorology and Vegetation of Saltpond

Saltpond is basically a low-lying area with loose quaternary sands which are cretaceous—Eocene marine sands within pebbly sands and some limestone. Due to its proximity to the Atlantic Ocean, it has mild temperatures, which range between 24° C and 28°C and has a relative average humidity of about 70 per cent. The district experiences double maxima rainfall during the year, with peaks in May—June and October. The periods December-February and July to early September are much drier than the rest of the year.

The vegetation in the study area is formed by dense scrub tangle and grass, which grow to an average height of 4.5 m. It is believed that Saltpond was once forested, but trees have

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been systematically destroyed through centuries of bad environmental practices. However, pockets of relatively dense forest can be found around fetish groves and isolated areas.

All the commented physical characteristics have combined effectively to offer opportunities in agriculture (farming) to the people. In addition, the proximity to the sea has made fishing a major activity of the population along the coast.

3.1.2. Jubilee Field

The Jubilee field is located in the western region of Ghana, is a small peninsula called Cape Three Points. It forms the southern-most tip of Ghana, and it's nearest a location in the sea which is at 0 latitude, 0 longitude, and 0 altitude. It experiences temperature range of 23.8–26.4 ^{o}C with mean temperature of about 24.9 ^{o}C. It has two main oil blocks, namely; West Cape Three Points and Deep Water Tano. Figure 4.3 shows the Ghana offshore activity map for Cape Three Points. The Jubilee Field (Fig. 4.3 and 4.4), an oil and gas reserve located offshore Ghana is approximately 60 km from the nearest coast and lies in deep water (1,100–1,700 m), straddling the two oil concession blocks (GNPC, 2013).

Tullow Ghana limited (TGL) is an oil and gas exploration and production company duly registered with the Ghana National Petroleum Corporation and the Petroleum Commission of Ghana. Tullow is the designated operator of the Jubilee field offshore the west coast of Ghana. The offshore oil and gas production facility (FPSO Kwame Nkrumah) has been in operation in the field since June 2010.

4.1.2.1 Geology of Jubilee Oilfield

The Tano-Cape Three Points Basin is a Cretaceous wrench modified pull-apart basin. The basin was formed as a result of trans-tensional movement during the separation of southern West Africa and northern South America. Active rifting resulted in the formation of a deep

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basin. With time the continental crust further thinned and sea floor spread. New oceanic crust were formed at the trailing edges of the two continental plates as they began separating and the two plates finally separated. Prevailing conditions at the time were ideal for the deposition of shales, thus, thick organic rich shale was deposited. Several river systems contributed significant clastic into the deep basin and led to deposition of large turbidite fan/channel complexes. Some sandstones were in tilted fault blocks as reservoirs. Trapping is both stratigraphic and structural. The hydrocarbon potential of Ghana's portion of the basin has been known since the 1890's based on onshore oil seeps but the first major discovery was made in 2007 at the Jubilee Field with oil production commencing in December, 2010 (MoF, 2014).

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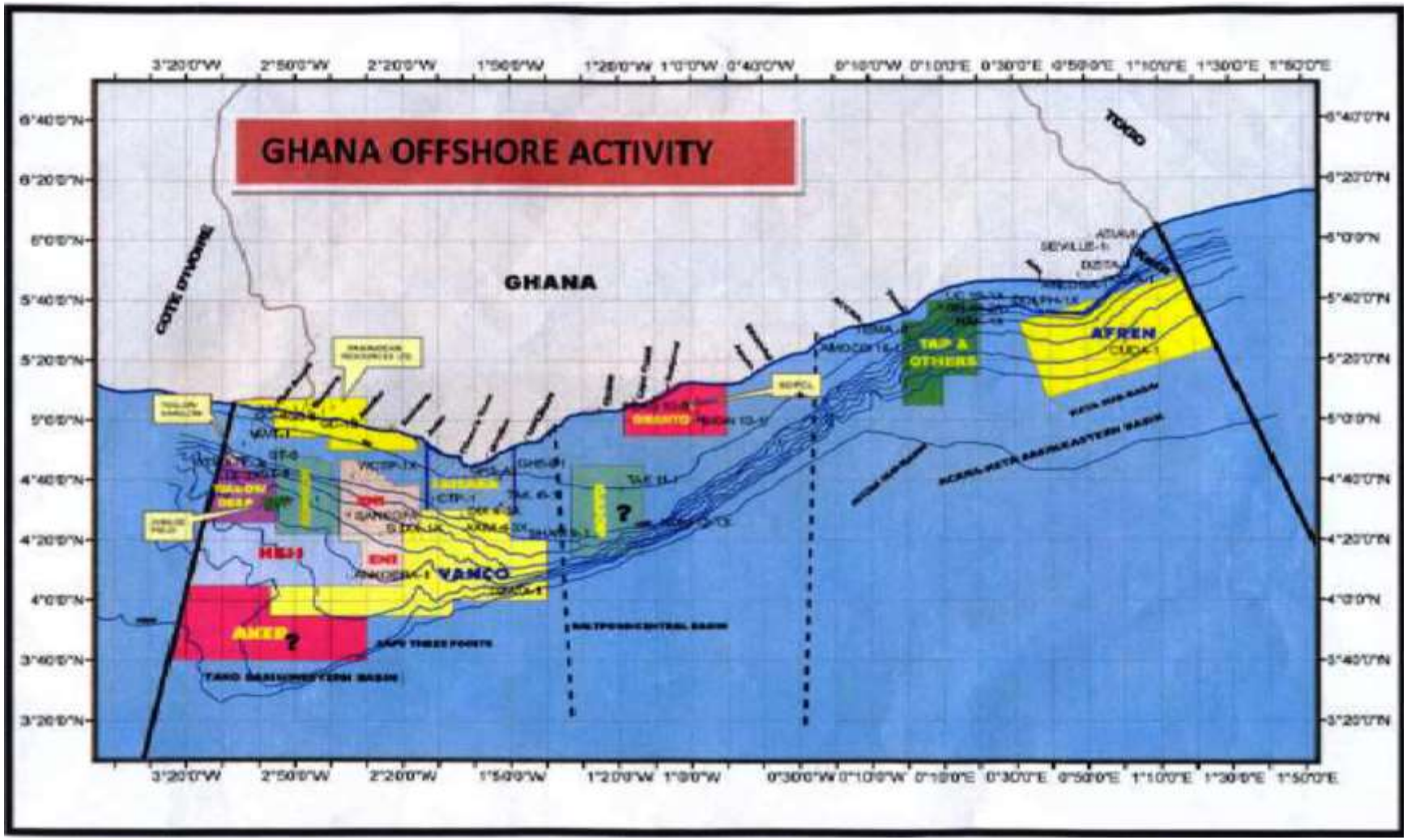

Figure 4.3: Ghana offshore activity map (GNPC, 2013)

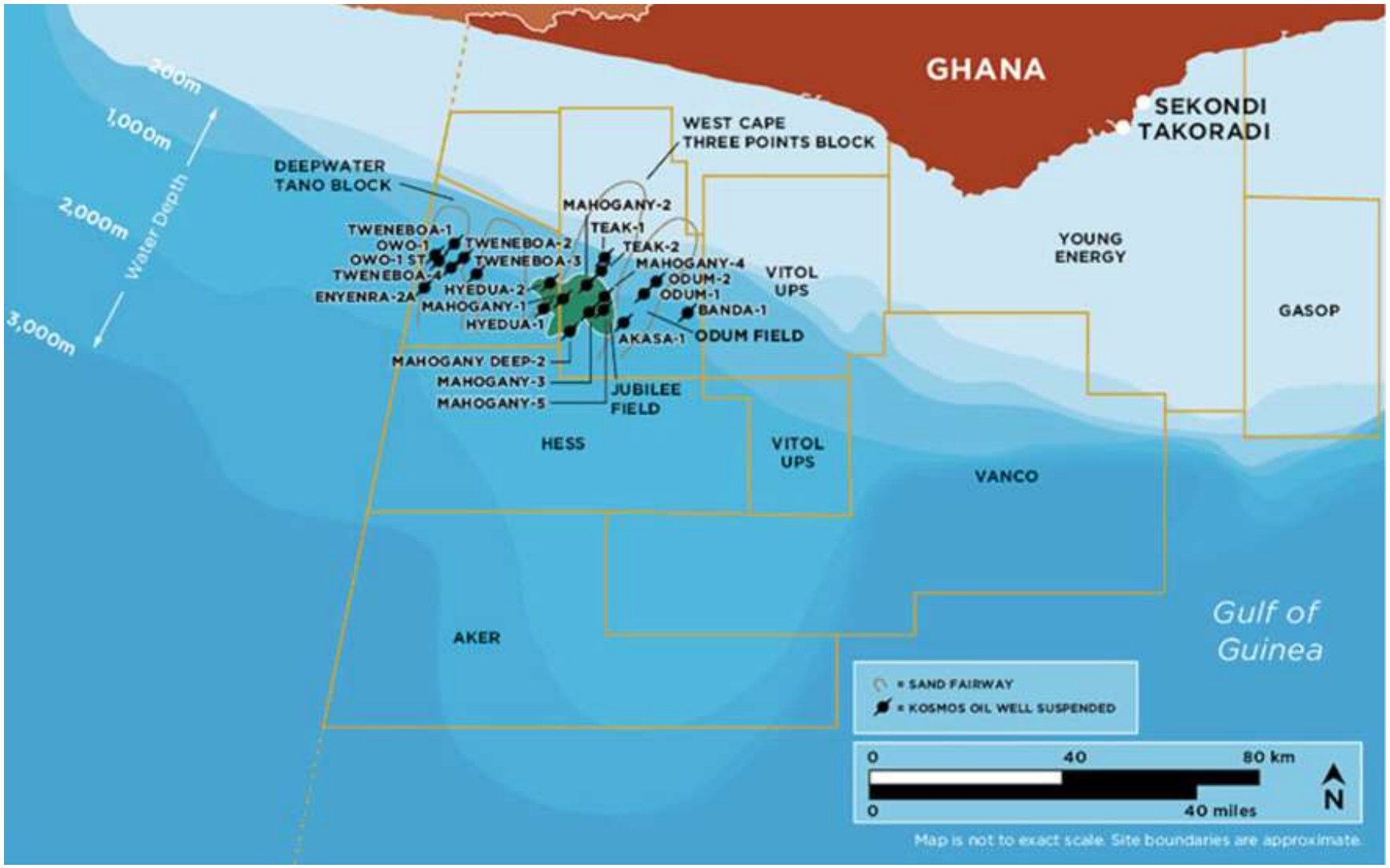

Figure 4.4: Jubilee oilfield straddling the two oil concession blocks (GNPC, 2013)

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4.2. Sample collection

Sampling was carried out at different periods spanning from June 2012 to January 2015 with five sampling campaigns (see table 4.1) throughout the project. The following significant exposure pathways were considered as the basis for the types of samples to be collected for the study.

1. Workers:
    - Direct gamma radiation exposure
    - Radon inhalation

2. The Public:
    - Direct gamma radiation exposure
    - Exposure to radon
    - Ingestion of contaminated water sources (surface water(e.g. rivers, streams, etc)and ground water (e.g. boreholes, wells)
    - Ingestion of sea food harvested from contaminated marine environment

In all, a total of ninety two (92) samples were collected from the study areas. This comprised 42 environmental samples (water, sediments, soils, etc.) and 50 NORM samples (produce water, sludge, scale, crude oil, etc) from the two oilfields and petroleum waste treatment facility located in the central and western region of Ghana.

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Table 4.1: Description of samples collected during each sampling campaign

Sample types (codes)	Description	Sampling Campaign
Soil (S1-S16) Water (W1-W8)	Soil and water samples from the four coastal communities along the coast of Saltpond oilfield (Figure 4.2)	First campaign – June 2012
Sludge (SLW1-SL3)	Sludge from the bottom of produce water separation tank from Jubilee field	Second campaign – October 2013
Produced water (JF1-JF5)	Produced water from Jubilee field (treated for discharge)	
Crude oil (JC1-JC5)	Crude oil from Jubilee field	
Produced water (SF6-SF9)	Produced water from Saltpond field (treated for discharge)	
Crude oil (SC6-SC8)	Crude oil from Saltpond field	
Sediments (SD17-SD34)	Beach sediments samples from the same four coastal communities as soil and water previously along coast of Saltpond oilfield (Figure 4.2)	
Produced water (SF10-SF13)	Produced water from Saltpond field (untreated)	Third campaign – April 2014
Crude oil (SC9-SC10)	Crude oil from Saltpond field	
Ash (AS1-AS6)	Incineration ash from various waste from offshore Jubilee field sampled from Zeal Environmental Technologies Ltd waste treatment facility	Fourth campaign-September 2014
Oil based mud (RM1-RM4)	Oily based mud separated from oily waste water from offshore Jubilee field sampled from Zeal Environmental Technologies Ltd waste treatment facility	
MB1-MB2	Blocks moulded from (RM) with addition of cement and hydrated lime sampled from Zeal Environmental Technologies Ltd waste treatment facility	
Oily waste water (OWW1-OWW3)	Oily waste water from offshore Jubilee field sampled from Zeal Environmental Technologies Ltd waste treatment facility	
Wash water (WW4)	Wash water to be discharged to general sewage after treatment and separation of Oily waste water sampled from Zeal Environmental Technologies Ltd waste treatment facility	
SC1-SC5	Scales from produce water pipeline from Jubilee field	Fifth campaign-January 2015
SL4-SLW6	Sludge from the bottom of produce water separation tank from Jubilee field	

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4.2.1 Sampling of environmental samples

A total of 42 samples comprising 8 water, 18 tidal area sediments and16 soils were collected within the Saltpond field study area (see Figure 4.2). The water samples included underground (borehole W1-W4), lagoon (W5-W7), and river (W8) water. The borehole and river water samples are used for domestic and drinking purposes . The lagoon has a link to the sea and it is used for fishing and swimming. Soil samples were taken mainly from areas used for agricultural or building material purposes. The sediments were taken from the beach and tidal flat of the same four coastal communities Ankaful, Nankesedo, Kormantse and Abandze just as for soils and waters (see Figure 4.2 and Appendix D for exact locations and coordinates for all environmental samples).

Due consideration was taken to avoid stagnant areas during collection of surface water from the river (W8) and lagoon (W5-W7). For the soil and beach sediments samples, at each location, an area of 15 × 15 m^2 was marked and 5–8 sub-samples were taken randomly with a coring tool at a depth down to 5 cm.

The pH of the water samples were measured on the field and in the laboratory using a pH Meter, model HANNA pH 211, calibrated with standard buffer solutions with pH 4.01, 7.0 and 9.21. The Total Dissolved Solids (TDS) and conductivity were also measured in the laboratory using a HACH multi-meter, model SanSion 5. This equipment was calibrated with 0.01M KCl and 0.1M KCl standard solutions.

4.2.2 NORM Sampling

NORM samples were collected from the two producing oilfields, namely; Saltpond and Jubilee oilfields, and Zeal Environmental Technologies Limited, a waste treatment facility which handles oil and gas waste from offshore. In all, 50 Samples were collected

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comprising 13 produced waters, 6 sludges, 5 Scales, and 10 crude oil samples from the Saltpond and Jubilee fields. Three (3) oily waste water, 1 wash water, 4 oil based mud, 2 mud blocks and 6 incinerated ash samples were also collected from the waste treatment facility of Zeal Environmental Technologies Limited.

Plate 4.1: Oil based mud processing and blocks moulding facility (Zeal Environmental Technologies Ltd)

Plate 4.2: Oily waste water treatment plant (Zeal Environmental Technologies Ltd)

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Plate 4.3: Dose rate measurement around well heads on the Saltpond oilfield platform

Plate 4.4: Dose rate measurement on the inner surface of scale contaminated pipe from Jubilee field

For produced water samples after homogenization, the physical parameters such as temperature, pH, conductivity, TDS and salinity were measured in the laboratory using HACH multi-meter with probes, model SanSion 5. Anions and cations were determined using a UV-VIS Spectrophotometer (Model UV-1201 by HIMADZU of Japan) and atomic absorption spectrometry (Model Varian AAS240FS). Morphological and elemental composition of an aliquot of solid dried fraction from produced water sample was analysed using a JEOL 6460LV scanning electron microscope (SEM). Quantitative elemental analyses were carried out using an Agilent 7500C ICP-QMS provided with an Octopole Reaction System (ORS). Element concentrations, quality checks and

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calculation of dead time or count rates corrections were carried out using a mix of single elemental standard solutions.

4.3 Sample preparation and measurement by alpha-particle spectrometry

The sample preparation and conditioning prior to the commencement of the measurement by alpha-particle spectrometry is not a trivial task. The application of radiochemical procedures for the isolation of the radionuclides of interest and specific source preparations to avoid self-absorption effects (see Figure 4.5) are unavoidable.

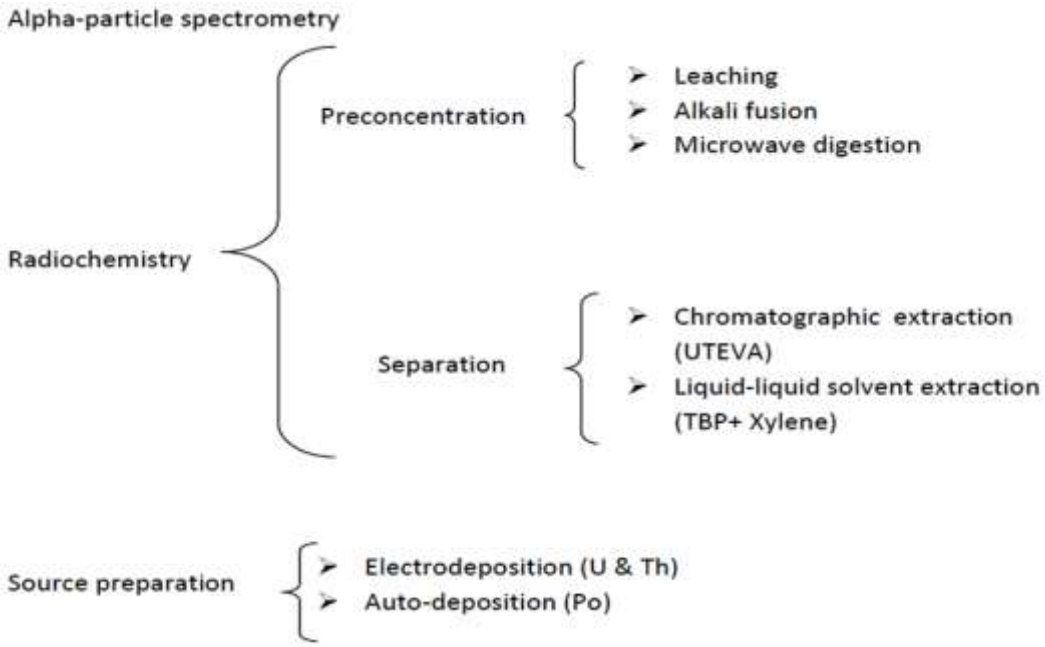

Figure 4.5: Summary of various analytical steps involved in Alpha Spectrometry used in this work.

Specifically, water samples were acidified immediately after sampling with concentrated HNO_3 (65%) to pH 2 to avoid the growth of microorganisms and to minimize the interactions with walls of the storage containers prior to the analysis in the laboratory. Afterwards, the liquid and solid matrix samples preparations for U and Th determination

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by alpha-particle spectrometry were carried out in three main steps: pre-concentration, radiochemical separation and electrodeposition.

The pre-concentration of U and Th from water samples was done by co-precipitating the actinides via the iron hydroxide method (Holm and Fukai, 1977a and 1977b). An amount of 0.5L of water taken from a previously shaken storage container were filtered and known amounts of tracers (^{232}U, ^{229}Th and ^{209}Po) were added with gently warming at 30 ^{o}C and stirring to ensure homogenization. Then, 2ml of a Fe^{3+} solution (5 mg/ml) were added and the pH adjusted to 8-8.5 with concentrated NH_3 (25%) resulting in the co-precipitation of actinides with iron hydroxide. The supernatant was then carefully removed after settling down of precipitate and the remained fraction was centrifuged at 4500 rpm for 10 minutes. The precipitate, containing the U and Th, was dried and finally dissolved in 5mL of 3M HNO_3 before starting the radiochemical separation stage.

In the case of solid matrix samples, 0.3 – 2g of dried homogenized solid sample aliquot were taken and calcinated at 600 ^{o}C for 24hrs after addition of the same tracers indicated above excluding samples in which polonium was analysed. The ashed material was then wet digested with aqua regia for 4h at 50 ^{o}C using the leaching technique. Afterwards, 12mL of H_2O_2 was added drop by drop and 45mL of concentrated HNO_3 (65%) was also added while the sample was stirred at room temperature for 12 hrs. Finally, 30mL of 8M HNO_3 was added and filtration was carried out. The filtered fraction was then evaporated to 10mL and topped to 50mL with distilled water. The resulting solution of 50mL was submitted to the same actinides co-precipitation iron hydroxide procedure described above for water samples.

For crude oil samples, they were digested using a microwave digester Anton Par applying the digestion programme code for light crude oil (0.4g crude + 8ml Conc.

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HNO_3 + 2ml H_2O_2 + 1ml HCl with digestión time of 30mins).The digested solution was diluted with distilled water to 50ml and was submitted to the same actinides co-precipitation iron hydroxide procedure described above for water samples.

The radiochemical separation stage for samples was done by applying Liquid-liquid solvent extraction (TBP+xylene) and/or commercial extraction chromatographic resins (called UTEVA from TRISKEM Co.). The step wise procedure used for both separation techniques are presented in Figure 4.6. 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 resins contain from the manufacturer. The column was rinsed twice afterwards with 5mL of 3M HNO_3 (these washings contain the Po) and afterwards the Th fraction initially retained in the column was stripped by loading 4mL of 9M HCl followed by 20mL of 5M HCl. The U fraction was obtained after that by loading 10 ml of 0.01M of HCl (Lehritani et al., 2012). Both obtained solutions (24 ml in case of Th, 10 ml in the case of U) are free from other interfering alpha emitters.

Source preparation for Po was done by self-deposition onto copper discs whiles U and Th were independently electrodeposited onto stainless steel discs by applying the well-known method of Hallstadius (Hallstadius, 1984). The U isotopes were electroplated at 1.2A for 1h, while the Th was electroplated at 1.5A for 2h and Po self-deposition was for 4hrs.

The measurement of the U, Th and Po isotopes electroplated and self-deposited on stainless steel discs and copper (25mm) were done using 450 mm^2 active surface PIPS detectors installed in the 8- chamber Alpha Analyst System (Canberra), presented in Chapter 3. In the laboratory, each chamber was devoted to the exclusive measurement of

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one element in order to avoid cross contamination. The measurements were carried out at a source to detector distance of 0.55 cm. The accumulation and analysis of Alpha spectra was done using Genie 2000 software with measurement time of about 200,000s.

The background spectrum was also used to determine the minimum detectable activity (MDA) of U and Th at the 95% confidence level (~0.1mBq) using a measuring time of 2-3days.

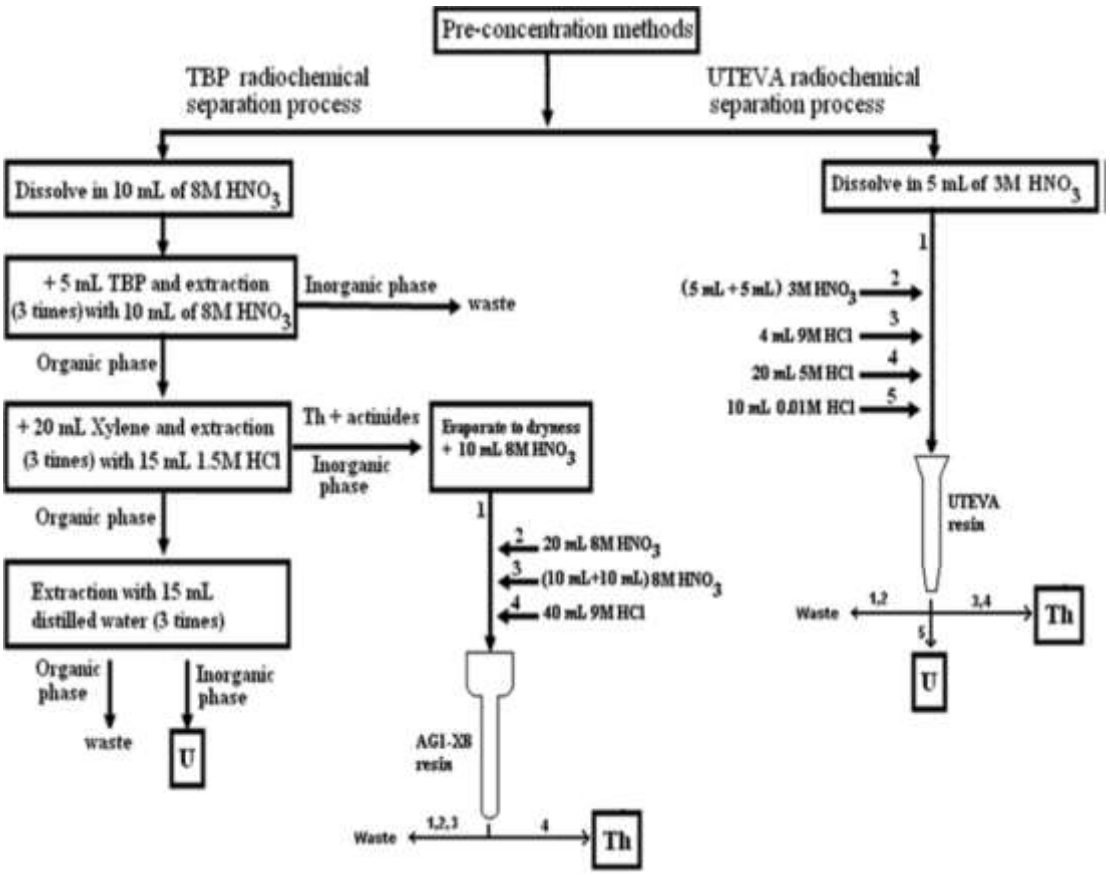

Figure 4.6: Radiochemical separation steps for UTEVA and TBP

Radiochemical analysis becomes essential when the activity concentration of the radionuclides is close to the detection limit of the direct measuring technique or when the levels of interference in the radionuclide assay process cannot be tolerated and also

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to allow the particles emitted to approach the detector. The interference may be due to matrix interference, in which the sample matrix absorbs the emitted particles, or spectral interference, where the spectra of other radionuclides prevent the accurate measurement of the radionuclides of interest. Radiochemical analysis is essential for quantitative α and β particles spectrometry of the different natural (such a U isotopes, Th isotopes, ^{210}Pb, ^{210}Po, ^{226}Ra, and ^{228}Ra) and artificial radionuclides (such as $^{239+240}$Pu, ^{238}Pu, ^{241}Am, and ^{244}Cm) in the different environmental matrixes. Also, improving sensitivity in radiochemical separations usually entails a more through elimination of interfering components.

In general, it is necessary to add isotopic or non-isotopic carriers before any radiochemical analysis is commenced. Isotopic carriers serve two functions: to provide additional mass of the element, which aids in the separation process, and to provide a means of measuring the chemical yield. Non-isotopic carriers serve only to aid in the separation of the desired nuclides.

4.4 Sample preparation and measurement by Gamma Spectroscopy

4.4.1 Sample preparation

In the laboratory, each of the soil/sediments samples was air-dried on trays for 7 days and then oven-dried at a temperature of 105^{o}C for between 3 and 4 hrs until all the moisture was completely lost. The samples were then ground into fine powder using a ball mill and sieved through a 500µm mesh size pore and stored in the geometries and containers selected. For solid NORM waste samples in which the radon emanation fraction was determined the dried samples were each transferred into measuring containers without any treatment and vacuum sealed. These containers, containing the samples, were completely sealed for 1 month to allow the short-lived daughters of ^{238}U

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and ^{232}Th decay series to attain equilibrium with their long-lived parent radionuclides. The liquid samples were prepared into one (1) litre Marinelli beaker after filtration to remove all solid particles in the water. Prior to the measurements, the detector and measuring assembly were calibrated for energy and efficiency to enable both qualitative and quantitative analysis of the samples to be performed as detailed in chapter three.

4.4.2 Analysis of samples

All solid and liquid matrix samples were non-destructively analysed by high-resolution gamma spectrometry using a p-type Extended Range Germanium coaxial detector (XtRa) with relative efficiency of 37.1% and with an energy resolution of 1.8 keV for gamma-ray energy of 1332 keV of ^{60}Co. The detector is housed in a 10 cm passive shielding of ancient lead and an active shielding made with an organic scintillation detector (Bicron BC-418) placed on the top of the lead shield and working in anticoincident mode with the Ge detector . This allows remarkable reduction in the environmental gamma-radiation measurements due to the very low background. The counting time was 180,000 seconds for each soil sample.

Plate 4.5: Gamma spectrometry system with a p-type Extended Range Germanium coaxial detector

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The identification of individual radionuclides was performed using their characteristic gamma-ray energies and the quantitative analysis of radionuclides was performed using the Genie 2000 gamma acquisition and analysis software. Background spectra were acquired and used to correct the net peak area of gamma rays of the measured isotopes. The background spectrum was also used to determine the minimum detectable activities presented earlier in chapter three.

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%). All the energies and intensities of the different radiations mentioned were taken from a well-known library (Chu et al., 1999).

4.5 Calculation of Activity Concentration

The activity concentration of radionuclides in the soil/sediments, water and petroleum samples for gamma measurements were calculated from the expression as shown in equation (4.1)

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$$A_{sp} = \frac{N.e^{\lambda_p t_d}}{p.T_c.\eta.m} \quad (4.1)$$

where;

A*sp* is the activity concentration

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

t_d 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,

T_c is the sample counting time,

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

exp ($\lambda_p T_d$) is the decay correction factor for delay between time of sampling and counting, and

λ_p is the decay constant of the parent radionuclide.

For alpha measurements the activity concentrations were calculated using the isotopic dilution techniques whiles the yield was calculated using equation (4.2)

$$A(Bq) = \frac{N}{t.\varepsilon.I.C_1} \quad (4.2)$$

where:

A is activity of tracer

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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 (%)

4.6 Determination of Hazard indices and risks

Soil/sediments and other solid waste materials in the study area could be used as construction materials for buildings and other purposes. For this reason, certain hazard parameters are defined to determine the suitability of these materials in order to reduce exposure of the public.

The radium equivalent activity (Ra_{eq}) is a radiation index, used to evaluate the actual radioactivity in the materials containing naturally occurring radionuclides. To compare the activity concentration of the soils containing ^{226}Ra, ^{232}Th and ^{40}K, the radium equivalent index $^{226}Ra_{eq}$ was used by applying the following expression

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K \quad (4.3)$$

Where; C_{Ra}, C_{Th} and C_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K respectively. In the definition of Ra_{eq}, it is assumed that 370 Bq/kg of ^{226}Ra, 259 Bq/kg of ^{232}Th and 4810 Bq/kg of ^{40}K produce the same gamma ray dose rate. The above criterion only considers the external hazard due to gamma rays in building materials. The maximum recommended value of Ra_{eq} in raw building materials and products must be less than 370 Bq/kg for safe use (OECD/NEA, 1979; Beretka and Mathew, 1985).

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Another criterion used to estimate the level of gamma ray radiation associated with natural radionuclides in specific construction materials is defined by the term external hazard index (H_{ex}) as shown equation (4.4) (OECD/NEA, 1979; Beretka and Mathew, 1985).

$$H_{ex} = \frac{C_{Ra}}{370} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \quad (4.4)$$

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 unity 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 (OECD/NEA, 1979; Beretka and Mathew, 1985).

Another hazard index known as internal hazard index due to radon and its daughters was calculated from equation (4.5). This is based on the fact that, radon and its short-lived products are also hazardous to the respiratory organs.

$$H_{in} = \frac{C_{Ra}}{185} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \quad (4.5)$$

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 unity (OECD/NEA, 1979; Beretka and Mathew, 1985).

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4.7 Radon Measurements

Air- borne radon activity concentrations were measured directly with a Genitron Alpha Guard, Model PQ 2000/mp50. The measurements were carried out outdoor and indoor in the field. The temperature, atmospheric pressure and relative humidity were also recorded during the measurement. The Alpha Guard is provided with a large surface glass fibre filter, which allows only the gaseous ^{222}Rn to pass through whilst the radon progeny are prevented from entering the ionisation chamber. The filter also protects the interior of the chamber from contamination by dusty particles. The data was evaluated using Alpha View/Expert Software, which automatically transforms radon daughter concentrations from working level (WL) to equilibrium equivalent concentration (ECC) in Bqm^{-3}.

The annual effective dose from radon gas in air was estimated from equation (4.6).

$$E_{inh}(Rn) = DCF_{Rn}.F_{Rn}.C_{Rn}.T_{\exp} \qquad (4.6)$$

where;

E_{inh} (Rn) is the annual effective dose from inhalation of radon,

DCF_{Rn} is the dose per unit intake of radon via inhalation in $nSv/Bqhm^{-3}$, (9 $nSv/Bqhm^{-3}$) (UNSCEAR, 2000),

F_{Rn} is equilibrium factor for outdoor and indoor occupancy, 0.6 and 0.4 respectively (UNSCEAR, 2000),

C_{Rn} is the radon activity concentration in Bqm^{-3}, and

T_{exp} is the exposure period of one year for outdoor occupancy, which is 1760 hours using outdoor occupancy factor of 0.2 (UNSCEAR, 2000).

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4.7.1 Determination of radon emanation fraction and radon mass exhalation rate

The soil and waste samples were air-dried and finally oven dried in some cases to remove any additional moisture from the samples. The dried samples were each transferred into measuring containers without any treatment and vacuum sealed. The EF measurements were carried out on scale, sludge, ash, mud and mud block samples.

The samples were each counted on a High Purity Germanium Detector (HPGE) 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 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 as follows;

$$C_1 = A_0 + N\left(1 - e^{-\lambda t_1}\right) \quad (4.7)$$

$$C_2 = A_0 + N\left(1 - e^{-\lambda t_2}\right) \quad (4.8)$$

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}).

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A_0 and N are determined by solving equations (4.7) and (4.8) as follows:

In order to simplify equations (3.16) and (3.17), x was put in place of $1-e^{-\lambda t}{}_1$ and y put in place of $1-e^{-\lambda t}{}_2$. The results for N, A_0 and EF are given in equations (4.9), (4.10) and (4.11).

$$N = \frac{C_1 - C_2}{x - y} \quad (4.9)$$

$$A_0 = \frac{xC_2 - yC_1}{x - y} \quad (4.10)$$

$$EF = \frac{N}{A_0 + N} \quad (4.11)$$

The emanation fraction (EF) was calculated from equation (4.11).

The mass exhalation rate or radon mass exhalation rate is the product of the emanation fraction and ^{222}Rn production rate (Chowdhury *et al*., 1998; Kpeglo et al., 2011). The mass exhalation rate (E_{Rn}, in Bq/kgs) was determined using the equation:

$$E_{Rn} = C_{Ra} \times EF \times \lambda_{Rn} \quad (4.12)$$

Where, C_{Ra} 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).

4.8 Gross alpha and beta measurements in water samples

The water and produced water samples were also analysed for gross alpha (α) and gross beta (β) radioactivity. To this end, 500mL of each water sample was acidified with 1 mL of concentrated HNO_3 and evaporated to near dryness on a hot plate in a fume hood. The residue in the beaker was rinsed with 1 M HNO_3 and evaporated again to near dryness.

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The residue was then dissolved in minimum amount of 1 M HNO_3 and transferred into a weighed 25 mm stainless steel planchet. The planchet with its content was heated until all moisture evaporates. It was then stored in a desiccator and allowed to cool and prevented from absorbing moisture. The prepared samples were then counted to determine alpha and beta activity concentrations using the low background Gas-less Automatic Alpha/Beta counting system (Canberra iMaticTM) calibrated with alpha (^{241}Am) and beta (^{90}Sr) standards. The system uses a solid state passivated implanted planar silicon (PIPS) detector for alpha and beta detection. The alpha and beta efficiencies were determined to be 36.39 ± 2.1% and 36.61 ± 2.2 %, respectively. The background readings of the detector for alpha and beta activity concentrations were 0.04 ± 0.01 and 0.22 ± 0.03 counts per minute (cpm) respectively

4.9 Scanning Electron Microscopy (SEM)

Morphological and elemental composition of solid NORM waste samples were performed using a JEOL 6460LV scanning electron microscope (SEM) with acquisition of digital images in both secondary (SEI) and backscattered (BEI) electron imaging modes (maximum resolution 3.5nm). This device was coupled to an EDX micro-probe and fitted with an ATW2 beryllium window (resolution 137eV at 5.9 keV).The semi-quantitative analysis was performed using the Oxford INCA software.

4.10 Estimation of massic elemental concentrations of primordial radionuclides

Considering the fact that the primordial radionuclides (^{238}U, ^{232}Th, and ^{40}K) exhibit a constant atomic abundance in nature, it is possible to convert the specific activities of ^{238}U, ^{232}Th, and ^{40}K into massic elemental concentrations of U, Th, and K respectively in order to compare the different techniques using the following formula (Tzortzis and Tsertos, 2004; Kpeglo et al., 2012)

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$$C_E = \frac{T_{1/2} \cdot \mathrm{R} \cdot \mathrm{M_a}}{P_a \cdot \mathrm{N_A} \cdot ln2} \cdot A_{sp} \qquad (4.13)$$

where, C_E is the elemental concentration in sample, M_a is the atomic mass (kgmol^{-1}), $T_{1/2}$ is the half-life (seconds), P_a is the fractional atomic abundance in nature (%), N_A is Avogadro's constant (6.023 x 10^{23} gmol^{-1}), A_{sp} is the measured activity concentration (Bqkg^{-1}) of the radionuclide considered (^{238}U, ^{232}Th, or ^{40}K), and *R* is a constant with a value of 1,000,000 for U and Th (concentration in μgg^{-1}) or 100 for K (concentration in % of mass fraction).

4.11 Estimation of the age of scale samples

For relatively newly formed scale (less than 10 years old), as in the present situation, the measured activity ratio of ^{224}Ra/^{228}Ra was used to estimate the average scale age of the oilfield equipment. This was conducted by applying the ingrowths decay ratio of ^{224}Ra and ^{228}Ra where the present activity of ^{224}Ra in scales is only from the decay of ^{228}Ra, with a half-life of 5.75 years, via ^{228}Th (half-life 1.9 years); thorium is not present in freshly produced scales. Taking into consideration the above assumptions, the average age of scales in the oilfield equipment was estimated by applying the following equation (Al-Masri and Aba, 2005):

$$T \text{ (years)} = -\ln[1-(^{224}\mathrm{Ra}/^{228}\mathrm{Ra})/1.49]4.098 \qquad (4.14)$$

were:

T is age of scale

^{224}Ra is activity concentration of ^{224}Ra in Bq/kg

^{228}Ra is activity concentration of ^{228}Ra in Bq/kg

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4.12 Calculation of external absorbed dose rate and annual effective dose due to radioactivity in solid matrix samples

The external gamma dose rate from the samples was calculated from the activity concentrations of the relevant radionuclides using equation (4.15) **(**UNSCEAR, 2000 and 2008):

$$D\left(nGyh^{-1}\right) = 0.0417A_K + 0.462A_U + 0.604A_{Th} \quad (4.15)$$

where;

A_K, A_U and A_{Th} are the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th respectively. Table 4.2 shows the dose conversion factors of ^{40}K, ^{238}U and ^{232}Th.

Table 4.2: Activity to dose rate conversion factors (UNSCEAR, 2000 and 2008)

Radionuclide	Dose Coefficient (nGy/h per Bq/kg)
^{40}K	0.0417
^{238}U	0.462
^{232}Th	0.604

The annual effective dose was calculated from the absorbed dose rate by applying the dose conversion factor of 0.7 Sv/Gy and an outdoor occupancy factor of 0.2 (UNSCEAR, 2000) for public exposure whiles an occupancy factor of 2000 hrs/yr was used for occupational exposure. In the case of the water samples, the committed effective doses (E_{ing}) were estimated from the activity concentrations of each individual radionuclide and applying the yearly water consumption rate for adults of 730 L/year (2

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L/day multiplied by 365 days) and the dose conversion factors of ^{238}U, ^{232}Th and ^{40}K taken from the BSS and UNSCEAR report, (IAEA, 1996 and UNSCEAR, 2000) using equation (4.16).

$$E_{Ing}(w) = A_{sp}(w).I_w.\sum_{j=1}^{3} DCF_{Ing}(U,Th,K) \qquad (4.16)$$

where, A*sp* (w) is the activity concentration of the radionuclides in a sample in Bq/L, I_w is the intake of water in litres per year, and DCF_{Ing} is the ingestion dose coefficient in Sv/Bq taken from the BSS (IAEA, 1996).

4.13 Calculation of effective doses and total annual effective dose

For the purpose of verifying compliance with dose limits, the total annual effective dose was determined. The total annual effective dose (E_T) to members of the public was calculated using ICRP dose calculation method (ICRP, 1991). The analytical expression for the total annual effective dose is determined by summing all the individual equivalent doses for the exposure pathways considered in this study. These include:

- External gamma irradiation from the gamma emitting radionuclides in the soil /sediments samples (E_γ(U, Th, K);
- Committed dose from ingestion of water containing ^{238}U, ^{232}Th and ^{40}K radionuclides E_{ing} (W);
- Inhalation of radon gas in air, E_{inh} (Rn) and

Thus;

$$E_T = E_\gamma(U,Th,K) + E_{ing}(W) + E_{inh}(Rn) \qquad (4.17)$$

where;

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E_T is the total annual effective dose in Sievert

E_γ (U, Th, K) is the external gamma ray annual effective dose from the soil/sediments,

E_{ing} (W) is the committed effective dose from consumption of water,

E_{inh} (Rn) is the annual effective dose from the inhalation of radon gas in air

For occupational exposure for workers working with oil waste was determined using equation (4.18):

$$E_T = E_\gamma(U, Th, K) + E_{inh}(Rn) \qquad (4.18)$$

where; E_T is the total effective dose in Sievert (Sv/y), E_γ (U, Th, K) is the external gamma effective dose from the sludge, scale, ash, mud and mud block samples, E_{inh} (Rn) is the effective dose from the inhalation of air borne ^{222}Rn.

In addition, the cancer and hereditary risks due to low doses without threshold dose known as stochastic effect were estimated using the ICRP cancer risk assessment methodology (ICRP, 2007). The nominal lifetime risk coefficients of fatal cancer recommended in the 2007 recommendations of the ICRP are 5.5 x 10^{-2} Sv^{-1} for members of the public and 4.1 x 10^{-2} Sv^{-1} for occupationally exposed workers. For heritable effects, the detriment- adjusted nominal risk coefficient is estimated at 0.2 x 10^{-2} Sv^{-1} for the whole population and 0.1 x 10^{-2} Sv^{-1} for adult workers as stated in ICRP recommendations for stochastic effects after exposure at low dose rates.

The risk to public in vicinities that may be impacted by the oil drilling activities and workers of NORM waste facility was then estimated using the 2007 recommended risk

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coefficients in ICRP report (ICRP, 2007) and an assumed 70 years lifetime of continuous exposure of the population to low level radiation according to the ICRP methodology:

Fatality Cancer Risk = Total Annual Effective Dose (Sv) x Cancer Risk Factor

Hereditary Effects = Total Annual Effective Dose (Sv) x Hereditary Effect Factor

4.14 Determination of annual effective dose from external gamma dose rate measurements

At each sampling location, outdoor external gamma dose rates were measured using a digital environmental radiation survey meter (RADOS, RDS-200, Finland). The dose rate meter was calibrated at the Secondary Standard Dosimetry Laboratory (SSDL) with a calibration factor provided. At each location, five measurements were made at 1 meter above the ground and the average value taken in μGy/h. The annual effective dose ($E_{\gamma, ext}$) was then estimated from the measured average outdoor external gamma dose rate using equation (4.19) below:

$$E_{\gamma,ext}(mSv) = D_{\gamma,ext}.T_{\exp}.DCF_{ext}.10^{-3} \quad (4.19)$$

Where;

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

T_{exp} is the exposure duration per year, 8760 hours (365 days) and applying an outdoor occupancy factor of 0.2 (UNSCEAR, 2000)

DCF_{ext} is the effective dose to absorbed dose conversion factor of 0.7 Sv/Gy for environmental exposure to gamma rays (UNSCEAR, 2000)

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4.15 Human Health Risk Assessment Model

In this section the concepts discussed in section 2.9 of Chapter 2 are used to develop a methodology to be applied in a hypothetical case study for the Saltpond oilfield. The primary objective was to assess the potential risk to human health from radium in discharge of produced water to sea via consumption of fish. This is also motivated by the fact that, the Saltpond field is in a water depth of 24.9 m and fishing around the platform is the only viable occupation to the critical group along the coastal communities of the shallow offshore oilfield. The developed framework for human health risk assessment methodology for fish consumption in this study is presented a flow chart shown in Figure 4.7. It consists of three main phases: (1) prediction of exposure concentration for the fish; (2) assessment of radium concentration in the edible part of the fish, and (3) characterization of the cancer risk in humans. These phases are discussed in the following sections.

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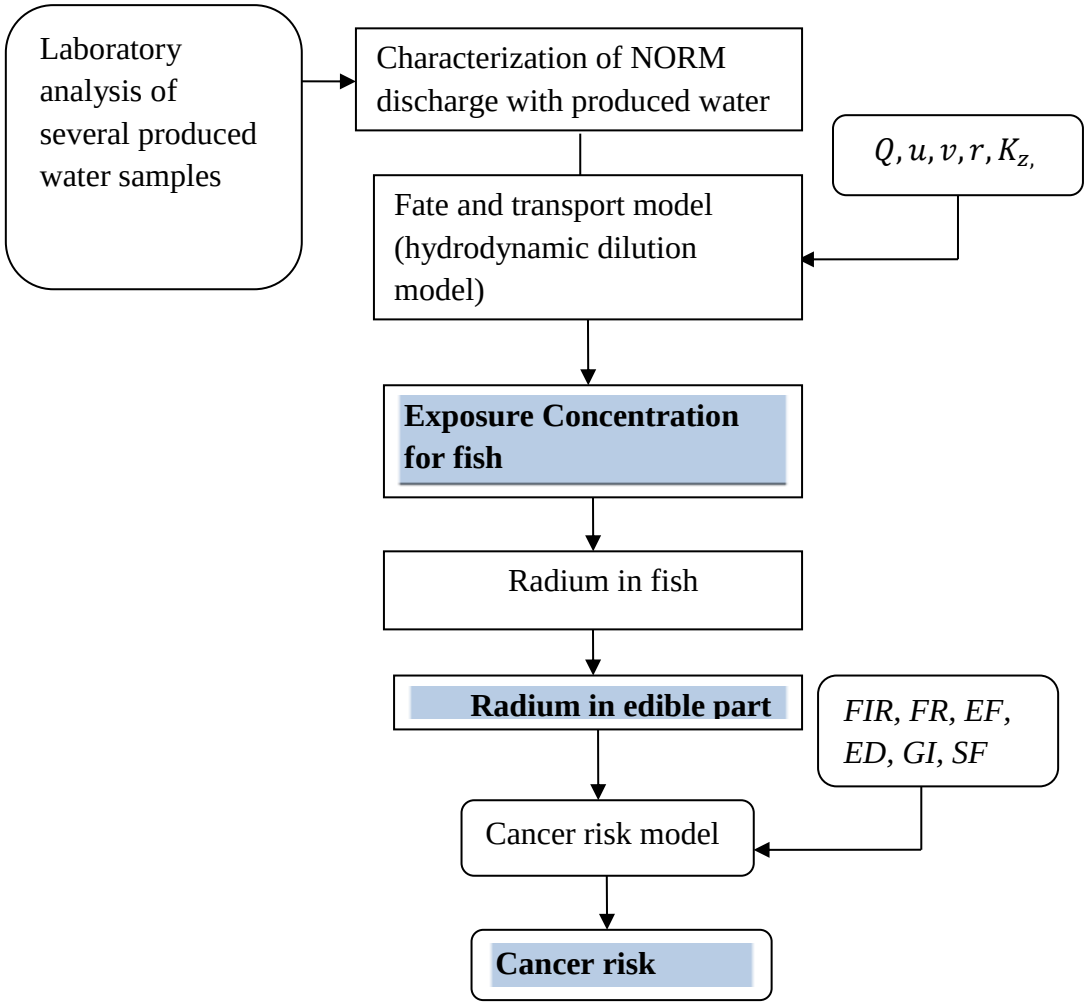

Figure 4.7: Human health risk assessment framework

4.15.1 Prediction of exposure concentration for the fish

This study considers a hypothetical discharge scenario for produced water from the Saltpond offshore oilfield to apply the proposed methodology. The hypothetical platform with a Gravity based Structure was considered with assumed ambient water depth of 25m and designed for a capacity of treating 0.104 m^3/s of produced water. The ambient sea water and discharge characteristics of platform were defined on the basis of limited available data (DFO 2003; Petro-Canada 1996; Mukhtasor 2001and Chowdhury et al., 2004).

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The estimated exposure pathway from produced water discharge to human uptake is shown in Figure 4.8. The produced water after treatment is discharged into the sea, where dilution occurs. In this dilution zone marine fishes grow and accumulate contaminants in their tissues. These commercial fishes subsequently make their way to the local fish market, supermarket and restaurants after being harvested.

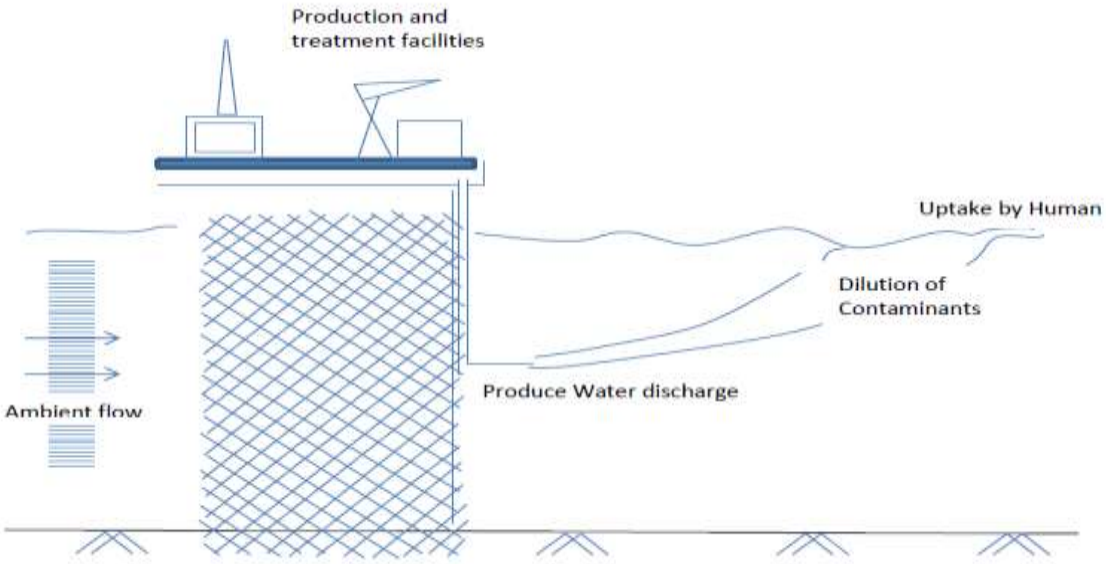

Figure 4.8: Exposure Pathways for Human Uptake

The hydrodynamic dilution model (equation 2.2) as described in Chapter 2 has been applied in this study to predict exposure concentration (C_f) for fish. The variables for the dilution are the horizontal diffusion velocity *(v),* the effluent discharge rate *(Q),* the horizontal length of consideration *(r),* and the ambient current velocity *(u).* The uncertainty of the ambient sea water was incorporated by using a log-normal flow velocity in m/s of (-3.29, 0.96), where the parameters –3.29 and 0.96 represent the natural logarithm of the median and the standard deviation of current speed respectively. Due to the limited data on the offshore produced water platform, for conservative analysis the effluent discharge rate of 0.104 m^3/s was considered for the risk analysis.

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The concentration of pollutants (^{226}Ra, ^{228}Ra) at the discharge point, C_o were taken from those obtained from analysis of produced water from Saltpond oilfield carried out earlier on several samples as part of this work. All input parameters and their characterisation for the model use for risk assessment are presented in Appendix A

Additionally, the following assumptions were made for the human health risk analysis in this study:

- Population demography considered consisted of adults only
- Distribution of contaminants in the dilution zone is steady and homogeneous
- The fishes stay and grow within the dilution zone during the simulation period
- As radium is soluble in water, 100% bioavailability has been assumed for a conservative calculation
- During cooking of fish or fish products, no loss of contaminants occurred
- The growth of fishes and dilution of contaminants remained the same all the year
- Acceptable risk was estimated as one in a million according to the USEPA

4.15.2 Prediction of Radium in the Edible Part of Fish

The growth of a fish continues throughout its whole life irrespective of its location, and therefore the growth and other physical changes (e.g. change in lipid and bone content) during the exposure period have an effect on the accumulation of contaminants. Using the whole fish bio-concentration factor, the total radium in fish is predicted as (Chowdhury et al., 2004):

$$W_{rad} = C_f \times BCF \times W_t \quad (4.20)$$

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where,

W_{rad} = total radium accumulated in fish *(*Bq*)*;

W_t = weight of fish *(*kg*)*;

C_f = exposure concentration for fish (Bq/kg) calculated using equation (2.2); and

BCF = whole fish bio-concentration factor for radium.

The equation for concentration distribution was developed using mass balance assuming no loss of radium in fish as: (Chowdhury et al., 2004):

$$x \times W_t \times C_{raded} + (1 - x) \times W_t \times C_{radned} = W_{rad}$$

$$x \times W_t \times C_{raded} + (1 - x) \times W_t \times y \times C_{raded} = W_{rad}$$

$$= C_{raded} = \frac{W_{rad}}{[x+(1-x)y]\times W_t} \quad (4.21)$$

where

C_{raded} = radium concentration in edible part of fish (Bq/kg)

C_{radned} = radium concentration in non-edible part of fish (Bq/kg)

W_{rad} = total radium in fish as calculated in equation (4.20) (Bq)

W_t = weight of fish (kg)

x = edible fraction of a fish

$y = C_{radned}/C_{raded}$

Using the value of W_{rad}, equations (4.20) and (4.21) can be re-written as:

$$C_{raded} = \frac{C_f \times BCF}{[x+(1-x)y]} \quad (4.22)$$

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The BCF, *x* and *y* have been found to follow ln(2.99, 0.92), ln(4.36, 0.063) and ln(2.29, 1.2) distributions, respectively; where the first and second parameters represent natural log of medians and standard deviations, respectively (Chowdhury et al., 2004).

4.15.3 Characterization of Cancer Risk

The total human intake of radium was calculated as (Chowdhury et al., 2004):

$$I_{\mathrm{T}} = C_{raded} \times \mathrm{FIR} \times \mathrm{EF} \times \mathrm{ED} \times \mathrm{FR} \times \mathrm{GI} \times 10^{-3} \qquad (4.23)$$

where

I_T = total intake radium intake (Bq)

C_{raded} = radium concentration in edible part of fish (Bq/kg)

FIR = daily fish ingestion rate (g/day)

EF = exposure frequency (days/yr)

ED = exposure duration (yrs)

FR = fraction of contaminated fish ingested

GI = gastrointestinal absorption factor

10^{-3} = conversion factor for *g*/kg

4.15.3.1 Fish ingestion rate (FIR)

USEPA (1999a), used 177 g/day as the 99th percentile fish ingestion for human health risk assessment. Meinhold *et al*. (1996) derived a lognormal (3.455, 0.622) distribution for fish caught near an open bay platform in Louisiana.

4.15.3.2 Fraction of contaminated fish ingested (FR)

Throughout the exposure period, it is unrealistic to assume that all the fish ingested are

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from the contaminated site. A study by USEPA (1997) for the age group 1-20 year old shows that 123 g/day marine fish was ingested from a total of 219g/day fish ingestion. In 1992, a survey of restaurants shows an average of 889 dishes out of 1500 total each week was served with seafood (Schultz *et al*. 1996). The available data (USEPA 1996b, 1997; Schultz *et al*. 1996) suggest that marine fish ingestion is almost 50% of the total fish ingestion. The total fish ingested from marine sources may not be exposed to a produced water plume and thus the use of 50% of the total ingested fish, as the contaminated fish will still provide a conservative prediction of cancer risk.

4.15.3.3 Exposure frequency (EF)

USEPA (1989, 1991, 1998a) recommended the exposure period for all exposure pathways as 350 days/year. In this recommendation, a minimum of 2 wk/yr absence from the exposure has been assumed.

4.15.3.4 Exposure duration (ED)

The US EPA Office of Solid Waste (OSW) recommends the use of a default reasonable maximum exposure (*RME*) for risk assessment. The US EPA OSW recommends the exposure duration for subsistence fisher and adult resident as 30 years (USEPA 1998a).

4.15.3.5 Gastrointestinal absorption factor (GI)

The fraction of chemical that is absorbed by blood from the intestinal tracts is known as the gastrointestinal absorption factor *(GI)*. The GI factor for radium of 0.3 for adolescent from USEPA (1999b) have been used in this study.

The cancer risk was calculated using (Chowdhury et al., 2004):

$$\mathrm{CR_{RAD}} = I_{\mathrm{T}} \times \mathrm{SF} \qquad (4.24)$$

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where

CR_{RAD} = cancer risk from radionuclides

I_T = total radium intake (Bq)

SF = slope factor $(Bq)^{-1}$(1.91×10^{-11} for ^{226}Ra and 5.29×10^{-11} for ^{228}Ra; USEPA, 1999b).

The total cancer risk was calculated using probabilistic summation concept assuming independence in occurrence of individual risks as:

$$\text{Total cancer risk} = R_A + R_B - R_A \times R_B \quad (4.25)$$

where,

R_A = cancer risk from ^{226}Ra, R_B = cancer risk from ^{228}Ra

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CHAPTER FIVE

RESULTS AND DISCUSSION

Overview

In this Chapter, the results, analysis and discussions of a total of Ninety-two (92) samples collected from the Jubilee oilfield, Zeal Environmental Technologies Limited, Saltpond oilfield and four coastal communities within Saltpond and its environs are presented. This included mainly 42 environmental samples, and 50 NORM waste samples details of which have been presented in Chapter 4.

5.1 Quality control and validation of Gamma and Alpha Spectrometric techniques

Prior to the analysis, analytical quality control procedures were carried out for the alpha and gamma spectrometry systems in order to authenticate the quality and reliability of measurements. Both gamma and alpha detectors were calibrated for energy and efficiency and results are presented in Figures 5.1 to 5.3 and Tables 5.1 and 5.2

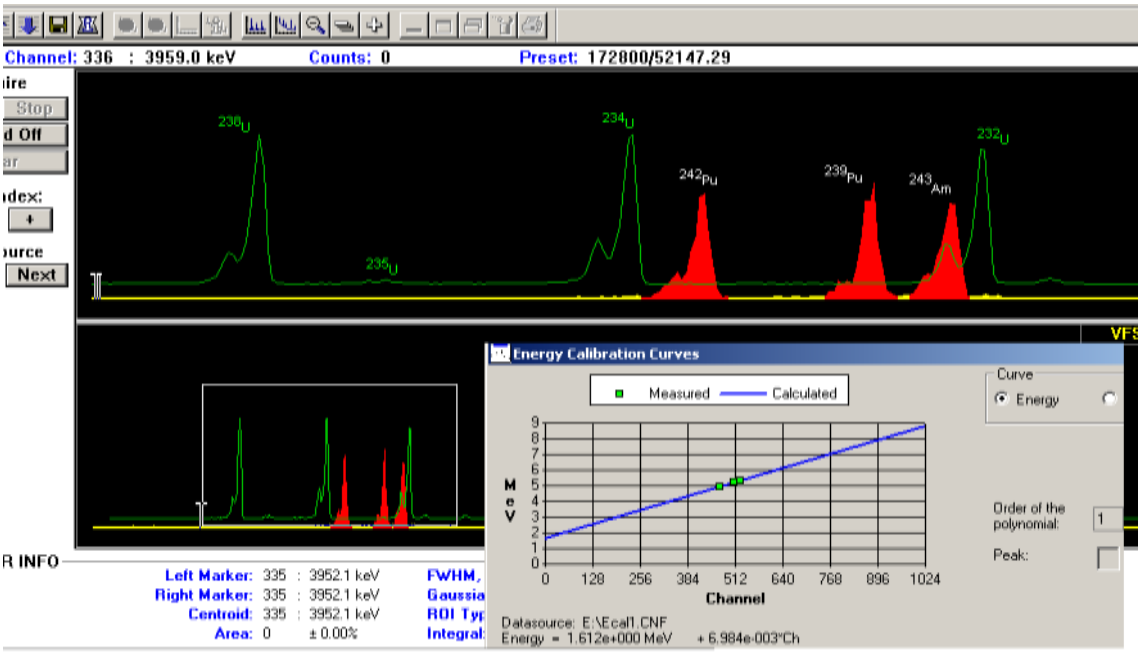

Figure 5.1: Energy calibration curve for alpha spectrometry system

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Table 5.1: 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 (%)	18.3±1.1	23.0±1.3	20.8±1.2	21.9±1.2	21.2±1.2	23.4±1.3	19.4±1.2	22.2±1.3

The efficiency values for all alpha chambers as shown in Table 5.1 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. However, these efficiency values were only used for estimation of the radiochemical yields but not the activity concentrations which were calculated based on isotopic dilution method.

Table 5.2: Geometries used for gamma measurements in different sample matrices

Matrix	Sample	Geometry
Solid	Soil, sediments, Scale , sludge, Ash, mud and mud block	Petri dish (55mm diameter by 12mm height)
Liquid	Produced water, oily waste water, wash water and crude oil	Marinelli beaker (1L)

The IAEA reference materials IAEA-RGU-1(U-ore) and IAEA-RGTh-1 (Th-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 into petri dish containers of the same type as that of solid matrix samples and 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 (^{210}Pb, ^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{60}Co and ^{88}Y,) was prepared into a 1L marinelli beaker with mean density of 1.0 g/cm^3 and used for efficiency calibration of the gamma system. Self-absorption corrections were carried out for low energy photo peaks ^{210}Pb and ^{234}Th, summing-up coincidence corrections were made for certified gamma cocktail in 1L marinelli geometry.

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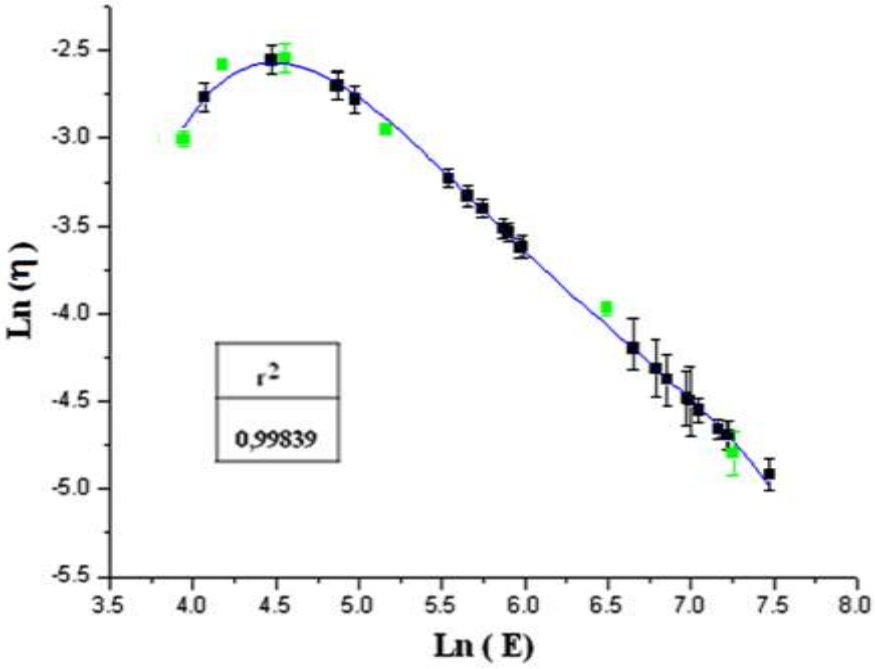

Figure 5.2: Efficiency calibration curve for liquid samples in 1L marinelli beaker geometry of HPGe detector using 5th order polynomial curve fitting

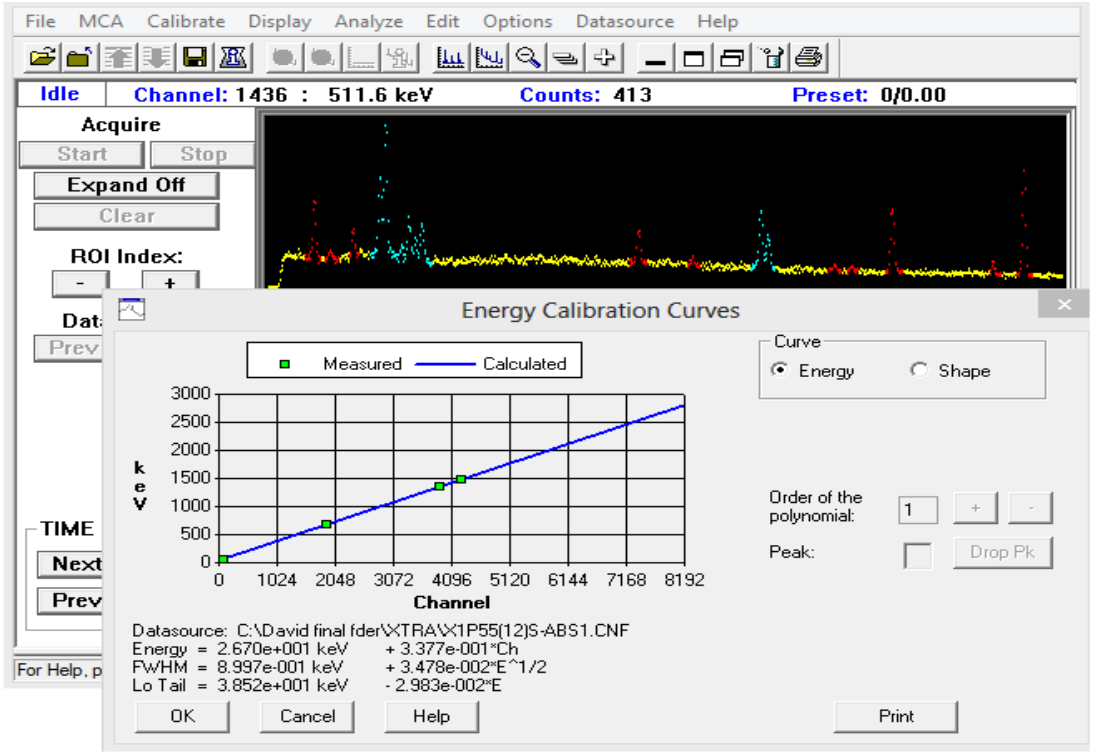

Figure 5.3: Energy calibration curve for gamma spectrometry system

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The accuracy and precision of analytical procedures used in this study for both gamma and alpha spectrometric techniques were also validated with the analysis of IAEA SRMs (IAEA381, IAEA375 and IAEA 414) under the same experimental conditions as the samples. The sensitivity of the method used in this work was in good agreement with the reference values for IAEA SRMs as shown in Tables 5.3 and 5.4.

Table 5.3: Analysis of reference material via gamma spectrometry

Sample	Matrix	Density ($g.cm^{-3}$)	Radionuclide	Reference Value ($Bq.kg^{-1}$)	Measured value ($Bq.kg^{-1}$)
IAEA381	liquid	1.02 ± 0.02	^{137}Cs	0.49 ± 0.01	0.52 ± 0.06
			^{40}K	11.4 ± 0.9	14.6 ± 2.0
IAEA375	Solid	1.69 ± 0.17	^{134}Cs	463 ± 9	452 ± 30
			^{137}Cs	5280 ± 106	4998 ± 107
			^{40}K	424 ± 8	408 ± 16
			$^{226}Ra(^{214}Pb)$	20 ± 2	19.5 ± 1.2
IAEA414	organic	0.55 ± 0.03	^{137}Cs	5.14 ± 0.13	4.95 ± 0.29
			^{40}K	480 ± 18	440 ± 29
			$^{226}Ra(^{214}Pb)$	1.40 ± 0.36	(MDA) 1.3

Table 5.4: Analysis of reference material via alpha spectrometry

Sample	Matrix	Radionuclide	Reference value ($Bq.kg^{-1}$)	Measured value ($Bq.kg^{-1}$)
IAEA 381	liquid	^{238}U	0.042 ± 0.004	0.038 ± 0.003
		^{234}U	0.051 ± 0.006	0.049 ± 0.003
IAEA414	organic	^{238}U	1.112 ± 0.050	1.17 ± 0.08
		^{234}U	1.22 ± 0.07	1.11 ± 0.07
		^{232}Th	0.029 ± 0.003	0.036 ± 0.015
CNS/CIEMAT-2011	liquid	^{238}U	0.249 ± 0.025	0.244 ± 0.044
		^{234}U	0.255 ± 0.025	0.246 ± 0.044
		^{230}Th	0.119 ± 0.011	0.118 ± 0.021
		^{210}Po	1.16 ± 0.05	1.18 ± 0.21
IAEA 375	Solid	^{238}U	24 ± 5	18 ± 3
		^{234}U	25 ± 7	19 ± 3
		^{232}Th	21 ± 1	22 ± 2

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The radiochemical recovery or yield in alpha spectrometric determination is also an important parameter in validating the reliability or authenticity of results obtained using alpha spectrometry. Generally, it is required that for alpha results to be acceptable and reliable the radiochemical yield should not be less than 30% (García Tenorio, 1983). Figure 5.4 presents average yield of radionuclides analyzed for samples via alpha spectrometry. The lowest average yield was 41.2% recorded for Po in produced water and the highest was 84% for Th in crude oil.

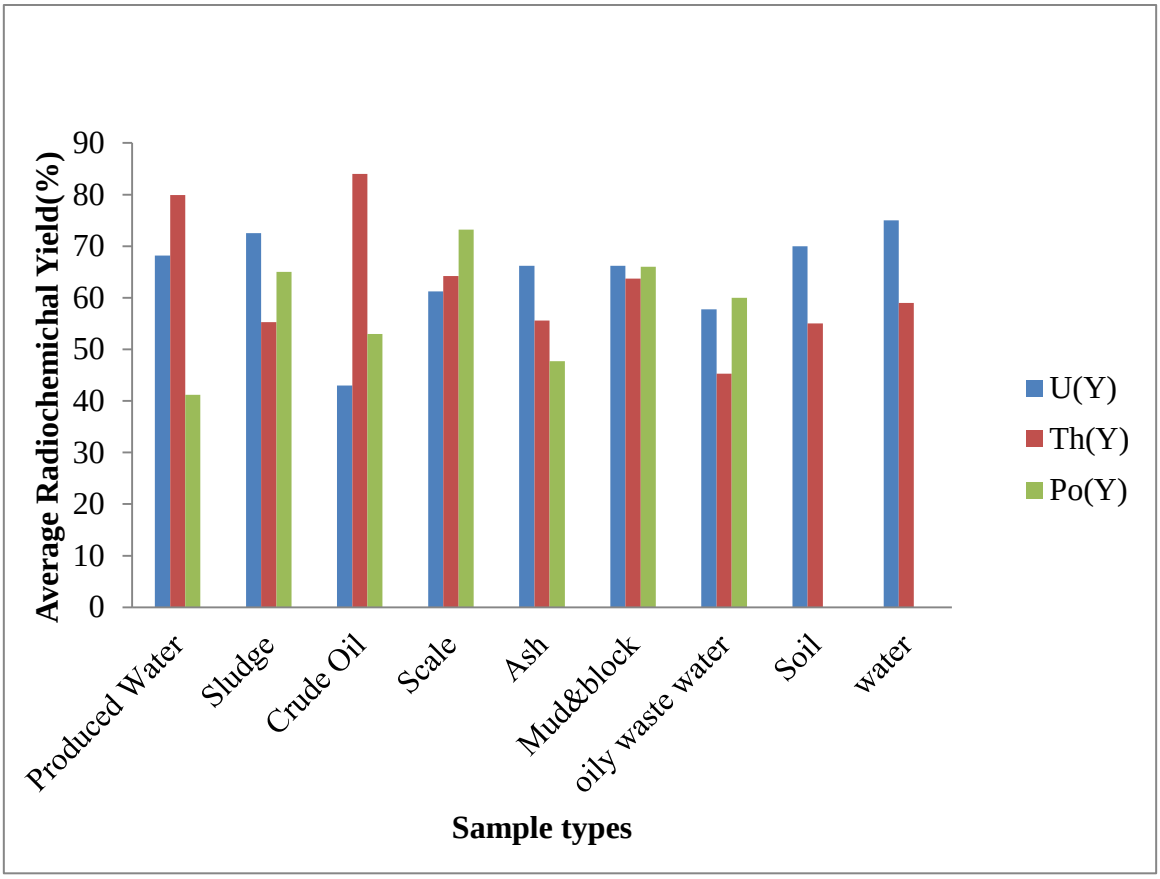

Figure 5.4: Average Radiochemical yield for samples determined via Alpha spectrometry

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5.2 Environmental samples

The environmental samples comprising soil, beach sediments and water (lagoon, river and borehole/well) from four communities (Ankaful, Nankesedo, Kormantse and Abandze all of which lie about 1.5km apart) located along the coast which could be affected by the activities of shallow water offshore oilfield at Saltpond have been analysed to evaluate the present radiological state of the critical population and coastal environment, to assess the impact of crude oil drilling activities from the saltpond field and to establish a baseline data for future studies.

5.2.1 Soil

The activity concentrations of ^{234}U, ^{238}U, ^{230}Th and ^{232}Th, in the soil samples determined by alpha-particle spectrometry, as well as, the corresponding $^{234}U/^{238}U$ activity ratios are presented in Table 5.5.

The average values of ^{234}U, ^{238}U, ^{230}Th and ^{232}Th were 7.5 ± 4.9 (in the range 2–19 $Bq.kg^{-1}$), 7.6 ± 4.9 (in the range 2.2 – 19.2 $Bq.kg^{-1}$), 6.3 ± 3.6 $Bq.kg^{-1}$ (in the range 2.5 – 15.8 $Bq.kg^{-1}$) and 6.4 ± 3.5 $Bq.kg^{-1}$ (in the range 2.9 –15.6 $Bq.kg^{-1}$), respectively. This are in good agreement with the results that have been found over the world for sandy soils as analyzed by UNSCEAR (2000). On the other hand, the $^{234}U/^{238}U$ activity ratios varied from 0.93 – 1.04 with an overall average of 0.98 ± 0.03 confirming the fact that, in the undisturbed earth's crust, ^{238}U is practically in radioactive equilibrium with its daughter ^{234}U. This notwithstanding, a clear dis-equilibrium was however observed for ^{238}U and its daughter ^{230}Th as can be seen from the results shown in Table 5.5.

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Table 5.5: Activity Concentrations of ^{238}U, ^{234}U, ^{230}Th and ^{232}Th, and $^{234}U/^{238}U$ activity ratio of the soil samples determined by alpha-particle spectrometry

Sample ID	Activity Concentration ($Bq.kg^{-1}$)				$^{234}U/^{238}U$
	^{234}U	^{238}U	^{230}Th	^{232}Th	
S1	5.4 ± 0.2	5.2 ± 0.2	5.9 ± 0.6	5.9 ± 0.6	1.04 ± 0.06
S2	2.5 ± 0.2	2.5 ± 0.2	4.0 ± 0.5	4.0 ± 0.5	1.00 ± 0.11
S3	9.0 ± 0.4	9.0 ± 0.4	5.0 ± 0.7	5.2 ± 0.8	1.00 ± 0.06
S4	4.0 ± 0.3	4.3 ± 0.3	2.9 ± 0.4	2.9 ± 0.4	0.93 ± 0.10
S5	11.3 ± 0.8	12.2 ± 0.8	15.8 ± 0.2	15.6 ± 0.2	0.93 ± 0.09
S6	9.2 ± 0.3	9.4 ± 0.3	6.2 ± 0.4	6.2 ± 0.4	0.98 ± 0.04
S7	5.7 ± 0.5	6.0 ± 0.5	13.4 ± 1.2	13.8 ± 1.2	0.95 ± 0.11
S8	13.2 ± 0.6	13.1 ± 0.6	6.3 ± 0.7	6.6 ± 0.7	1.01 ± 0.07
S9	2.3 ± 0.2	2.4 ± 0.2	2.9 ± 0.5	2.9 ± 0.5	0.96 ± 0.12
S10	2.1 ± 0. 2	2.2 ± 0.2	2.5 ± 0.7	3.3 ± 0.8	0.95 ± 0.09
S11	3.9 ± 0.3	3.8 ± 0.3	4.6 ± 0.3	4.4 ± 0.3	1.02 ± 0.11
S12	3.6 ± 0.2	3.7 ± 0.2	5.6 ± 0.8	6.0 ± 0.8	0.97 ± 0.08
S13	6.5 ± 0.4	6.5 ± 0.4	5.6 ± 0.6	5.5 ± 0.6	1.00 ± 0.09
S14	13.7 ± 0.5	13.7 ± 0.5	6.7 ± 1.3	7.5 ± 1.4	1.00 ± 0.05
S15	19.0 ± 1.3	19.2 ± 1.4	6.0 ± 0.8	6.1 ± 0.8	0.99 ± 0.10
S16	7.9 ± 0.5	8.2 ± 0.5	7.8 ± 0.9	7.2 ± 0.8	0.96 ± 0.08
Mean	7.5	7.6	6.3	6.4	0.98
SD	4.9	4.9	3.6	3.5	0.03
Range	2.1 - 19.0	2.2 - 19.2	2.5 - 15.8	2.9 - 15.6	0.93 - 1.04

Figure 5.5 shows in addition the obtained $^{235}U/^{238}U$ activity ratios for the soil samples. These activity ratios ranged from 0.02 – 0.08, with relatively high uncertainties due to the low counting rate of the ^{235}U in the obtained alpha spectra, with the average of 0.045 ± 0.020, which is consistent with the expected value of 0.046 for natural uranium (UNSCEAR 1993).

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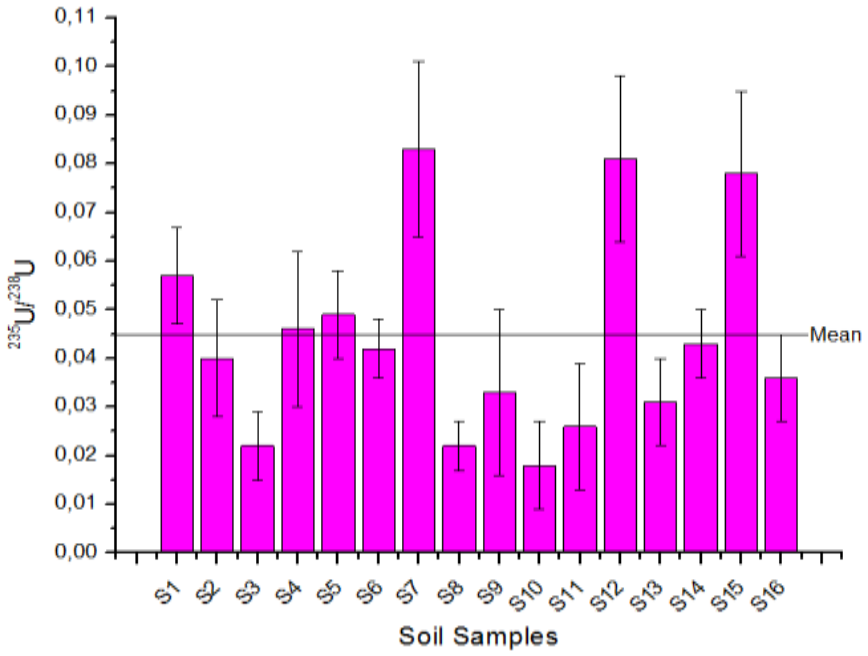

Figure 5.5: $^{235}U/^{238}U$ activity ratios determined in the soil samples.

The activity concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K, ^{210}Pb, ^{238}U and ^{137}Cs, in the same soil samples, and determined by gamma-ray spectrometry are shown in Table 5.6. The average value of the activity concentration of ^{226}Ra is 22.6 ± 13.8 $Bq.kg^{-1}$ (in a range of 5.5–60.2 $Bq.kg^{-1}$); while for ^{228}Ra, the average activity concentration is 17.9 ± 11.5 $Bqkg^{-1}$ (in a range of 6.0–53.6 $Bq.kg^{-1}$); and for ^{228}Th, the average is 19.7 ± 11.5 $Bq.kg^{-1}$ (in a range of 5.7–51.9 $Bq.kg^{-1}$). In the case of ^{40}K the average activity concentration is 156 ± 87 $Bq.kg^{-1}$ (in a range of 70.4–360.6 $Bq.kg^{-1}$). For ^{210}Pb, the average is 67 ± 29 $Bqkg^{-1}$(in a range of 30.8–131.0 $Bq.kg^{-1}$); and for ^{238}U determined from ^{234}Th assuming secular equilibrium between them, the average is 9.4 ± 7.4 $Bq.kg^{-1}$ (in a range of 0.5–27.6 $Bq.kg^{-1}$). The only artificial gamma emitter detected was ^{137}Cs with an average activity concentration in the analyzed soils of 1.2 ± 0.4 $Bq.kg^{-1}$ (in a range of 0.3–1.9 $Bq.kg^{-1}$).

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Table 5.6: Activity concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K, ^{210}Pb, ^{234}Th and ^{137}Cs in the soils, determined by gamma-ray spectrometry.

Sample ID	Activity Concentration (Bq.kg^{-1})						
	Th-234	Ra-226	Pb-210	Ra-228	Th-228	Cs-137	K-40
S1	4.0 ± 1.6	14.3 ± 0.9	63.6 ± 4.2	15.3 ± 2.2	20.6 ± 2.3	1.2 ± 0.2	260.5 ± 30.1
S2	0.5 ± 1.4	9.1 ± 0.9	50.0 ± 3.5	9.0 ± 0.6	9.9 ± 1.0	0.3 ± 0.1	86.4 ± 14.7
S3	9.5 ± 3.2	24.0 ± 0.1	131.0 ± 7.8	32.3 ± 2.9	37.0 ± 3.5	1.9 ± 0.3	149.0 ± 23.2
S4	3.1 ± 1.9	13.6 ± 0.8	56.7 ± 4.5	16.6 ± 1.7	17.7 ± 0.6	1.6 ± 0.3	139.3 ± 22.1
S5	15.4 ± 2.8	30.6 ± 0.1	60.1 ± 4.4	25.1 ± 2.7	29.0 ± 0.1	1.8 ± 0.3	132.5 ± 22.7
S6	15.9 ± 3.1	22.9 ± 1.6	82.1 ± 5.8	15.7 ± 2.8	15.9 ± 1.3	1.5 ± 0.3	87.4 ± 11.3
S7	13.3 ± 2.8	19.3 ± 1.3	90.9 ± 6.0	16.4 ± 1.0	19.6 ± 3.2	1.3 ± 0.2	86.4 ± 10.4
S8	13.3 ± 2.8	34.2 ± 1.4	90.9 ± 6.0	16.3 ± 3.9	17.7 ± 3.3	1.1 ± 0.3	256.4 ± 27.7
S9	0.6 ± 1.1	8.1 ± 1.0	30.8 ± 2.4	7.8 ± 0.8	8.6 ± 3.6	0.5 ± 0.2	70.4 ± 8.6
S10	1.0 ± 1.3	5.5 ± 0.1	47.4 ± 3.5	6.0 ± 1.7	5.7 ± 1.3	1.1 ± 0.2	75.3 ± 9.3
S11	5.2 ± 1.7	14.0 ± 1.0	50.1 ± 3.6	14.6 ± 1.3	16.1 ± 0.8	1.7 ± 0.2	129.1 ± 14.6
S12	3.8 ± 1.6	12.3 ± 0.4	38.2 ± 3.1	8.0 ± 1.1	9.8 ± 0.9	0.9 ± 0.2	114.9 ± 17.5
S13	10.2 ± 2.0	28.0 ± 0.8	64.6 ± 4.0	18.8 ± 3.1	19.2 ± 1.9	0.8 ± 0.2	211.9 ± 24.7
S14	12.8 ± 2.1	32.5 ± 0.3	63.8 ± 4.0	14.2 ± 1.6	17.2 ± 0.6	1.2 ± 0.4	263.6 ± 30.1
S15	27.6 ± 4.1	60.2 ± 2.8	119.0 ± 7.4	17.0 ± 0.8	19.7 ± 0.6	1.5 ± 0.2	360.6 ± 41.7
S16	13.9 ± 2.7	32.2 ± 2.7	32.7 ± 3.2	53.6 ± 2.3	51.9 ± 2.4	1.1 ± 0.8	77.9 ± 10.2
Mean	9.4	22.6	67.0	17.9	19.7	1.2	156.4
SD	7.4	13.8	29.0	11.5	11.5	0.4	87.6
Range	0.5 – 27.6	5.5 – 60.2	30.8 – 131.0	6.0 – 53.6	5.7 – 51.9	0.3 – 1.9	70.4 – 360.6

The average activity concentrations determined in the soils are lower than the published worldwide average activity concentration of 33 Bqkg^{-1}for ^{238}U, 32 Bq.kg^{-1} for ^{226}Ra, 45 Bq.kg^{-1}for ^{232}Th and 412 Bq.kg^{-1} for ^{40}K (UNSCEAR, 2008). However, the values obtained in this study are comparable with published data from other works in Ghana (Faanu et al., 2013; Faanu et al., 2011; Darko et al., 2010; and Darko et al., 2005). All these information indicate that the study area has not been affected until now by the NORM activities starting in that environment.

The superficial soils analyzed were characterized for presenting a notable dis-equilibrium between the activity concentrations of ^{226}Ra and ^{238}U with ^{226}Ra/^{238}U activity ratios, these are clearly higher than one (see Figure 5.6). This cannot be associated with possible analytical problems as can be deduced through the comparison of results obtained by two totally different techniques (alpha- and- gamma-spectrometry). As shown in Figure 5.6, the activity concentrations of ^{238}U have been

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determined independently in all the soils by applying both techniques and the results are generally in agreement. The dis-equilibrium existing between ^{238}U and ^{226}Ra, is a phenomenon reflecting the previous loss of U from the soil in dissolved form, either by plants uptake or accompanying the waters interacting with the soils mainly in the rainy seasons.

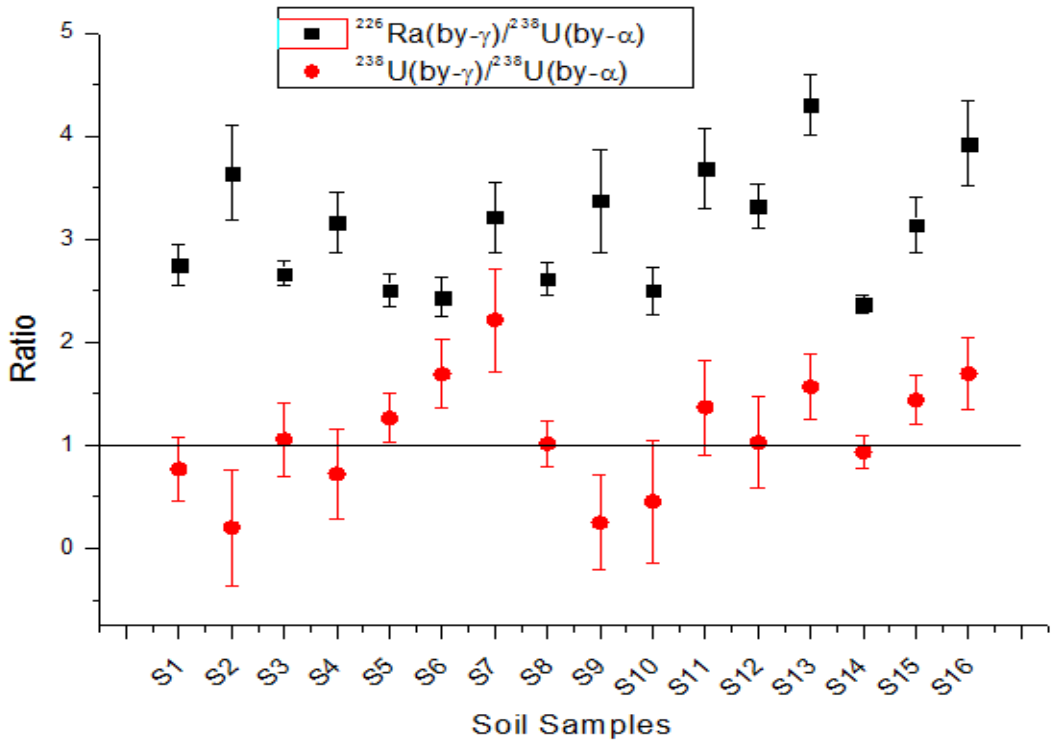

Figure 5.6: Graph showing the ratios of ^{226}Ra (by-γ)/^{238}U (by-α) and ^{238}U (by-γ)/^{238}U (by-α) for the soil samples.

Table 5.7 shows the absorbed dose rate measured experimentally in air at 1 m above the ground and the corresponding calculated annual effective doses for the soil sampling points in the four coastal communities considered. From Table 5.7, it can be seen that measured absorbed dose rates varied in a range of 20–180 nGy.h^{-1}, with an average value of 70 ± 20 nGy.h^{-1}. The corresponding average annual effective dose was calculated as 0.086 ± 0.025 mSv in a range of 0.043– 0.129 mSv.

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Table 5.7: Average absorbed dose rate in air at 1 m above sampling points in the study areas and associated annual effective dose

Sample ID	Absorbed dose rate ($nGyh^{-1}$)		Annual effective dose (mSv)
	Range	Mean ± SD	
S1	30-110	71 ± 33	0.087
S2	20-80	48 ± 25	0.059
S3	30-150	93 ± 49	0.114
S4	30-100	65 ± 29	0.080
S5	40-130	88 ± 42	0.108
S6	30-110	68 ± 33	0.083
S7	30-100	65 ± 29	0.080
S8	30-110	74 ± 35	0.091
S9	20-70	40 ± 22	0.049
S10	20-60	35 ± 19	0.043
S11	30-90	58 ± 25	0.071
S12	20-90	55 ± 27	0.067
S13	30-120	81 ± 38	0.099
S14	30-130	83 ± 41	0.102
S15	40-160	95 ± 50	0.117
S16	30-180	105 ± 63	0.129
Mean ± SD		70 ± 20	0.086 ± 0.025

For comparison purposes, and with basis in the experimental radionuclide determinations carried out in each sampling point, the external absorbed gamma dose rate and the external annual effective dose due to terrestrial gamma- rays have been calculated following the methodology described in chapter 4. The results have been compiled in Table 5.8.

The average external absorbed dose rate (calculated from soil concentrations) in the study area was calculated to be 43.6 ± 21.3 $nGyh^{-1}$, ranging from 13.2 to 88.3 $nGy.h^{-1}$. This average value is also lower than the worldwide average value of 60 $nGyh^{-1}$ (UNSCEAR 2000), indicating the peculiarities of the terrestrial zone under study. Due to its geochemical and morphological composition, it presents low activity concentrations of the radionuclides from the uranium and thorium series, in which gamma emitters are the principal contributors to the external gamma doses. The corresponding average

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annual effective dose estimated from the soil activity concentrations is 0.053 ± 0.026 mSv, ranging from 0.02 to 0.110 mSv at the different soil sampling points analyzed. The mean absorbed dose rate calculated from soil activity concentrations was a factor of about 38% less than the dose rate experimentally measured in outdoor air at1 m above the ground for soil sampling point. The difference could be attributed to contribution from cosmogonic radionuclides in addition to terrestrial radionuclides for the in-situ gamma dose rate measurement.

In addition, airborne ^{222}Rn concentrations were measured in the coastal communities and results ranged from 20.9 – 37.8 Bq.m^{-3} with an average of 26.5 ± 5.5 Bq.m^{-3} as presented in Figure 5.7. The corresponding calculated annual effective dose from inhalation of outdoor ^{222}Rn concentration measured were in the range of 0.20 – 0.36 mSv with an average of 0.25 ± 0.05 mSv. The results in this study compare well with results published in UNSCEAR (1996 ; 2000) reports for normal areas around the world with values in a range of 2-30 Bq/m^3 in air (UNSCEAR, 2000).

Table 5.8: External gamma absorbed dose rate and external annual effective dose calculated for all the soil sampling points analyzed in this work from activity concentrations of radionuclides

Sample ID	$D_{\gamma r}$ (nGy.h^{-1})	$E_{\gamma, ext}$ (mSv.y^{-1})	Sample ID	$D_{\gamma r}$ (nGy.h^{-1})	$E_{\gamma, ext}$ (mSv.y^{-1})
S1	41.00	0.050	S9	16.86	0.020
S2	19.45	0.020	S10	13.21	0.020
S3	63.55	0.080	S11	32.80	0.040
S4	34.24	0.040	S12	22.98	0.030
S5	59.45	0.070	S13	49.44	0.060
S6	40.66	0.050	S14	50.90	0.060
S7	40.41	0.050	S15	77.77	0.090
S8	46.30	0.060	S16	88.27	0.110
Mean	43.6	0.053			
SD	21.3	0.026			
Range	13.2 – 88.3	0.020 – 0.110			

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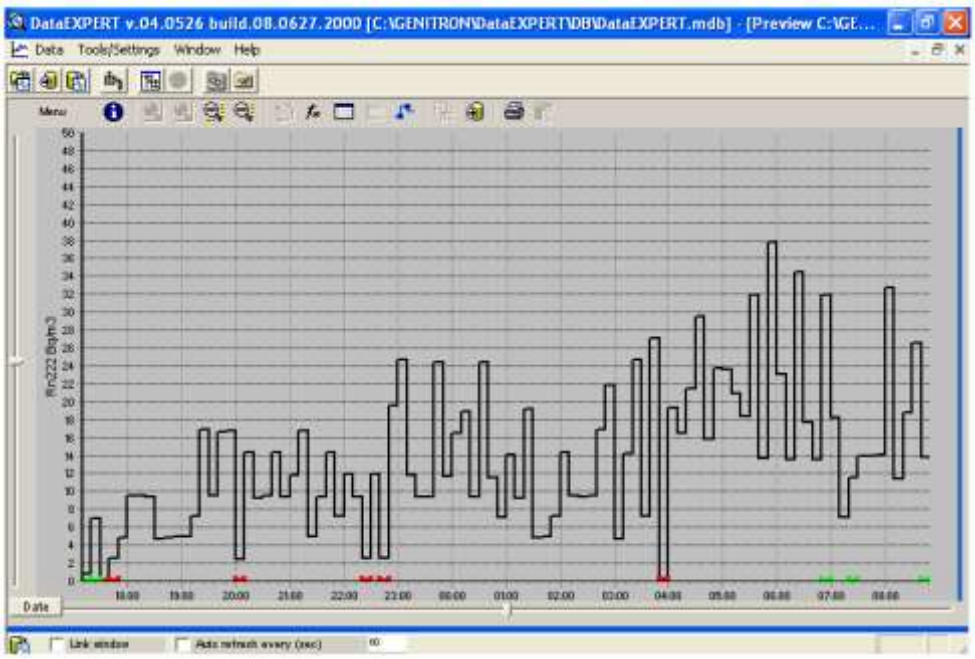

Figure 5.7: Ambient ^{222}Rn concentration measured at coastal communities along the coast of Saltpond oilfield using alpha guard

The low values found in the soil samples for the activity concentrations of the different natural radionuclides analysed imply low values of the associated hazard indices: the radium equivalent (Ra_{eq}) activity in Bq.kg^{-1}, and the external (H_{ex}) and the internal hazards (H_{in}). The values of these indices associated with each sampling point are presented in Table 5.9. The mean radium equivalent activity was 97 ± 48 Bq.kg^{-1}, with the individual values ranging from 29 to 203 Bq.kg^{-1}, the mean external hazard index was 0.26 ± 0.13, ranging from 0.08 to 0.55, and the mean internal hazard index was 0.35 ± 0.18 ranging from 0.10 to 0.70. All these average values are below the acceptable or reference values (370 Bq.kg^{-1}, in the case of Ra_{eq}, 1.0 in the case of H_{ex} and H_{in}), indicating that the soils do not pose any significant radiological radiation hazard and thus, regarded safe, for example, for use as building materials. At any of the sampling points the individual values calculated for the hazard indices did not exceed the fixed reference values.

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Table 5.9: Radium equivalent activity in Bq.kg^{-1} (Ra_{eq}), external (H_{ex}) hazard index and internal (H_{in}) hazard index calculated at each soil sampling point

Sample ID	R_{aeq} (Bq/kg)	H_{ex}	H_{in}
S1	89.70	0.24	0.29
S2	43.30	0.12	0.14
S3	144.07	0.39	0.48
S4	76.48	0.21	0.25
S5	133.57	0.36	0.49
S6	90.72	0.25	0.35
S7	90.73	0.25	0.33
S8	100.96	0.27	0.36
S9	37.57	0.10	0.12
S10	29.03	0.08	0.10
S11	73.04	0.20	0.25
S12	50.40	0.14	0.18
S13	108.8	0.30	0.40
S14	110.50	0.30	0.42
S15	168.05	0.45	0.70
S16	202.96	0.55	0.67
Mean	97.0	0.26	0.35
SD	48.0	0.13	0.18
Range	29.0 – 203.0	0.08 – 0.55	0.10 – 0.70

5.2.2 Beach sediments

The activity concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K, ^{210}Pb and ^{238}U in beach sediments from the coast of same communities as the soil samples discussed above are presented in Table 5.10. The results in the beach sediments are generally lower than that of the soil. However, it was seen from Table 5.10, that the concentrations obtained for ^{228}Ra and ^{228}Th from Th- series in the sediments were similar within one sigma uncertainty and thus suggest secular equilibrium between them but on the other hand it is clearly seen from the Table 5.10, the disequilibrium between the U-series members ^{226}Ra, ^{210}Pb and ^{238}U in the same beach sediments. This could be attributed to high solubility of U in medium compared to that of Th and the presence of a fraction of 210Pb with atmospheric origin.

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Table 5.10: Activity Concentration of ^{40}K, ^{238}U, ^{232}Th series radionuclides in beach Sediments samples by Gamma Spectrometry

Sample ID	Concentration (Bq.kg^{-1})					
	^{238}U	^{226}Ra	^{210}Pb	^{228}Ra	^{228}Th	^{40}K
SD17	2.6 ± 1.3	2.9 ± 0.1	10.2 ± 3.4	2.4 ± 0.6	2.0 ± 1.3	92.0 ± 10.3
SD18	1.8 ± 0.3	5.8 ± 1.5	18.0 ± 1.8	4.3 ± 0.3	4.0 ± 0.1	97.6 ± 15.6
SD19	2.2 ± 1.0	2.9 ± 0.6	6.8 ± 1.9	2.3 ± 0.2	2.1 ± 0.9	93.8 ± 10.5
SD20	2.7 ± 0.3	5.9 ± 0.1	29.2 ± 3.0	4.8 ± 1.5	4.2 ± 0.5	95.8 ± 10.7
SD21	2.5 ± 1.4	3.8 ± 0.7	10.1 ± 1.0	2.7 ± 1.5	3.3 ± 0.4	101 ± 11
SD22	2.8 ± 1.1	6.4 ± 1.0	25.6 ± 2.6	6.7 ± 0.6	4.9 ± 0.1	97.7 ± 10.8
SD23	2.6 ± 1.4	3.0 ± 0.1	8.6 ± 0.9	2.4 ± 0.5	2.2 ± 0.6	103 ± 15
SD24	3.2 ± 1.5	6.7 ± 1.2	27.6 ± 2.8	5.5 ± 1.5	5.5 ± 1.1	92.6 ± 12.7
SD25	8.4 ± 1.2	18.8 ± 1.0	12.4 ± 1.8	27.1 ± 2.4	26.8 ± 1.3	576 ± 64
SD26	6.9 ± 0.8	14.6 ± 0.7	12.1 ± 2.2	18.9 ± 0.7	21.3 ± 2.1	729 ± 80
SD27	2.5 ± 1.1	2.9 ± 0.8	11.8 ± 0.3	2.4 ± 0.4	2.5 ± 0.8	51.4 ± 5.9
SD28	3.6 ± 1.2	7.6 ± 0.8	13.6 ± 1.6	5.6 ± 0.9	5.9 ± 0.5	71.4 ± 9.2
SD29	5.7 ± 1.1	12.4 ± 1.1	10.0 ± 1.9	15.5 ± 0.6	16.3 ± 1.2	628 ± 69
SD30	3.0 ± 0.4	7.5 ± 0.3	11.9 ± 1.7	6.6 ± 0.6	6.3 ± 0.7	67.1 ± 7.4
SD31	2.9 ± 0.3	9.2 ± 0.6	15.8 ± 1.6	11.0 ± 0.9	8.9 ± 0.3	71.6 ± 11.0
SD32	2.2 ± 0.2	5.9 ± 1.5	7.7 ± 0.8	4.5 ± 1.6	3.8 ± 1.5	47.8 ± 10.6
SD33	3.6 ± 1.8	7.1 ± 0.2	6.0 ± 1.5	6.6 ± 0.2	7.1 ± 0.3	62.4 ± 7.1
SD34	2.6 ± 0.3	7.6 ± 1.2	8.4 ± 2.8	4.8 ± 0.4	5.7 ± 0.2	51.0 ± 5.8

Corresponding average hazard indices, external absorbed dose and annual effective dose estimated from the beach sediments activity concentrations are presented in Table 5.11 with all indices being below the acceptable values as discussed above.

Table 5.11: 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 beach Sediments samples

Samples		R_{aeq} (Bq.kg^{-1})	H_{ex}	H_{in}	$D_{\gamma r}$ (nGy.h^{-1})	$E_{\gamma, ext}$ (mSv.y^{-1})
Sediments	Range	15 – 160	0.04 – 0.43	0.05 – 0.51	7 – 76	0.008 – 0.09
	mean	45 ± 43	0.12 ± 0.11	0.15 ± 0.13	21 ± 20	0.030 ± 0.020

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In addition, the activity concentrations of ^{234}U, ^{238}U, ^{230}Th and ^{232}Th in the sediments samples were determined by alpha-particle spectrometry and results are presented in Tables 5.12, 5.13 and 5.14.

In order to compare the two sequential radiochemical separation methods UTEVA and TBP, both separation procedures were applied to the same set of sediments and results for U and Th isotopes are presented in Tables 5.12 and 5.1.3 respectively.

Table 5.12: Activity Concentrations of ^{238}U and ^{234}U and chemical yields in beach sediments samples analysed by alpha-particle spectrometry using the UTEVA and TBP radiochemical separation procedures

Sample ID	^{234}U (Bq.kg^{-1})		^{238}U(Bq.kg^{-1})		Chemical yield (%)	
	UTEVA	TPB	UTEVA	TPB	UTEVA	TPB
SD17	1.4 ± 0.2	1.2 ± 0.2	1.2 ± 0.1	1.1 ± 0.1	91	40
SD18	1.6 ± 0.1	1.6 ± 0.1	1.4 ± 0.1	1.4 ± 0.1	78	68
SD19	1.2 ± 0.1	1.2 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	65	55
SD20	2.0 ± 0.2	1.9 ± 0.2	1.8 ± 0.2	1.7 ± 0.2	82	62
SD21	1.2 ± 0.1	1.0 ± 0.1	1.3 ± 0.2	1.0 ± 0.1	69	52
SD22	1.6 ± 0.1	1.7 ± 0.1	1.5 ± 0.1	1.5 ± 0.1	89	62
SD23	1.7 ± 0.4	1.7 ± 0.1	1.0 ± 0.3	1.2 ± 0.1	95	87
SD24	1.0 ± 0.1	1.8 ± 0.1	1.0 ± 0.1	1.6 ± 0.1	90	70

Table 13: Activity Concentrations of ^{232}Th and ^{230}Th and chemical yields in beach sediments samples analysed by alpha-particle spectrometry using the UTEVA and TBP radiochemical separation procedures

Sample ID	^{230}Th (Bq.kg^{-1})		^{232}Th (Bq.kg^{-1})		Chemical yield (%)	
	UTEVA	TPB	UTEVA	TPB	UTEVA	TPB
SD17	1.2 ± 0.2	1.4 ± 0.2	0.5 ± 0.1	0.6 ± 0.1	40	68
SD18	1.8 ± 0.2	1.7 ± 0.2	1.6 ± 0.2	1.6 ± 0.2	58	62
SD19	1.1 ± 0.2	1.3 ± 0.1	1.0 ± 0.2	1.1 ± 0.1	37	61
SD20	1.6 ± 0.4	2.4 ± 0.2	1.9 ± 0.3	2.0 ± 0.2	58	85
SD21	1.2 ± 0.2	1.1 ± 0.3	1.0 ± 0.2	1.0 ± 0.3	51	60
SD22	1.9 ± 0.4	2.0 ± 0.3	1.6 ± 0.3	1.6 ± 0.3	32	41
SD23	1.2 ± 0.1	1.9 ± 0.2	1.5 ± 0.2	1.7 ± 0.2	51	68
SD24	2.5 ± 0.2	3.0 ± 0.3	1.7 ± 0.1	2.5 ± 0.2	96	62

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Table 5.14: Activity Concentrations of ^{238}U, ^{234}U, ^{230}Th and ^{232}Th in beach Sediments samples determined by alpha-particle spectrometry using the TBP radiochemical separation procedure

Sample ID	Concentration ($Bq.kg^{-1}$)				
	^{234}U	^{238}U	^{230}Th	^{232}Th	Yield (%) U/Th
SD25	6.6 ± 0.4	7.2 ± 0.5	7.8 ± 0.8	6.2 ± 0.4	83/68
SD26	5.9 ± 0.4	7.5 ± 0.5	8.2 ± 0.6	9.1 ± 0.5	66/72
SD27	1.7 ± 0.2	2.0 ± 0.2	1.8 ± 0.4	1.3 ± 0.3	69/83
SD28	2.2 ± 0.2	1.3 ± 0.1	2.5 ± 0.3	1.0 ± 0.2	76/80
SD29	4.5 ± 0.4	4.9 ± 0.4	3.0 ± 0.3	3.6 ± 0.4	71/65
SD30	2.9 ± 0.3	3.3 ± 0.3	3.3 ± 0.6	3.3 ± 0.5	55/63
SD31	2.8 ± 0.3	2.6 ± 0.2	2.6 ± 0.3	2.2 ± 0.2	63/58
SD32	1.5 ± 0.3	1.8 ± 0.3	1.7 ± 0.4	2.0 ± 0.3	55/64
SD33	1.9 ± 0.3	1.8 ± 0.3	2.0 ± 0.2	2.5 ± 0.4	55/52
SD34	2.2 ± 0.3	1.5 ± 0.3	1.9 ± 0.2	1.4 ± 0.1	58/66

It is seen from Table 5.12 that, the results obtained for U isotopes (^{234}U and ^{238}U) for both UTEVA and TBP methods are in agreement. However it was also clear that, radiochemical yields in sediments samples were higher in the UTEVA radiochemical procedure (82.4 ±10.9%) than that of TBP (62.0 ± 14.0%). On the other hand, ^{230}Th and ^{232}Th concentrations as shown in Table 5.13, recorded higher chemical yield for TBP (63.4 ±12.1%) than UTEVA (53.0 ± 20.0%) radiochemical procedure dough the results were generally in agreement.

A comparison of other aspects to consider in making a choice between the two radiochemical separation procedures in terms of time consumption, reagents needed and waste generated for both techniques are summarized in Table 5.15.

For the TBP method, U and Th separation needs three steps of 30min for each step. Additionally, the Th purification stage, 90mL of different solution are passed through AG1-X8 resin with a flow rate of $1mLmin^{-1}$, needs 1.5h. Taking into account additional laboratory works, TBP procedure needs about 3.5-4h per sample. The UTEVA

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procedure however, consists of the automatic elution of 50mL of different solutions through the resin that takes 1.5h per sample.

Table 5.15: Time, reagents and waste generated for TBP and UTEVA separation techniques

Concept	TBP + Th purification	UTEVA
Time for separation process	3.5h (1.75h TBP + 1.75h AG1-X8)	1.5h
Reagents needed	5mL of TBP 20mL of Xylene 70mL of 8M HNO_3 45mL of 1.5M HCl 45mL of distilled H_2O 40mL of 9M HCl 7.5g of AG1-X8 resin	15mL 3M HNO_3 4mL of 9M HCl 20mL of 5M HCl 10mL of 0.01M HCl 1 UTEVA column
Generated waste	TBP +Xylene(25mL) AG1-X8 resin(7.5g) 40mL of 8M HNO_3	UTEVA column

Additionally, it is possible to work in the laboratory with many samples at the same time (parallel) in an easier way using UTEVA columns instead of glass decantation funnels used for TBP procedure. This fact will lead also to save manpower. It is clear therefore that, radiochemical procedure using chromatographic resins is less time consuming, and requires fewer amounts of reagents, thus generating lower amounts of waste. Another point worth noting is the potential drawback of high cost associated with UTEVA resins. However, a careful economical study considering the cost associated with the materials and reagents for all steps for both TBP and UTEVA (excluding personnel) performed recently (Lehritani et al., 2012), resulted in a general cost saving of 10% in UTEVA compared to TBP.

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5.2.3 Water

In addition to the soil samples, several water samples with different origin were collected along same coastal communities in the studied area from which soil and beach sediments were taken. A total of 8 water aliquots were analyzed, made up of 4 underground water (W1 to W4), 3 lagoon water (W5 to W7), and the remaining one is river water (W8).

The radioactivity content of these waters was first of all screened by determining their gross-α and gross-β activities. The results obtained are compiled in Table 5.16, with the gross-α activities found in the range of 0.005 $Bq.L^{-1}$(surface water) to 0.048 $Bq.L^{-1}$(underground water) and the gross-β activities in the range of 0.014$Bq.L^{-1}$(lagoon water) to 0.180 $Bq.L^{-1}$(underground).

Table 5.16: Gross -α and gross-β activities in the different waters samples analyzed in this work (W1-W4=underground, W5-W7= lagoon, W12 = river)

Sample ID	Activity concentration ($Bq.L^{-1}$)	
	Gross -α	Gross-β
W1	0.020	0.090
W2	0.048	0.180
W3	0.017	0.060
W4	0.009	0.035
W5	0.031	0.073
W6	0.030	0.141
W7	0.012	0.022
W8	0.005	0.014
Mean	0.022	0.077
SD	0.014	0.058
Range	0.005 – 0.048	0.014 – 0.180
GSA* limit	0.100	1.000
WHO* limit	0.500	1.000

**GSA-Ghana Standards Authority*
**WHO- World Health Organisation*

All the values found were clearly below the World Health Organisation (WHO) and Ghana Standards Authority (GSA) screening levels for drinking water below which, no

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further action is required (0.5 Bq.L^{-1}for gross-α and 1.0 Bq.L^{-1}for gross-β (WHO 2011; GSA 2005)).The guidance values ensure an exposure lower than 0.1 mSv.y^{-1} assuming a consumption rate of 2 L.d^{-1} of each of the analysed water samples. All the water sources in the study area can be designated for drinking and domestic purposes from radiological point of view since the results show insignificant levels of natural radioactivity. This fact indicates that the analysed water samples have not been affected by the NORM with the commencement of operations of the oil industry in the study area.

In order not to address only radiological information at this stage (because the levels of radioactivity in the water samples are very low), but also to obtained baseline data for purposes of comparison in future, the activity concentrations of the U-Th series have been determined in all the water samples in order to evaluate eventual future radiological impacts due to NORM activities. The set of data obtained are provided in Table 5.17.

Table 5.17: ^{234}U, ^{238}U, ^{230}Th, ^{232}Th and ^{226}Ra activity concentrations as well as ^{234}U/^{238}U activity ratios determined in the water samples analyzed

Sample ID	Activity Concentration (mBq.L^{-1})					^{234}U/^{238}U
	^{234}U	^{238}U	^{230}Th	^{232}Th	^{226}Ra	
W1	8.6 ± 2.0	6.8 ± 1.8	6.5 ± 1.4	0.6 ± 0.6	7.0 ± 3.0	1.26 ± 0.44
W2	27.5 ± 2.3	27.8 ± 2.3	<0.04	<0.04		0.99 ± 0.12
W3	8.8 ± 2.9	4.6 ± 2.0	<0.04	<0.04	18.0 ± 5.0	1.91 ± 1.04
W4	5.6 ± 1.6	3.9 ± 1.3	5.3 ± 3.5	<0.04	16.0 ± 4.0	1.44 ± 0.63
W5	23.2 ± 2.2	23.4 ± 2.2	2.2 ± 1.3	2.2 ± 1.3		0.99 ± 0.13
W6	21.2 ± 2.1	20.1 ± 2.1	<0.04	6.7 ± 4.0		1.05 ± 0.15
W7	3.1 ± 0.7	1.8 ± 0.5	<0.04	<0.04		1.72 ± 0.62
W8	1.6 ± 0.8	1.3 ± 1.0	2.3 ± 1.3	<0.04		1.23 ± 1.13
Mean	12.5	11.2	2.1	1.2	13.7	1.32
SD	10.0	10.7	2.6	2.3	5.9	0.34
Range	1.6 – 27.5	1.3 – 27.8	<0.04 – 6.5	<0.04 – 6.7	7.0 – 18.0	0.99 – 1.91
*WHO GL	1000	10000	1000	1000	1000	

*WHO GL: World Health Organisation Guidance levels

Table 5.17 shows the activity concentrations of ^{234}U, ^{238}U, ^{230}Th and ^{232}Th in the water samples determined by alpha spectrometry as well as ^{234}U/^{238}U activity ratio. The

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activities of ^{234}U were in the range 1.6–27.5 mBq.L^{-1}, the activities of ^{238}U in the range 1.3–27.8 mBq.L^{-1}, the activities of ^{230}Th in the range <0.04–6.5 mBq.L^{-1} and the activities of ^{232}Th in the range <0.04–6.7 mBq.L^{-1}respectively. In Table 5.16, the ^{226}Ra activity concentrations determined for some underground water sources are also provided and these varied from 7.0 to18.0 mBq.L^{-1}.

From the results shown in Table 5.17, it can easily be shown that about 50% of the water samples analysed have ^{230}Th and ^{232}Th activity concentrations below the minimum detectable activity (MDA), while the activity concentrations of ^{234}U, ^{238}U and ^{226}Ra are clearly higher and in all the cases detectable. These results cannot be considered surprising and could be attributed to the well-known fact that uranium and radium are considered soluble species from geochemical point of view, with typical natural activity concentrations greater than 1 mBql^{-1} in surface waters whiles on the other hand thorium is quite insoluble in the same medium. The uranium and radium in the water, represent elevated proportions of the alpha-radioactivity associated with the analyses, as it can easily be deduced from Figure 5.8, by comparing the gross-α activities with the ^{234}U activity concentrations , it is possible to observe a quite good correlation.

Table 5.17 also indicate the WHO Guidance levels for drinking water quality. It can be observed that the activity concentrations of all the measured radionuclides in the water samples obtained from this work were all far lower than the World Health Organization (WHO) recommended guidance levels for drinking water (WHO 2011). In general, higher activity concentration values of radionuclides in water samples were obtained for the underground water sources (borehole) followed by lagoon and river.

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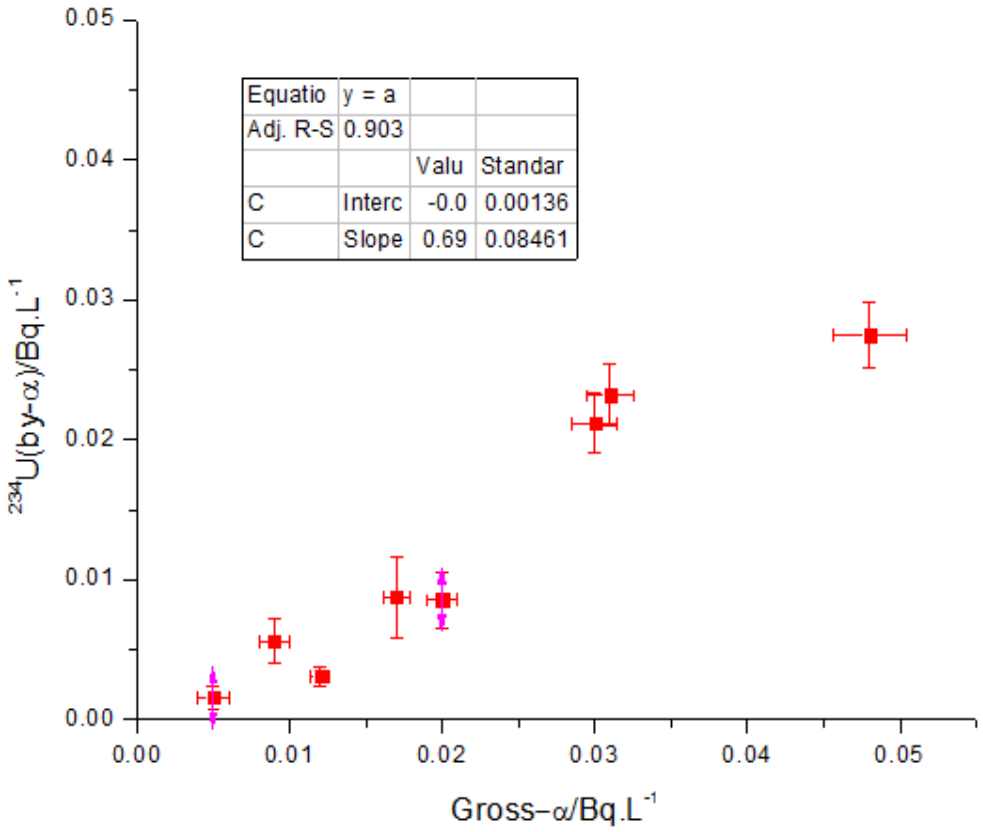

Figure 5.8: Comparison between the Gross-α activities and the ^{234}U activity concentrations determined in all the water samples analyzed in this work

Finally, it is interesting to note that the $^{234}U/^{238}U$ activity ratios found in all the water samples analysed varied from 0.99 to 1.91 with an overall average of 1.32 ± 0.03. Higher values were observed for the underground waters. These results showed the well-known preferential incorporation of ^{234}U to the waters from the substratus, being ^{234}U recoil, crystal damage and leaching the main mechanisms responsible for the $^{234}U/^{238}U$ disequilibrium in ground water (Barr et al., 1979; Ivanovich et al., 1992). These activity ratios are, on the other hand, consistent with the values found in water not affected by uranium inputs from NORM activities.

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5.3 NORM waste samples

5.3.1 Produce water, oily waste water, and crude oil

5.3.1.1 Radioactivity measurements in produced water

The produced water samples were collected from separators after treatment to meet oil in water content prior to discharge to marine waters from both the Saltpond and Jubilee oilfields platforms.

The activity concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th, ^{224}Ra and ^{40}K in produced water samples from the two oilfields, determined by gamma-ray spectrometry, are presented in Table 5.18. The average value of the activity concentration of ^{226}Ra is 15.2 ± 7.1 Bq.L^{-1} (in a range of 6.2–22.3 Bq.L^{-1}); while for ^{228}Ra, the average activity concentration is 23.0 ± 13.5 Bq.L^{-1} (in a range of 6.4–35.5 Bq.L^{-1}); and for ^{228}Th, the average is 3.8 ± 2.4Bq.L^{-1} (in a range of 0.7–6.4 Bq.L^{-1}). In the case of ^{224}Ra the average activity concentration is 3.8 ± 2.5 Bq.L^{-1} (in a range of 0.7–7.0 Bq.L^{-1}); whiles for ^{40}K, the average is 16.6 ± 7.9 Bq.L^{-1}(in a range of 5.9–23.9 Bq.L^{-1}). Comparison of the mean specific activities of radionuclides for the two oilfields as seen in Figure 5.9 shows that the activity concentrations for produced water from the Saltpond field were three orders of magnitude higher than that for the Jubilee field and this can be attributed to factors such as the maturity of the Saltpond field than Jubilee field, the geological characteristics of reservoir rocks, the type of hydrocarbons produced and the operating conditions for the oilfields.

The average concentrations of both ^{226}Ra and ^{228}Ra for the two oilfields obtained in this study all exceeded the aqueous Derived Release Limit (DRL) of Canadian guideline governing liquid discharges (Health Canada, 2011) as presented in Figure 5.9. Furthermore, results shown in Table 5.19 indicate that produced water from the two Ghanaian oilfields are relatively high in Radium concentration compared to Radium concentrations for other oilfields reported from most countries (Table 5.19) including the

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Gulf of Mexico which is reported in literature (Vegueria et al., 2002; Meinhold et al., 1996; Chowdhury et al., 2004; Neff, 2002; Stephenson, 1992) as having higher radium concentration in produced water. The results, nevertheless, are within the reported worldwide range of 0.002–1200 Bq.L^{-1} for ^{226}Ra and 0.3 – 180 Bq.L^{-1} for ^{228}Ra (Jonkers *et al.*, 1997) as shown in Table 5.19.

Table 5.18: Activity Concentration of ^{40}K, ^{238}U, ^{232}Th series radionuclides and ^{228}Ra/^{226}Ra ratio in Produced water samples by Gamma Spectrometry

Sample ID	Concentration Bq/l					^{228}Ra/^{226}Ra
	^{226}Ra	^{228}Ra	^{228}Th	^{40}K	^{224}Ra	
JF1	6.7 ± 0.2	6.6 ± 0.2	0.82 ± 0.01	6.3 ± 0.5	0.82 ± 0.01	0.99
JF 2	7.6 ± 0.3	6.9 ± 0.1	1.22 ± 0.03	8.3 ± 0.8	1.43 ± 0.04	0.91
JF 3	6.2 ± 0.1	6.4 ± 0.1	0.71 ± 0.01	7.7 ± 0.7	0.69 ± 0.01	1.03
JF 4	6.6 ± 0.1	6.6 ± 0.1	0.81 ± 0.01	5.9 ± 0.4	0.78 ± 0.01	1.00
JF 5	6.8 ± 0.2	6.7 ± 0.1	0.92 ± 0.01	7.3 ± 0.5	0.92 ± 0.02	0.99
SF 6	20.1 ± 0.5	33.5 ± 1.0	5.7 ± 0.2	23.4 ± 2.4	5.8 ± 0.3	1.67
SF7	22.2 ± 0.9	34.2 ± 1.6	5.5 ± 0.2	22.3 ± 2.3	5.4 ± 0.1	1.54
SF 8	19.5 ± 0.5	32.3 ± 0.9	5.0 ± 0.2	22.1 ± 2.3	5.1 ± 0.1	1.66
SF 9	22.1 ± 0.5	33.6 ± 1.5	5.4 ± 0.2	22.2 ± 2.4	5.6 ± 0.2	1.52
SF 10	19.7 ± 0.8	33.1 ± 1.0	6.0 ± 0.2	22.3 ± 2.5	6.0 ± 0.3	1.68
SF 11	22.3 ± 0.9	35.5 ± 1.7	6.4 ± 0.3	23.9 ± 2.4	7.0 ± 0.5	1.59
SF 12	19.6 ± 0.6	32.5 ± 1.3	4.7 ± 0.1	22.2 ± 2.5	4.7 ± 0.1	1.66
SF 13	18.7 ± 0.2	31.6 ± 1.4	5.7 ± 0.2	22.5 ± 2.3	5.8 ± 0.2	1.69

JF-Jubilee Field and SF-Saltpond Field

In addition the radium isotopic ratios, ^{228}Ra/^{226}Ra were also calculated for the two oilfields as shown in Table 5.18. The ratios ranged from 0.91 – 1.03 with an average of 0.98 ± 0.05 for the Jubilee field and 1.52 – 1.69 with an average of 1.63 ± 0.07 for the Saltpond field. The ratios obtained give an indication of different oil-producing wells from different geological formation reservoirs with different source rocks types having different U and Th concentrations, reflecting the Th/U ratio of the reservoir lithologies.

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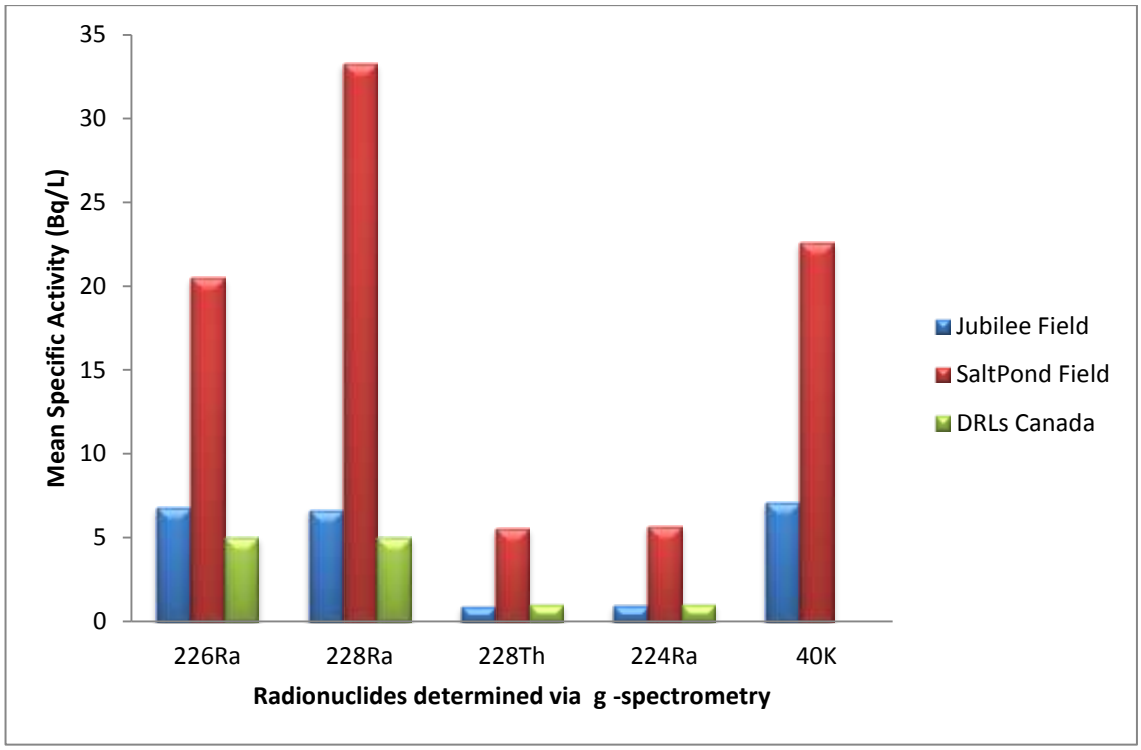

Figure 5.9: Comparison of mean specific activity of radionuclides in propduced water for the two Ghanian oilfields with the Canadian Derived Release Limits- Diffuse NORM Sources

Table 5.20 shows the activity concentrations of ^{234}U, ^{238}U, ^{210}Po, ^{230}Th and ^{232}Th in the produced water samples determined by alpha spectrometry. The activities of ^{234}U were in the range <DL–6.1 $mBq.L^{-1}$ with average 3.4 ± 1.5 $mBq.L^{-1}$, the activities of ^{238}U in the range <DL–5.5 $mBq.L^{-1}$ with average 3.4 ± 1.2 $mBq.L^{-1}$, the activities of ^{210}Po in the range 22 – 145 $mBq.L^{-1}$ with average 70 ± 43 $mBq.L^{-1}$, the activities of ^{230}Th in the range 2.9 to 15.0 $mBq.L^{-1}$ with average 7.6 ± 3.5 $mBq.L^{-1}$ and the activities of ^{232}Th in the range 1.6–5.6 $mBq.L^{-1}$ with average 3.1 ± 1.2 $mBq.L^{-1}$ respectively

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Table 5.19: 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	Salpond	18.7 - 22.3	20.5	31.6 - 33.5	33.3	*Present study*
	Jubilee	6.2 - 7.6	6.8	6.4 - 6.9	6.6	*Present study*
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 - 10.4	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 and 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	Bacia de Campos	<0.01 – 6.0		<0.05 –12.0		Jeres Vegueira *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

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Table 5.20: Activity Concentrations of ^{238}U, ^{234}U, ^{210}Po, ^{230}Th and ^{232}Th in the Produced water samples determined by alpha-particle spectrometry

Sample ID	Concentration mBq/l				
	^{234}U	^{238}U	^{210}Po	^{230}Th	^{232}Th
JF1	6.1 ± 2.1	5.5 ± 2.2	22 ± 2	6.4 ± 1.3	2.1 ± 0.8
JF 2	2.5 ± 0.5	2.3 ± 0.5	43 ± 4	4.6 ± 1.3	1.7 ± 0.5
JF 3	1.6 ± 0.5	1.5 ± 0.5	39 ± 4	8.0 ± 1.2	1.6 ± 0.5
JF 4	5.5 ± 2.3	5.0 ± 2.1	40 ± 3	6.8 ± 1.0	5.6 ± 1.2
JF 5	4.8 ± 1.7	4.3 ± 1.8	48 ± 5	5.6 ± 1.3	2.7 ± 0.5
SF 6	<DL	2.9 ± 0.5	82 ± 7	5.6 ± 0.8	4.2 ± 0.7
SF 7	2.8 ± 0.5	4.2 ± 1.2	46 ± 3	4.7 ± 0.7	3.6 ± 0.5
SF8	2.5 ± 0.5	<DL	35± 11	2.9 ± 1.0	2.4 ± 0.5
SF 9	2.1 ± 0.9	<DL	82 ± 12	8.0 ± 1.1	3.4 ± 0.6
SF 10	3.2 ± 0.6	2.9 ± 0.4	135 ± 12	11.9 ± 1.8	2.1 ± 0.5
SF 11	<DL	2.7 ± 0.2	139 ± 9	12.0 ± 1.4	3.0 ± 0.9
SF 12	4.1 ± 0.6	3.8 ± 0.5	145 ± 14	15 ± 2.0	5.1 ± 0.5
SF 13	2.5 ± 0.5	2.7 ± 0.2	55± 11	7.0 ± 1.5	3.4 ± 1.7
*DRLs	10000	10000	1000	5000	1000

*DRLs: Canadian Derived Release Limits- Diffuse NORM Sources
**DL: Minimum detection limit

Generally activity concentrations of U and Th-isotopes as well as ^{210}Po in produced water for both oilfields in this study were lower than that of radium isotopes discussed above. Also, all the radionuclides in all the samples were several orders of magnitude below the aqueous Derived Release Limit (DRL) of Canadian guideline governing liquid discharges (Health Canada, 2011) as shown in Table 5.20.

Analyses of NORM from many different oil and gas fields show that the solids found in the downhole and surface structures of oil and gas production facilities do not include ^{238}U and ^{232}Th **(**Jonkers et al., 1997**)**. These elements are not mobilized from the reservoir rock that contains the oil, gas and formation water. The formation water contains cations of calcium, strontium, barium and radium dissolved from the reservoir rock. As a consequence, formation water contains the radium isotopes ^{226}Ra from the ^{238}U series, and ^{228}Ra and ^{224}Ra from the ^{232}Th series. All three radium isotopes, but not their parents, thus appear in the water co-produced with the oil or gas. They are referred

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to as 'unsupported' because their long lived parents ^{238}U and ^{232}Th, and also ^{228}Th remain in the reservoir.

Prior to the analysis of samples via Alpha spectrometry, the samples were screened for gross-α and gross-β activities and results are presented in Table 5.21. The gross-α activities for the Jubilee and Saltpond oilfields ranged from 5.8 – 7.4 $Bq.L^{-1}$ with average 6.6 ± 0.8 $Bq.L^{-1}$and 14.9 – 26.1 with average 20.5 ± 7.8 $Bq.L^{-1}$ respectively. For the gross-β activities they ranged from 14.3– 22.8 $Bq.L^{-1}$ with average 18.1 ± 4.3 $Bq.L^{-1}$and 61.4 – 87.7 with average 74.2 ± 18.2 $Bq.L^{-1}$ respectively.

Table 5.21: Average Gross -α and gross-β activities in Produced waters samples

	Gross –α ($Bq.L^{-1}$)		Gross-β($Bq.L^{-1}$)	
	JF	SF	JF	SF
Mean	6.6 ± 0.8	20.5 ± 7.8	18.1 ± 4.3	74.2
Range	5.8 – 7.4	14.9 – 26.1	14.3 – 22.8	61.4 – 87.1

Comparing the total alpha and beta activities as shown in Tables 5.21 with that of the individual radionuclides as presented earlier in Tables 5.18 and 5.20, it can be seen clearly that ^{226}Ra and ^{228}Ra are the major contributors to total alpha and total beta activities respectively. It is well known the general good correlation existing between gross alpha and beta activities with ^{226}Ra and ^{228}Ra concentrations respectively in these types of samples, which have been established even by USEPA the measurement of gross alpha and beta as a method of screening samples for the presence of radium (Hess et al., 1985)

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5.3.1.2 Correlation of Ra with chemical and physical properties of produced water

The results of chemical and physical properties as well as trace metal content of produce water samples from the two oilfields in this study are presented in Tables 5.22 – 5.24. Correlation between Ra and physical parameters have been documented in a number of studies (Neff, 2002; Kraemer and Reid, 1984), however most of this studies focused mainly on salinity (TDS) and Cl^- with Ra. In this current study, other physical and chemical parameters (Tables 5.22 and 5.23) in addition to TDS and Cl^- determined for all produced water samples have been related to Ra content. Origin 8.0 (a computer program for data analysis and graphing) was applied in our study to determine correlations and curve fittings. Figures 5.10 – 5.14 show correlations between Ra and physico-chemical parameters.

Table 5.22: Physical Parameters measured for Produced waters samples

ID	pH	Tp (^oC)	Density (kg/m^3)	Oil in water (mg/L)	Condty (mS/cm)	TDS (mg/L)	TSS (mg/L)	Salinity (ppt)	Alkalinity (mg/L)	Turbidity (FAU)
JF1	7.07	26.1	1023	20	56.4	30650	17100	45.6	740	9
JF 2	7.25	26.1	1023	21	60.8	31800	17200	52.8	765	14
JF 3	7.30	26.0	1022	22	50.5	28700	18800	33.5	780	5
JF 4	6.35	26.3	1022	22	54.7	30170	18680	36.7	420	7
JF 5	6.70	26.3	1023	20	60.2	31240	17600	48.4	480	12
SF 6	4.12	26.7	1142	45	123.2	66400	35800	544	199	170
SF 7	4.08	26.4	1148	42	125.0	70100	35400	578	198	192
SF8	4.62	26.3	1142	50	118.5	64500	36600	479	225	140
SF 9	4.15	26.4	1148	40	124.4	69500	35500	527	202	179
SF 10	4.73	26.3	1142	150	122.6	65300	36100	574	240	164
SF 11	4.13	26.1	1148	120	125.5	70300	35300	595	202	201
SF 12	3.90	26.3	1148	150	121.4	64800	36300	486	160	156
SF 13	3.98	26.3	1142	140	110.3	61000	36800	470	160	116

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Table 5.23: Anions and cations for Produced waters samples

Sample	F^- (mg/L)	Cl^- (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	HCO_3^- (mg/L)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)
JF1	1.38	9811	0.12	23.81	6.35	425	10635	168	68
JF 2	1.51	9998	0.09	22.20	5.24	294	14290	157	59
JF 3	1.29	9637	0.22	32.90	7.32	951	7400	280	112
JF 4	1.33	9717	0.13	24.52	6.61	512	9580	176	70
JF 5	1.44	9902	0.10	22.75	5.82	362	12870	161	64
SF 6	9.7	39518	3.85	18.40	44.01	167	16185	3882	1482
SF 7	10.0	44110	3.74	16.25	43.24	159	17460	3795	1409
SF8	9.0	29485	4.81	21.20	46.94	194	14840	4354	1680
SF 9	9.8	41230	3.80	17.10	43.72	162	16950	3840	1435
SF 10	9.3	37430	4.01	19.95	44.98	181	15440	3911	1504
SF 11	10.1	42880	3.68	15.84	42.95	157	18130	3769	1396
SF 12	9.0	35580	4.03	20.65	45.86	195	14960	3968	1566
SF 13	9.1	24189	5.42	21.80	48.30	195	14780	4672	1850

Table 5.24: Trace metals in Produced waters samples determined via (ICP-QMS)

elements	Unit	Jubilee field		Saltpond Field	
		Range	Mean	Range	Mean
K	(mg/L)	197 - 210	204 ± 9.2	448 - 500	475 ± 22
Fe	(mg/L)	9 -10	9.5 ± 0.7	131 - 143	137 ± 5
Br	(mg/L)	56 - 57	56.5 ± 0.7	977 - 1065	1024 ± 43
Sr	(mg/L)	18 - 20	19 ± 1.4	989 - 1101	1051 ± 58
Ba	(mg/L)	29 - 31	30 ± 1.4	48 - 55	51 ± 3
Mn	(mg/L)	0.13 – 0.31	0.22 ± 0.12	37 - 41	39 ± 1.6
Pb	(ug/L)	10 - 37	24 ± 19	<1.09 - 6	3 ± 2
Zn	(ug/L)	<3.3 - 154	154 ± 95	4 - 66	39 ± 26
Hg	(ug/L)	9 -11	10 ± 1.4	4 - 10	6 ± 2
As	(ug/L)	10 - 12	11 ± 1.4	413 - 545	471 ± 59
Ni	(ug/L)	15 - 51	33 ± 25	791 - 963	893 ± 90
V	(ug/L)	20 - 21	20.5 ± 0.7	111 - 124	116 ± 5
Sc	(ug/L)	37 - 38	37.5 ± 0.7	135 - 151	143 ± 7
Cu	(ug/L)	56 - 68	62 ± 8	60 - 82	72 ± 11
Al	(ug/L)	320 - 674	497 ± 250	40 - 132	88 ± 44

The anions HCO_3^-, SO_4^{2-} and Cl^- showed good linear correlation with both ^{226}Ra and total Ra (^{226}Ra+^{228}Ra) as presented in Figures 5.10 and 5.11. The highest R^2 was obtained for Cl^- (>0.92). As expected for produced water, the Cl^- content in all samples increased with increasing Radium content whiles radium decreased with increasing

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SO_4^{2-} and HCO_3^- content which is due to the well-known fact of radium co-precipitation with $BaSO_4$, $SrSO_4$, $CaSO_4$ and $CaCO_3$ to form scales in the presence of Ca, Ba and Sr ions in produce water. The sulphate concentration of produced water is a major controlling factor in the scaling tendency of sulphate minerals.

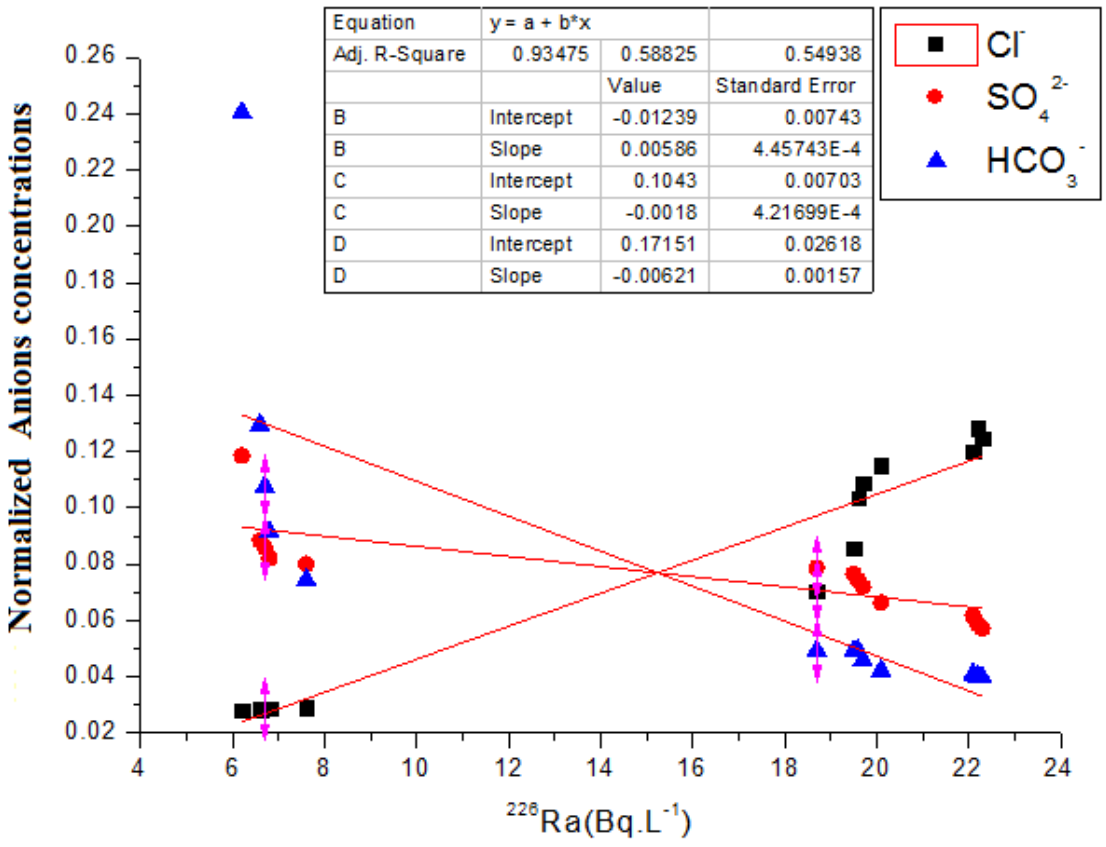

Figure 5.10: Correlation between ^{226}Ra with HCO_3^-, SO_4^{2-}, Cl^- in produced water

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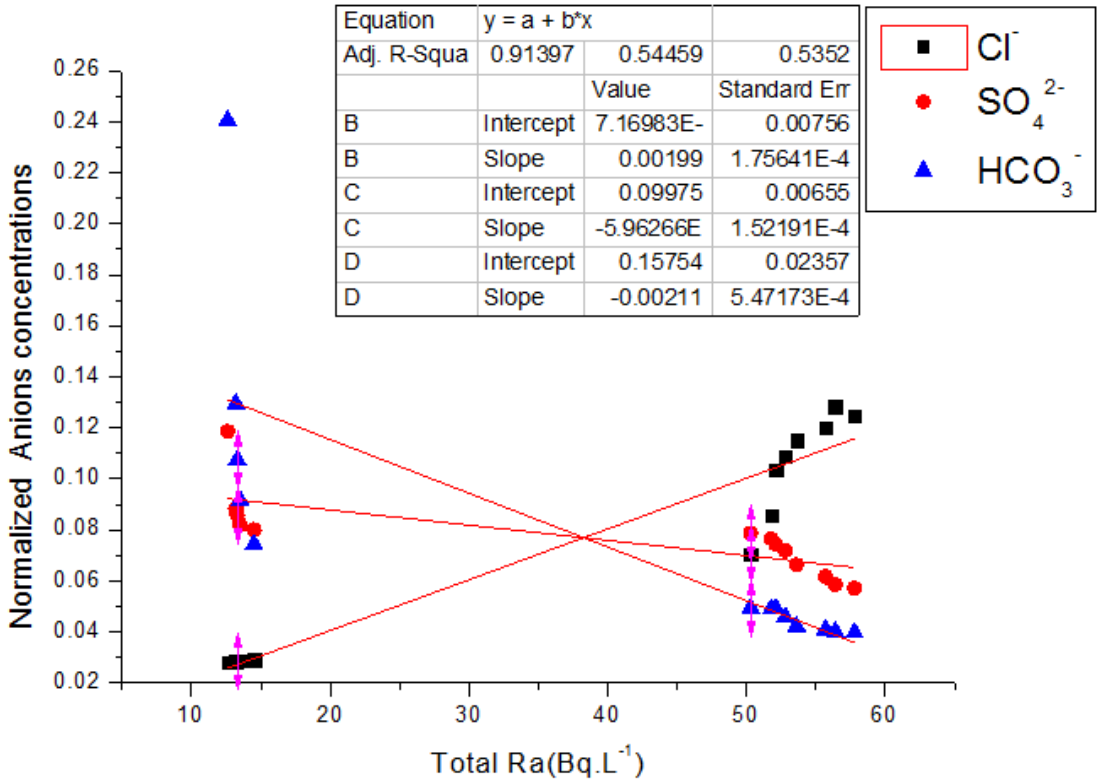

Figure 5.11: Correlation between total Radium with HCO_3^-, SO_4^{2-}, Cl^- in produced water

TDS had the closest correlations with both ^{226}Ra and total Ra with R^2 of linear fittings of both parameters greater than 0.997, followed by conductivity (>0.92), Ca (>0.92), and Na (>0.73) as shown in Figures 5.12 and 5.13. The conductivity, TDS, Ca and Na showed an increasing trend with increasing radium. However comparing the data set for the two fields separately Ca showed an increasing trend with decreasing radium which could be associated to the formation of $CaSO_4$ and $CaCO_3$ and co-precipitation with radium.

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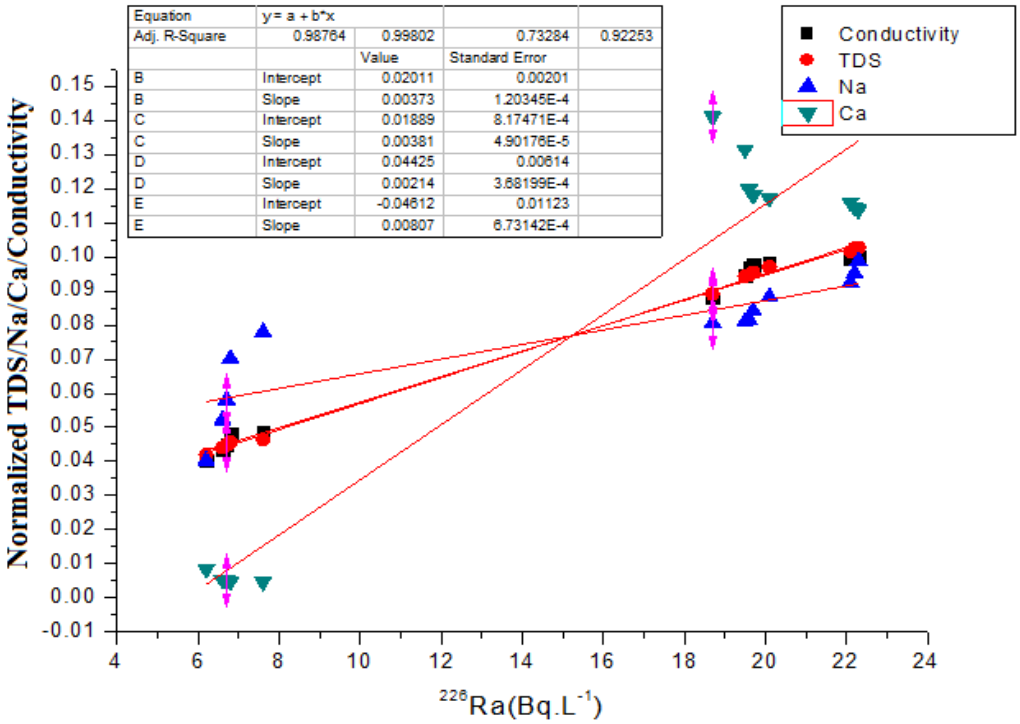

Figure 5.12: Correlation between ^{226}Ra with TDS, conductivity, Na and Ca in produced water

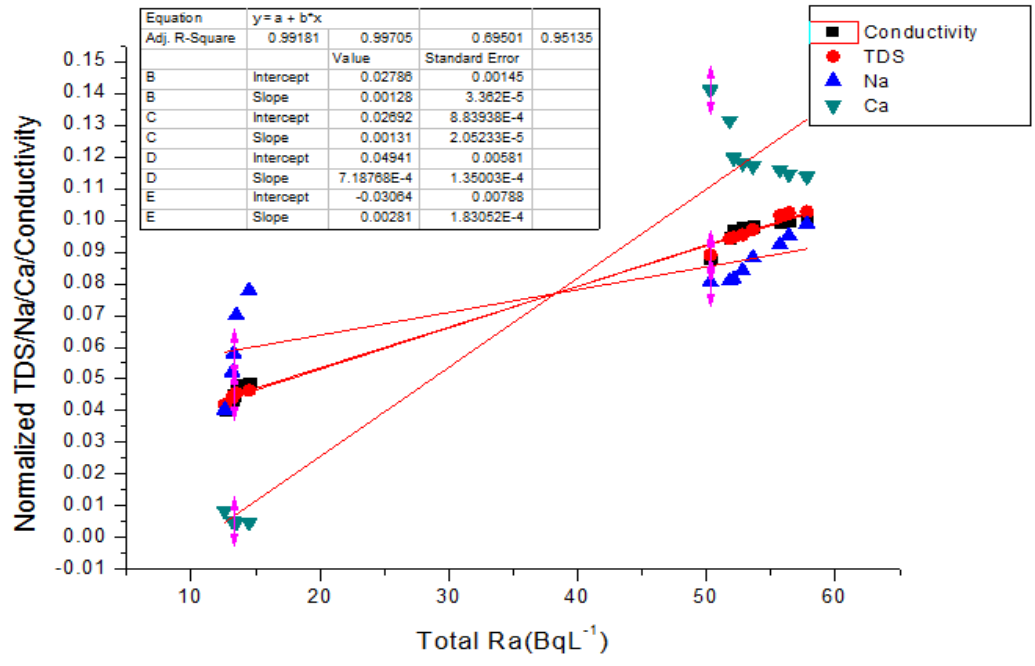

Figure 5.13: Correlation between total Radium with TDS, conductivity, Na and Ca in produced water

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A very interesting linear correlation was found for produced water samples in this study between NO_3^-, PO_4^{3-}, F^- and total radium as presented in Figure 5.14 with F^- having the highest R^2 of 0.999, followed by NO_3^- (0.968) and PO_4^{3-} (0.898). An increasing trend with radium was observed for F^-, NO_3^- and PO_4^{3-}, considering both data sets on a whole for the two fields. On the other hand, comparing the data set for the two fields separately, a decreasing trend was observed for both NO_3^- and PO_4^{3-} with increasing radium considering the anions within each of the two oilfields.

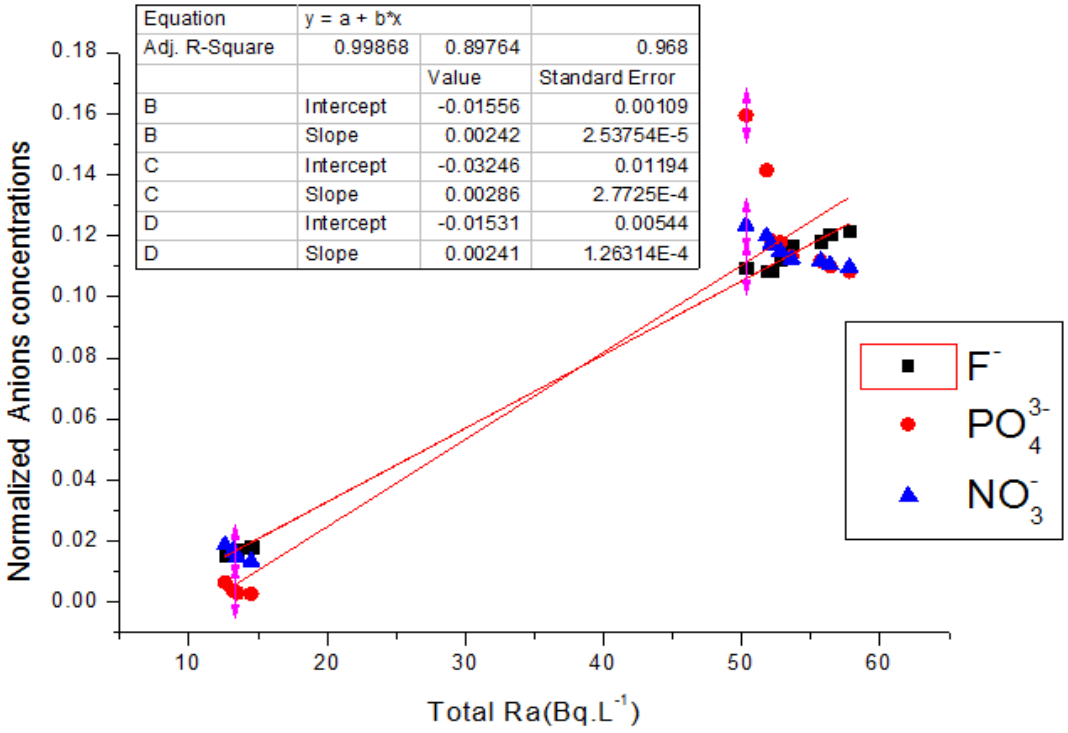

Figure 5.14: Correlation between total Radium with NO_3^-, PO_4^{3-}, F^- in produced water

In Figure 5.15, correlations of F^- with other physico-chemical parameters are presented. The figure shows that the TDS (R^2=0.99) and pH (R^2=0.94) may be possible contributing factors for the good correlation obtained between F^- and radium. This is also confirmed with the good correlations found between F^- and Ca (R^2=0.95), Cl (R^2=0.90), Mg (R^2=0.94) and Na (R^2=0.70), which contribute significantly to TDS as well as HCO_3^- (R^2=0.52) and SO_4^{2-} (R^2=0.53).

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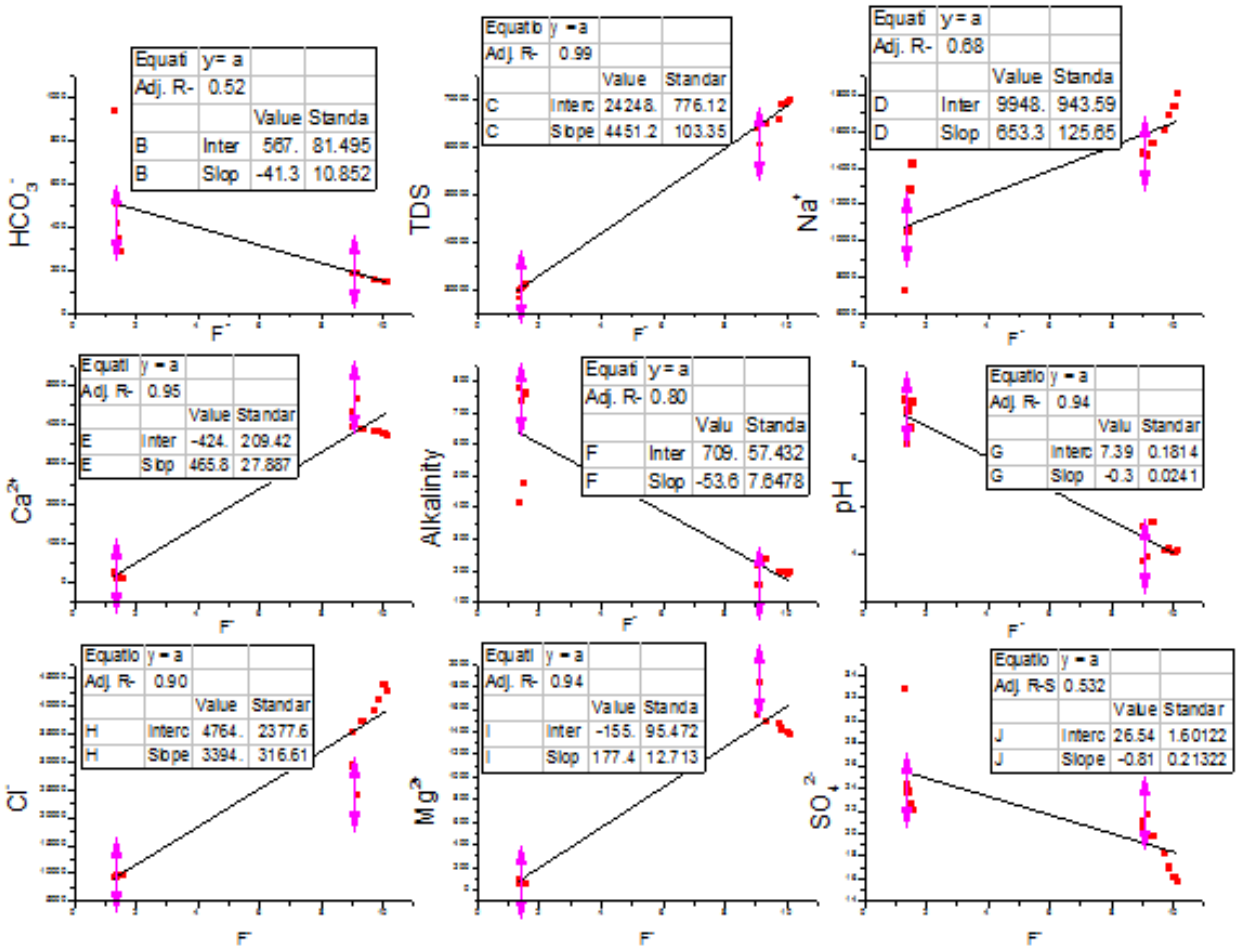

Figure 5.15: Correlation between F^- with other physico- chemical parameters in produced water

It has been reported (Gao et al., 2007) that the Na ions increase sharply and Ca ions decrease when seawater intrudes underground water. A series of field work and experiments have confirmed that fluorine increases with increasing Na ions and Na/Ca (Gao et al., 2007). Furthermore, Ca ions can restrict fluorine dissolution. Tang and Wang, 2005 observed that fluorine released from rocks increases with $(Na^+ + K^+)/Ca^{2+}$. Gao et al. (2007) even observed that complexes as NaF increase, those of HF, CaF^+ decrease when Na ions are added into water.

In addition, trace elemental concentrations were determined in aliquots of the produced water samples using ICP-QMS and results are presented in Table 5.24 earlier above. In all a total of 15 trace elements namely Al, As, Ba, Br, Cu, Fe, Hg, K, Mn, Ni, Pb, Sc, Sr,

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V and Zn were analysed. The quite high concentrations of Ba and Sr in produced water samples as shown in Table 5.23, is in agreement with the previous comments on scaling tendency of the oilfield equipment. Also, in order to compare the two analytical tools ICP-QMS and gamma spectrometry, elemental K was calculated from ^{40}K activity concentrations obtained via gamma spectrometry using relation in presented in chapter 4 and results compared well with uncertainty range of 15%.

Finally, additional information about the morphology and elemental composition of a solid dried fraction from a produced water sample was obtained using a scanning electron microscope (SEM), with some results shown in Figures 5.16 and 5.17. As it is shown in Figure 5.17 it is possible to find the presence of particles in the dried residue dominated mostly by Ba and Sr in agreement with the results obtained by ICP-QMS and with the high activity concentrations of Ra found in the waters (Sr, Ba and Ra members of the alkali earth metal group, with a similar behaviour).

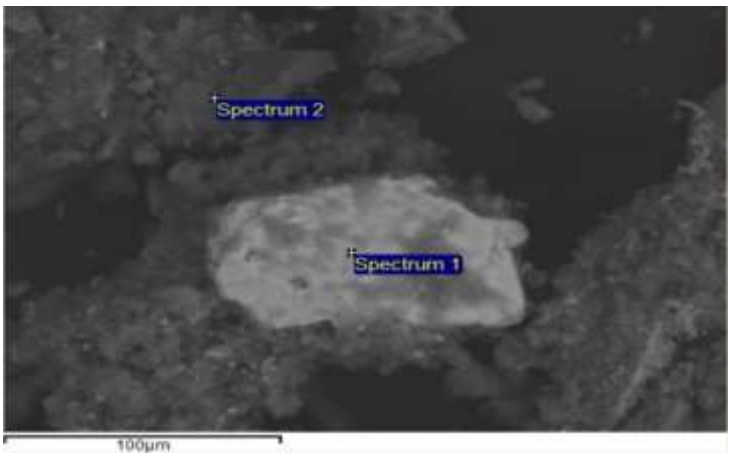

Figure 5.16: BEI image of particulate matter in produced water via SEM

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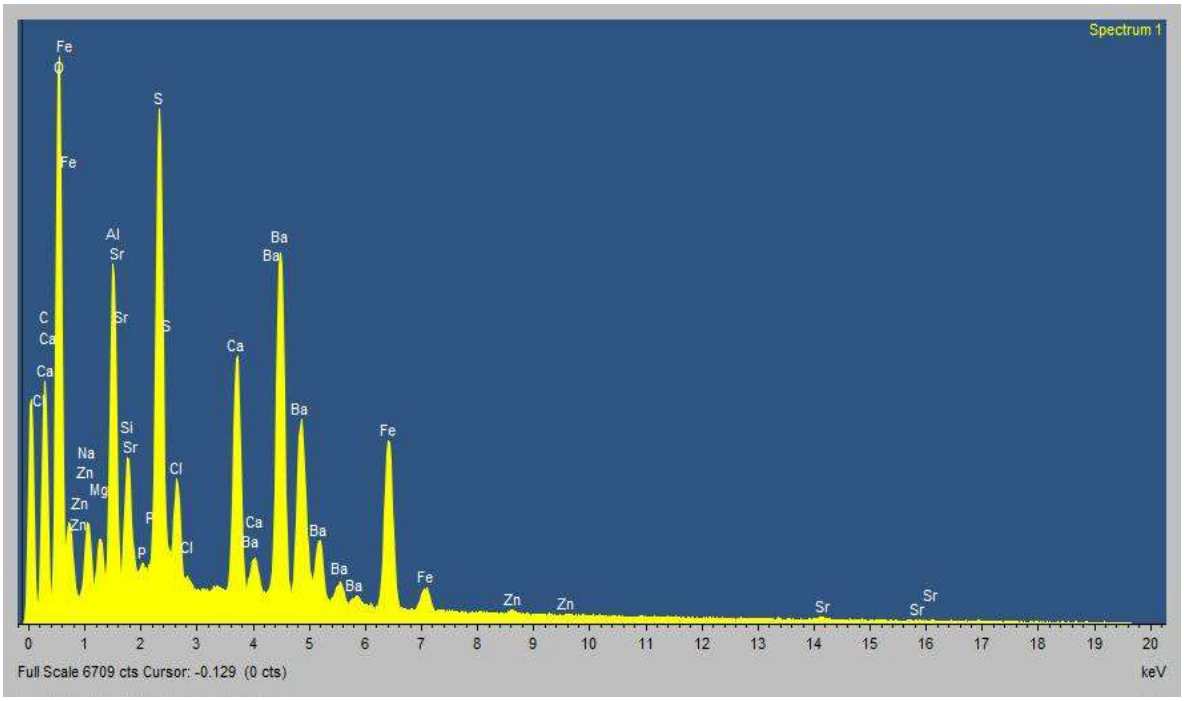

Figure 5.17: Elemental composition of particulate matter in produced water via SEM

5.3.1.3 Crude oil

Crude oil samples were collected the same time as the produced water from the same oilfield platforms.

Activity Concentrations of ^{40}K, ^{238}U and ^{232}Th series radionuclides by gamma and alpha Spectrometry in crude oil samples from the two oilfields are presented in Tables 5.25 and 5.26. Specific activities of ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th, ^{234}Th, ^{224}Ra and ^{40}K for crude oil samples from both fields were below the MDA (Table 25) for two days counting in 1L marinelli beaker geometry.

The activities of ^{210}Po for Jubilee field crude oil were in the range 408 – 434 $mBq.L^{-1}$ with average 418 ± 10 $mBq.L^{-1}$, the activities of ^{230}Th in the range 215 – 242 $mBq.L^{-1}$ with average 228 ± 11 $mBq.L^{-1}$, the activities of ^{232}Th in the range 58–67 $mBq.L^{-1}$ with average 62 ± 4 $Bq.L^{-1}$ and the activities of ^{234}U and ^{238}U were below MDA respectively.

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Table 5.25: Minimum detectable activity Concentration of ^{40}K, ^{238}U and ^{232}Th series radionuclides in crude oil by Gamma Spectrometry

	Activity Concentration ($Bq.L^{-1}$)						
	Th-234	Ra-226	Pb-210	Ra-228	Th-228	Ra-224	K-40
MDA	<0.55	<0.11	<1.10	<0.12	<0.06	<0.05	<0.91

Table 5.26: ^{234}U, ^{238}U, ^{230}Th, ^{232}Th and ^{210}Po activity concentrations determined in the crude oil samples analysed

Sample ID	Activity Concentration ($mBq.L^{-1}$)				
	^{234}U	^{238}U	^{230}Th	^{232}Th	^{210}Po
JC1	<5.29	<3.75	237 ± 45	61 ± 26	408 ± 76
JC2	<9.28	<5.73	222 ± 43	58 ± 24	416 ± 78
JC3	<5.91	<5.38	242 ± 47	67 ± 28	434 ± 80
JC4	<4.98	<5.23	215 ± 41	64 ± 25	421 ± 78
JC5	<5.75	<5.54	225 ± 43	59 ± 25	411 ± 76
SC6	158 ± 44	149 ± 38	135 ± 46	53 ± 11	385 ± 72
SC7	206 ± 87	131 ± 42	147 ± 67	55 ± 10	465 ± 83
SC8	116 ±37	101 ± 32	93 ± 29	50 ± 12	419 ± 101
SC9	188 ±75	158 ± 47	118 ± 39	56 ± 14	504 ± 105
SC10	296 ±91	168 ± 61	127 ± 49	58 ± 20	561 ± 107

*JC -Jubilee crude oil; SC-Saltpond crude oil

For Saltpond field crude oil, the activities of ^{234}U were in the range 116–296 $mBq.L^{-1}$ with average 179 ± 75 $mBq.L^{-1}$, the activities of ^{238}U in the range 101–168 $mBq.L^{-1}$ with average 141 ± 26 $Bq.L^{-1}$, the activities of ^{210}Po in the range 385 – 561 $mBq.L^{-1}$ with average 467 ± 69 $mBq.L^{-1}$, the activities of ^{230}Th in the range 93 – 147 $mBq.L^{-1}$ with average 124 ± 20 $mBq.L^{-1}$ and the activities of ^{232}Th in the range 50–58 $Bq.L^{-1}$ with average 54 ± 3 $Bq.L^{-1}$ respectively. It was observed that the activities in crude oil from both fields were insignificant, however the Saltpond field crude oil were generally higher than that of Jubilee field similarly as discussed above for produced water samples for both fields. The results of Crude oil for both oilfields were comparable with a reported worldwide range by Jonkers et al., 1997 as presented earlier in the literature review (Table 2.6).

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5.3.1.4 Oily waste water and wash water

The oily waste water samples were collected from Zeal environmental Technologies an onshore oil waste treatment facility. All oily waste water were from the Jubilee field only and wash water is the final waste water discharged to the general sewage after treating the oily waste water at the onshore waste facility which involves separating the oily waste into oil based mud, wash water and traces of recovered oil.

Table 5.27 presents activity concentrations of radionuclides ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th, ^{234}Th, ^{224}Ra and ^{40}K in oily waste water and wash water samples determined by gamma spectrometry. The mean activity concentration of ^{226}Ra for oily waste water samples was 7.6 ± 1.4 Bq.L^{-1} (in a range of 6.4–9.1 Bq.L^{-1}); for ^{210}Pb, the average was 4.5 ± 0.9 Bq.L^{-1} (in a range of 3.7–5.5 Bq.L^{-1}); while for ^{228}Ra, the average activity concentration was 4.4 ± 0.3 Bq.L^{-1} (in a range of 4.1–4.7 Bq.L^{-1}); and for ^{228}Th, the average was 5.4 ± 0.2 Bq.L^{-1} (in a range of 5.2–5.6 Bq.L^{-1}). In the case of ^{234}Th, the average was 3.0 ± 1.0 Bq.L^{-1} (in a range of 2.0–4.0 Bq.L^{-1}); for ^{224}Ra, the average activity concentration was 5.3 ± 0.3 Bq.L^{-1} (in a range of 5.1–5.6 Bq.L^{-1}); whiles for ^{40}K, the average was 25.7 ± 2.0 Bq.L^{-1}(in a range of 24.0 – 28.0 Bq.L^{-1}).

Generally specific activities in oily waste water samples (from Jubilee field) were quite similar to that of produced water concentrations from the Jubilee field discussed above.

Comparison of results of ^{234}Th (^{238}U) obtained via gamma with results of ^{238}U via alpha measurements show good agreement as seen in Tables 5.27 and 5.28

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Table 5.27: Activity Concentration of ^{40}K, ^{238}U, ^{232}Th series radionuclides in oily waste water and wash water samples by Gamma Spectrometry

Sample ID	Concentration (Bq.L^{-1})						
	^{234}Th	^{226}Ra	^{210}Pb	^{228}Ra	^{228}Th	^{40}K	^{224}Ra
OW1	2.0 ± 0.1	7.2 ± 0.5	5.5 ± 0.4	4.1 ± 0.1	5.2 ± 0.1	25 ± 3	5.1 ± 0.1
OW2	4.0 ± 0.2	9.1 ± 1.0	4.4 ± 0.3	4.7 ± 0.2	5.6 ± 0.2	28 ± 2	5.6 ± 0.2
OW3	3.0 ± 0.1	6.4 ± 0.8	3.7 ± 0.2	4.5 ± 0.2	5.4 ± 0.1	24 ± 3	5.3 ± 0.1
WW4	<0.64	0.06 ± 0.01	<1.22	0.11 ± 0.04	0.05 ± 0.01	24 ± 3	0.06 ± 0.01

*WW-wash water; OW- oily waste water

The average concentrations of all radionuclides from Table 5.27 except ^{228}Ra and ^{234}Th for the oily waste water obtained in this study also exceeded the aqueous Derived Release Limit (DRL) of Canadian guideline governing liquid discharges (Health Canada, 2011). However it is worth noting that, per the current regulations of the EPA of Ghana, the oily waste water are not to be discharged to sea but are brought onshore to oil and gas waste management company for treatment which involves mainly separating oily waste water into oil based mud, water (wash water) and recovered crude oil.

The activity concentrations of radionuclides in the wash water sample presented also shown in Table 5.27 were generally low compared to the oily waste water and the aqueous Derived Release Limit (DRL) of Canadian guideline governing liquid discharges (Health Canada, 2011) which ideally should be the case since the wash water is discharged to the general sewage after separation from oily waste water.

Table 5.28 shows the activity concentrations of ^{234}U, ^{238}U, ^{210}Po, ^{230}Th and ^{232}Th in the oily waste water and wash water samples determined by alpha spectrometry. The activities of ^{234}U were in the range 3.1–3.9 Bq.L^{-1} with average 3.5 ± 0.4 Bq.L^{-1}, the activities of ^{238}U in the range 2.3–3.7 Bq.L^{-1} with average 2.9 ± 0.7 Bq.L^{-1}, the activities of ^{210}Po in the range 5.0 – 5.4 Bq.L^{-1} with average 5.2 ± 0.2 Bq.L^{-1}, the activities of ^{230}Th in the range 3.0 – 4.30 Bq.L^{-1} with average 3.5 ± 0.7 Bq.L^{-1} and the activities of ^{232}Th in the range 1.9–3.0 Bq.L^{-1} with average 2.4 ± 0.6 Bq.L^{-1} respectively. Similarly,

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the wash water concentrations were lower compared to oily waste water with concentrations ranging from <0.01 to 1.0 m Bq.L^{-1}. However, concentrations of ^{234}U, ^{238}U, ^{210}Po, ^{230}Th and ^{232}Th generally higher in oily waste water compared to produced water from the same field.

Table 5.28: Activity Concentrations of ^{238}U, ^{234}U, ^{210}Po, ^{230}Th and ^{232}Th in oily waste water and wash water samples determined by alpha-particle spectrometry.

Sample ID	Concentration (Bq.L^{-1})						
	^{234}U	^{235}U	^{238}U	^{210}Po	^{230}Th	^{232}Th	Y(U/Th/Po)
OW1	3.1 ± 0.2	0.24 ± 0.04	2.3 ± 0.2	5.0 ± 0.5	3.0 ± 0.4	1.9 ± 0.1	62/48/67
OW2	3.9 ± 0.3	0.35 ± 0.06	3.7 ± 0.4	5.4 ± 0.5	4.3 ± 0.5	3.0 ± 0.3	60/40/62
OW3	3.5 ± 0.2	0.22 ± 0.05	2.8 ± 0.3	5.1 ± 0.5	3.3 ± 0.2	2.2 ± 0.2	59/55/64
WW4*	4.2 ± 0.8	<0.01	1.5 ± 0.2	1.0 ± 0.1	2.2 ± 0.5	<0.01	50/38/47

*WW4 Concentrations are in mBq.L^{-1}

5.3.2 Scale, Sludge, Ash, Mud and Mud block

All solid waste samples are associated to the Jubilee field only. The scale samples were collected from produced water pipes at storage and maintenance facility onshore. The sludge was obtained from the bottom of the produced water treatment tank from Jubilee field platform. The mud and mud block taken from zeal environmental technologies facility were obtained after separation of oily waste water discussed above. The Ash obtained from incineration of various waste from Jubilee field were also collected from Zeal environmental technologies.

The results of radioactivity concentrations of radionuclides ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th, ^{224}Ra and ^{40}K in scale and sludge samples determined by gamma spectrometry are presented in Table 5.29. The average value of the activity concentration of ^{226}Ra for Scale samples was 43.9 ± 8.1 kBq.kg^{-1} (in a range of 38.5–58.3kBq.kg^{-1}); for ^{210}Pb, the average was 0.36 ± 0.15 kBqkg^{-1}(in a range of 0.20–0.60 kBq.kg^{-1}); while for ^{228}Ra, the

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average activity concentration was 30.3 ± 5.1 kBq.kg^{-1} (in a range of 26.8 – 39.2 kBq.kg^{-1}); and for ^{228}Th, the average was 11.2 ± 2.8 kBq.kg^{-1} (in a range of 8.6–15.9 kBq.kg^{-1}). In the case of ^{224}Ra the average activity concentration was 11.2 ± 2.6 kBq.kg^{-1} (in a range of 8.8–15.4 kBq.kg^{-1}); whiles for ^{40}K, the average is 1.8 ± 0.4 kBq.kg^{-1} (in a range of 1.3–2.3 kBq.kg^{-1}).

Tables 5.29: Activity Concentration of ^{40}K, ^{238}U, ^{232}Th series radionuclides in Scales and sludge samples by Gamma Spectrometry

Sample ID	Concentration (kBq.kg^{-1})					
	^{226}Ra	^{210}Pb	^{228}Ra	^{228}Th	^{40}K	^{224}Ra
SC1	38.5 ± 0.4	0.4 ± 0.01	26.8 ± 0.1	9.8± 0.8	1.8 ± 0.2	9.6 ± 0.9
SC2	41.5 ± 0.4	0.3 ± 0.01	28.2 ± 0.5	11.0 ± 0.6	1.8 ± 0.1	10.9 ± 0.8
SC3	40.7 ± 0.4	0.2 ± 0.01	27.6 ± 0.5	10.9± 0.5	1.3 ± 0.2	11.2 ± 0.7
SC4	40.7 ± 0.1	0.3 ± 0.01	29.9 ± 0.5	8.6 ± 0.6	2.0 ± 0.3	8.8 ± 0.6
SC5	58.3 ± 0.2	0.6 ± 0.1	39.2 ± 0.7	15.9 ± 1.2	2.3 ± 0.3	15.4 ± 0.9
SLW1	0.60 ± 0.01	0.04 ± 0.01	0.30 ± 0.01	0.14 ± 0.01	0.05 ± 0.01	0.13 ± 0.01
SL2	0.90 ± 0.02	0.05 ± 0.01	0.62 ± 0.01	0.22 ± 0.01	0.07 ± 0.01	0.22 ± 0.01
SL3	0.95 ± 0.03	0.07 ± 0.01	0.73 ± 0.02	0.35 ± 0.01	0.09 ± 0.02	0.36 ± 0.01
SL4	7.4 ± 0.1	0.15 ± 0.01	4.9 ± 0.4	1.6 ± 0.1	0.4 ± 0.04	1.7 ± 0.1
SL5	8.4 ± 0.2	0.23 ± 0.02	5.6 ± 0.2	1.8 ± 0.2	0.5 ± 0.05	1.9 ± 0.3
SLW6	5.4 ± 0.1	0.12 ± 0.01	3.7 ± 0.01	1.2 ± 0.1	0.3 ± 0.1	1.2 ± 0.1

*SC -Scale; SL-Sludge (dry); SLW-Sludge (wet)

For sludge samples, the average specific activity of ^{226}Ra was 3.9 ± 3.6 kBq.kg^{-1} (in a range of 0.6–8.4kBq.kg^{-1}); for ^{210}Pb, the average is 0.11 ± 0.07 kBqkg^{-1}(in a range of 0.04–0.23 kBq.kg^{-1}); while for ^{228}Ra, the average activity concentration was 2.6 ± 2.4 kBq.kg^{-1} (in a range of 0.3–5.6 kBq.kg^{-1}); and for ^{228}Th, the average was 0.9 ± 0.7 kBq.kg^{-1} (in a range of 0.1–1.8 kBq.kg^{-1}). In the case of ^{224}Ra the average activity concentration was 0.9 ± 0.8 kBq.kg^{-1} (in a range of 0.1–1.9 kBq.kg^{-1}); whiles for ^{40}K, the average was 0.24 ± 0.19 kBq.kg^{-1} (in a range of 0.05–0.50 kBq.kg^{-1}). The specific activity of ^{234}Th for both scale and sludge was below minimum detectable activity value of ~ 0.01 kBq.kg^{-1}

Table 5.30 presents the specific activities of ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th, ^{234}Th, ^{224}Ra and ^{40}K in Ash, Mud and Mud block samples determined by gamma spectrometry. The mean activity concentration of ^{226}Ra for Ash samples was 17.3 ± 2.4 Bq.kg^{-1} (in a range of

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14.0–21.0 Bq.kg^{-1}); for ^{210}Pb, the average was 14.2 ± 3.0 Bqkg^{-1}(in a range of 10.0–19.0 Bq.kg^{-1}); while for ^{228}Ra, the average activity concentration was 11.0 ± 1.4 Bq.kg^{-1} (in a range of 9.0–13.0 Bq.kg^{-1}); and for ^{228}Th, the average was 13.5 ± 1.9 Bq.kg^{-1} (in a range of 11.0–16.0 Bq.kg^{-1}). In the case of ^{234}Th, the average was 8.3 ± 2.6 Bqkg^{-1}(in a range of 5.0–12.0 Bq.kg^{-1}); for ^{224}Ra, the average activity concentration was 12.5 ± 1.9 Bq.kg^{-1} (in a range of 10.0–15.0 Bq.kg^{-1}); whiles for ^{40}K, the average was 110.5 ± 9.5 Bq.kg^{-1} (in a range of 74.0–150.0 Bq.kg^{-1}).

Table 5.30: Activity Concentration of ^{40}K, ^{238}U, ^{232}Th series radionuclides in Ash, Mud and Mud block samples by Gamma Spectrometry

Sample ID	Concentration (Bq.kg^{-1})						
	^{234}Th	^{226}Ra	^{210}Pb	^{228}Ra	^{228}Th	^{40}K	^{224}Ra
AS1	9 ± 2	14 ± 2	19 ± 2	11 ± 4	11 ± 1	120 ± 10	13 ± 4
AS2	5 ± 1	16 ± 2	13 ± 1	9 ± 3	12 ± 1	135 ± 10	11 ± 2
AS3	6 ± 1	17 ± 2	15 ± 2	10 ± 1	13 ± 1	150 ± 17	12 ± 2
AS4	10 ± 1	19 ± 1	13 ± 1	12 ± 1	15± 1	86 ± 8	14 ± 2
AS5	12 ± 2	21 ± 4	15 ± 2	13 ± 1	16 ± 2	98 ± 10	15 ± 3
AS6	8 ± 1	17 ± 3	10 ± 1	11 ± 1	14± 1	74 ± 7	10 ± 3
RM1	8 ± 2	14 ± 2	7 ± 2	7 ± 1	8 ± 1	60 ± 5	7.8 ± 0.2
RM2	7 ± 1	12 ± 1	6 ± 1	6.5 ± 0.3	6.8 ± 0.4	48 ± 4	7.0 ± 0.2
RM3	6 ± 1	10 ± 2	4 ± 1	4.8 ± 0.1	5.8 ± 0.2	27 ± 2	5.9 ± 0.2
RM4	6.2 ± 0.5	11 ± 2	5 ± 1	6.0 ± 0.2	6.3 ± 0.2	37 ± 3	6.1 ± 0.2
MB1	7 ± 2	23 ± 1	22 ± 2	14 ± 3	13 ± 3	230 ± 30	12 ± 4
MB2	4.0 ± 0.1	16 ± 4	10 ± 1	9 ± 1	9 ± 3	160 ± 18	8 ± 3

*AS -Ash; RM-oil based mud; MB-oil based mud block

For mud samples, the mean specific activity of ^{226}Ra was 11.8 ± 1.7 Bq.kg^{-1} (in a range of 10.0–14.0 Bq.kg^{-1}); for ^{210}Pb, the average was 5.5 ± 1.3 Bqkg^{-1} (in a range of 4.0–7.0 Bq.kg^{-1}); while for ^{228}Ra, the average activity concentration was 6.1 ± 0.9 Bq.kg^{-1} (in a range of 4.8–7.0 Bq.kg^{-1}); and for ^{228}Th, the average was 6.7 ± 0.9 Bq.kg^{-1} (in a range of 5.8–8.0 Bq.kg^{-1}). In the case of ^{234}Th, the average was 6.8 ± 1.0 Bqkg^{-1}(in a range of 6.0–8.0 Bq.kg^{-1}); for ^{224}Ra, the average activity concentration was 6.7 ± 0.9 Bq.kg^{-1} (in a

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range of 5.9–7.8 Bq.kg^{-1}); whiles for ^{40}K, the average was 43.0 ± 14.2 Bq.kg^{-1} (in a range of 27.0 – 60.0 Bq.kg^{-1}).

For mud block samples, the average specific activity of ^{226}Ra was 19.5 ± 5.0 Bq.kg^{-1} (in a range of 16.0–23.0 Bq.kg^{-1}); for ^{210}Pb, the average was 16.0 ± 8.5 Bqkg^{-1} (in a range of 10.0–22.0 Bq.kg^{-1}); while for ^{228}Ra, the average activity concentration was 11.5 ± 3.5 Bq.kg^{-1} (in a range of 9.0–14.0 Bq.kg^{-1}); and for ^{228}Th, the average was 11.0 ± 2.8 Bq.kg^{-1} (in a range of 9.0–13.0 Bq.kg^{-1}). In the case of ^{234}Th, the average was 5.5 ± 2.1 Bqkg^{-1}(in a range of 4.0–7.0 Bq.kg^{-1}); for ^{224}Ra, the average activity concentration was 10.0 ± 2.8 Bq.kg^{-1} (in a range of 8.0–12.0 Bq.kg^{-1}); whiles for ^{40}K, the average was 195.0 ± 49.5 Bq.kg^{-1} (in a range of 160.0 – 230.0 Bq.kg^{-1}).

To summarize the general trend of specific activity levels of ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th, and ^{224}Ra in the sample types, Figure 5.18 was used to compare the average concentrations in the five solid NORM waste sample types investigated. The comparison shows scales recorded highest concentrations followed by sludge, mud block, and ash and lowest being mud. The higher concentrations of radionuclides in mud block than the mud which was used for the moulding could be attributed to radioactivity concentration contributed by Portland limestone cement added to the mud during block moulding. Natural radionuclide Concentrations of U, Th –series and ^{40}K of Ghanaian cements has been presented quite recently (Kpeglo et al., 2011; 2012).

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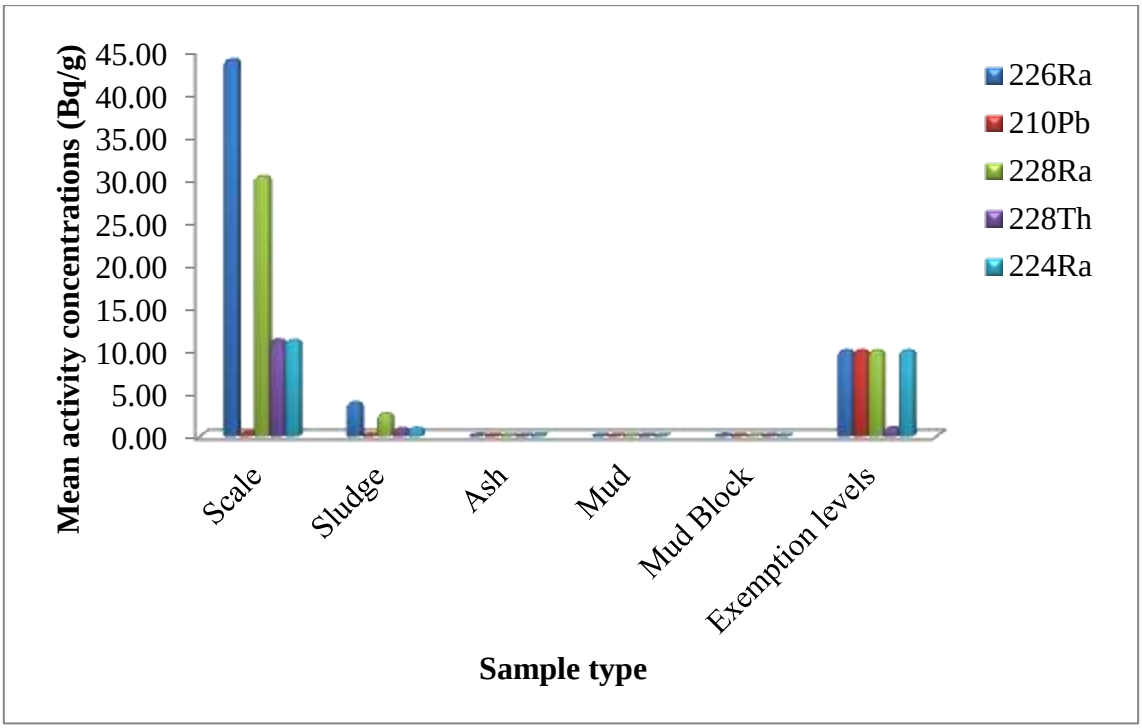

Figure 5.18: Comparison of mean specific activity of radionuclides in waste samples with the Exemption levels

The significant variations observed for sludge samples as shown in Table 5.29 suggest the following interesting points; firstly, the radioactivity of the NORM is higher in the dry phase of sludge than the wet phase which is evident from the low specific activity recorded for wet sludge samples SLW1 and SLW6 in the both categories of sludge samples. Secondly, an increasing NORM radioactivity with production and age of wells is observed as samples (SL4-SLW6) collected in about one year interval after sample (SLW1-SL3) from the same separation tank and same wells showed very wide increase in activity concentration. In this regard regular monitoring of specific activity in the sludge from the oilfield may be necessary in order to proper manage the disposal of sludge in future.

It was also clear from Figure 5.18 that all radionuclides except ^{210}Pb compared for scale samples exceeded the IAEA Basic Safety Standards (BSS) exemption levels and hence there may be need to exert regulatory control of the NORMs residues.

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The results of ^{226}Ra and ^{228}Ra in scale and sludge were compared with data from other countries as shown in Table 5.31. The specific activities compare well with data from other countries around the world**.**

The range of activity concentration of ^{226}Ra and ^{228}Ra in Scale from the Jubilee oilfield of Ghana (this study) was higher than the range of values reported in Scale from other studies carried out in other Oilfields in Norway**,** Congo, Egypt and Kazakhstan **(**Lysebo et al., 1996; Testa et al., 1994; Abo-Elmagd et al., 2010; and Kadyrzhanov et al., 2005). On the other hand, the range of ^{226}Ra and ^{228}Ra specific activities found for scales in this work were lower than those recorded in some other work undertaken in various oil fields in the United Kingdom**,** United States of America, Egypt**,** Tunisia**,** Algeria**,** Syria**,** Malaysia and Brazil(E & P forum, 1987; White and Rood, 2001; Shawky et al., 2001; Heaton and Lambley, 1995; Hamlat et al., 2001; Al-Masri and Suman, 2003; Omar et al., 2004; Godoy and Crux, 2003; Gazineu and Hazin, 2008)**.**

For sludge, a similar comparison was also seen, whiles the range of ^{226}Ra and ^{228}Ra specific activities found in this work were higher than those recorded for other studies in Algeria, Malaysia, Norway and Syria (Heaton and Lambley, 1995; Omar et al., 2004; Lysebo et al., 1996 and Al-Masri and Suman, 2003), another study also carried out in Brazil (Godoy and Crux, 2003), is significantly higher than those found in this study for the oilfield of Ghana.

The variation in activity concentration of natural radionuclide content in NORM waste of different origins can be attributed to factors such as the geochemical and geological characteristics of reservoir rocks, age, the type of hydrocarbons produced and operating conditions for the oilfields.

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Table 5.31: Comparison of ^{226}Ra and ^{228}Ra in Scale and Sludge from Ghanaian oilfields with others published in literature

Country	Material	^{226}Ra ($kBq.kg^{-1}$)	^{228}Ra ($kBq.kg^{-1}$)	Reference
Algeria	Scale	1 – 950	-	Hamlat et al., 2001
Australia	Scale	21 – 250	48 – 300	APPEA, 2002
Brazil	Scale	19.1 – 323	4.2 – 235	Godoy and Crux, 2003
Brazil	Scale	121 – 3500	148 – 2195	Gazineu et at., 2005
Brazil	Scale	77.9 – 2110	101.5 – 1550	Gazineu and Hazin, 2008
Congo	Scale	0.097 – 0.151	-	Testa et al., 1994
Egypt	Scale	0.493 – 0.519	0.032 – 0.05	Abo-Elmagd et al., 2010
Egypt	Scale	7.541 – 143.262	35.46 – 368.654	Shawky et al., 2001
Ghana	Scale	38.5 – 58.3	26.8 – 39.2	Present study
Kazakhstan	Scale	0.51 - 51	0.2 – 10	Kadyrzhanov et al., 2005
Malaysia	Scale	114.3 – 187.75	130.12 – 206.63	Omar et al., 2004
Norway	Scale	0.3 – 32.3	0.3 – 33.5	Lysebo et al., 1996
Syria	Scale	147 – 1050	43 – 181	Al-Masri and Suman, 2003
Tunisia	Scale	4.3 – 658		Heaton and Lambley, 1995
UK	Scale	1 – 1000		E & P forum, 1987
USA	Scale	15.4 – 76.1		White and Rood, 2001
Algeria	Sludge	0.069 – 0.393		Heaton and Lambley, 1995
Brazil	Sludge	0.36 – 367	0.25 – 343	Godoy and Crux, 2003
Ghana	Sludge	0.6 – 8.4	0.3 – 5.6	Present study
Malaysia	Sludge	0.006 – 0.56	4.52	Omar et al., 2004
Norway	Sludge	0.1 – 4.7	0.1 – 4.6	Lysebo et al., 1996
Syria	Sludge	0.47 – 1	0.359 – 0.66	Al-Masri and Suman, 2003

The average age of the five scale samples which was estimated using relation explained earlier in chapter 4, were determined and found to be 1.13, 1.23, 1.30, 1.0 and 1.25 years, respectively. The age of scale samples gives vital information that will help in future planning and carrying out maintenance on production lines likely to be contaminated with scales.

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Table 5.32 presents specific activities of ^{234}U, ^{238}U, ^{210}Po, ^{230}Th and ^{232}Th determined using alpha spectrometry for scale, sludge, Ash, Mud and Mud block samples.

The activities of ^{234}U for scale samples were in the range 0.9–4.5 $Bq.kg^{-1}$ with average 1.9 ± 1.5 $Bq.kg^{-1}$, the activities of ^{238}U in the range 1.6–4.6 $Bq.kg^{-1}$ with average 2.5 ± 1.2 $Bq.kg^{-1}$, the activities of ^{210}Po in the range 66 – 166 $Bq.kg^{-1}$ with average 99 ± 39 $Bq.kg^{-1}$, the activities of ^{230}Th in the range 1.2 – 3.9 $Bq.kg^{-1}$ with average 1.9 ± 1.2 $Bq.kg^{-1}$ and the activities of ^{232}Th in the range 0.9–4.5 $Bq.kg^{-1}$ with average 1.9 ± 1.5 $Bq.kg^{-1}$ respectively.

For sludge , the specific activities of ^{234}U were in the range 3.0–13.3 $Bq.kg^{-1}$ with average 8.7 ± 3.9 $Bq.kg^{-1}$, the activities of ^{238}U in the range 2.0–12.0 $Bq.kg^{-1}$ with average 7.1 ± 4.1 $Bq.kg^{-1}$, the activities of ^{210}Po in the range 21 – 80 $Bq.kg^{-1}$ with average 51 ± 20 $Bq.kg^{-1}$, the activities of ^{230}Th in the range 0.8 – 5.8 $Bq.kg^{-1}$ with average 3.6 ± 1.9 $Bq.kg^{-1}$ and the activities of ^{232}Th in the range 0.4–13.0 $Bq.kg^{-1}$ with average 6.0 ± 5.5 $Bq.kg^{-1}$ respectively.

For ash samples, the activity concentrations of ^{234}U were in the range 4.5–8.5 $Bq.kg^{-1}$ with average 6.8 ± 1.4 $Bq.kg^{-1}$, the activities of ^{238}U in the range 4.5–9.1 $Bq.kg^{-1}$ with average 6.8 ± 1.7 $Bq.kg^{-1}$, the activities of ^{210}Po in the range 6.0 – 16.5 $Bq.kg^{-1}$ with average 9.4 ± 3.7 $Bq.kg^{-1}$, the activities of ^{230}Th in the range 4.8 – 8.8 $Bq.kg^{-1}$ with average 6.2 ± 1.5 $Bq.kg^{-1}$ and the activities of ^{232}Th in the range 1.4–6.0 $Bq.kg^{-1}$ with average 4.0 ± 1.6 $Bq.kg^{-1}$ respectively.

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Table 5.32: Activity Concentrations of ^{238}U, ^{235}U, ^{234}U, ^{210}Po, ^{230}Th and ^{232}Th in Scale, sludge, ash, mud and mud blocks samples determined by alpha-particle spectrometry

Sample ID	Concentration (Bq.kg^{-1})				
	^{234}U	^{238}U	^{210}Po	^{230}Th	^{232}Th
SC1	2.1 ± 0.2	1.6 ± 0.1	97 ± 4	1.3 ± 0.2	0.9 ± 0.1
SC2	2.9 ± 0.3	2.3 ± 0.5	66 ± 3	3.9 ± 0.3	4.5 ± 0.3
SC3	3.1 ± 0.3	2.4 ± 0.3	83 ± 5	1.3 ± 0.2	1.8 ± 0.3
SC4	5.5 ± 0.4	4.6 ± 0.4	82 ± 2	1.2 ± 0.1	1.1 ± 0.1
SC5	2.2 ± 0.2	1.8 ± 0.2	166 ± 7	1.7 ± 0.2	1.0 ± 0.1
SLw1	3.0 ± 0.1	2.0 ± 0.1	21 ± 3	2.9 ± 0.2	6.8 ± 0.3
SL2	7.0 ± 0.3	4.6 ± 0.3	50 ± 3	5.8 ± 0.5	13.0 ± 8
SL3	6.3 ± 0.3	4.0 ± 0.3	40 ± 3	5.4 ± 0.6	12.0 ± 1.0
SL4	11.6 ± 0.7	10.2 ± 0.6	80 ± 4	4.2 ± 0.4	2.5 ± 0.3
SL5	13.3 ± 0.8	12.0 ± 0.7	55 ± 2	0.8 ± 0.1	0.4 ± 0.01
SLw6	11.1 ± 0.5	9.9 ± 0.5	60 ± 2	2.4 ± 0.2	1.5 ± 0.1
AS1	7.1 ± 0.5	6.7 ± 0.4	16.5 ±1.1	5.8 ± 0.9	3.6 ± 0.7
AS2	4.5 ± 0.3	4.5 ± 0.3	6.0 ± 0.4	4.8 ± 0.3	1.4 ± 0.1
AS3	6.1 ± 0.4	5.2 ± 0.3	8.4 ± 0.5	5.0 ± 0.8	3.5 ± 0.7
AS4	7.4 ± 0.3	7.9 ± 0.4	8.6 ± 0.3	6.8 ± 0.3	4.9 ± 0.4
AS5	8.5 ± 0.5	9.1 ± 0.8	9.2 ± 0.6	8.8 ± 0.6	6.0 ± 0.5
AS6	6.9 ± 0.3	7.3 ± 0.4	7.5 ± 0.4	6.1 ± 0.6	4.6 ± 0.5
RM1	5.9 ± 0.3	5.8 ± 0.3	6.0 ± 0.5	5.5 ± 0.3	3.0 ± 0.2
RM2	5.9 ± 0.4	5.1 ± 0.4	6.6 ± 0.5	8.8 ± 0.7	2.3 ± 0.3
RM3	3.7 ± 0.2	3.6 ± 0.2	5.2 ± 0.3	3.2 ± 0.4	1.7 ± 0.3
RM4	5.4 ± 0.5	5.7 ± 0.6	6.0 ± 0.4	5.2 ± 0.5	1.1 ± 0.2
MB1	6.9 ± 0.3	6.2 ± 0.3	7.7 ± 0.5	6.5 ± 0.3	4.2 ± 0.2
MB2	4.2 ± 0.2	4.1 ± 0.2	4.7± 0.3	4.3 ± 0.3	2.0 ± 0.2

For Mud samples, the activity concentrations of ^{234}U were in the range 3.7–5.9 Bq.kg^{-1} with average 5.2 ± 1.0 Bq.kg^{-1}, the activities of ^{238}U in the range 3.6–5.8 Bq.kg^{-1} with average 5.1 ± 1.0 Bq.kg^{-1}, the activities of ^{210}Po in the range 5.2 – 6.6 Bq.kg^{-1} with average 6.0 ± 0.6 Bq.kg^{-1}, the activities of ^{230}Th in the range 3.2 – 8.8 Bq.kg^{-1} with average 5.7 ± 2.3 Bq.kg^{-1} and the activities of ^{232}Th in the range 1.1–3.0 Bq.kg^{-1} with average 2.0 ± 0.8 Bq.kg^{-1} respectively.

For mud block samples, , the activity concentrations of ^{234}U were in the range 4.2–6.9 Bq.kg^{-1} with average 5.6 ± 1.9 Bq.kg^{-1}, the activities of ^{238}U in the range 4.1–6.2 Bq.kg^{-1} with average 5.2 ± 1.5 Bq.kg^{-1}, the activities of ^{210}Po in the range 4.7 – 7.7 Bq.kg^{-1} with

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average 6.2 ± 2.1 Bq.kg^{-1}, the activities of ^{230}Th in the range 4.3 – 6.5 Bq.kg^{-1} with average 5.4 ± 1.6 Bq.kg^{-1} and the activities of ^{232}Th in the range 2.0–4.2Bq.kg^{-1} with average 3.1 ± 1.6 Bq.kg^{-1} respectively.

In comparison of the activity concentration values of radionuclides between the samples as shown in Figure 5.19, it can be observed that the activity concentrations of ^{210}Po decreased in the order Scale>Sludge>Ash>Mud block>Mud. For ^{234}U, ^{238}U, ^{230}Th and ^{232}Th the trend increased in the order of Scale<Mud<Mud block<Ash<Sludge.

It was also clear from Figure 5.19 that, ^{210}Po level was highest in all the solid waste samples via alpha, an indication that ^{210}Po may contribute significantly to total alpha activity. This could be a significant source of exposure to workers via internal contamination by inhalation during maintenance, decommissioning operations and waste processing and disposal.

Generally activity concentrations of U and Th-isotopes as well as ^{210}Po for all solid NORM waste samples in this study were much lower compared to that of radium isotopes discussed earlier above.

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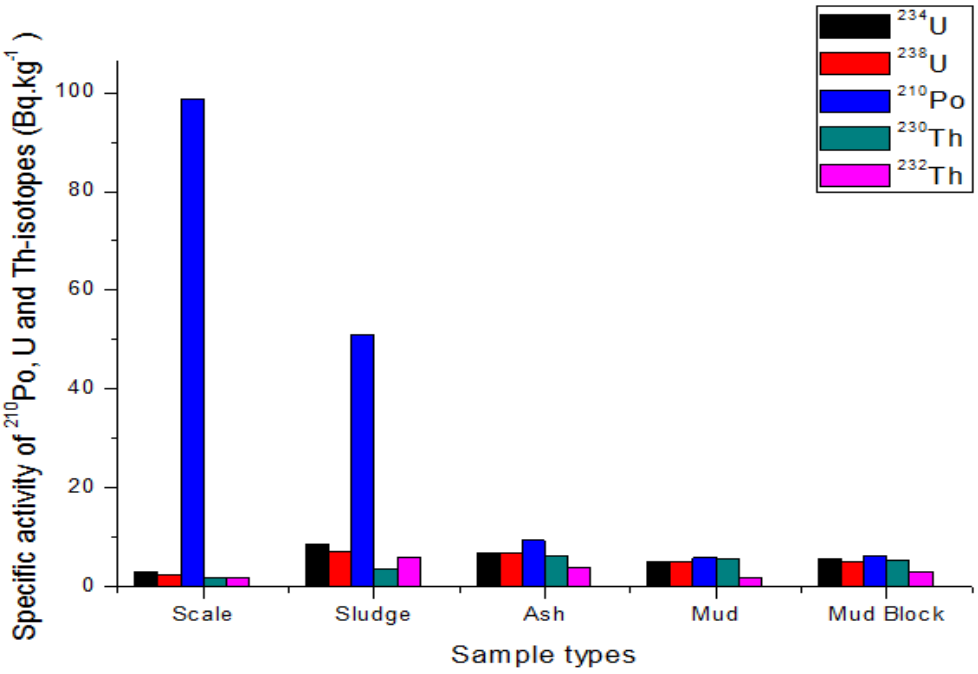

Figure 5.19: Comparison of mean specific activities of radionuclides in waste samples

Scale, Sludge, ash, mud block and mud materials that may contain significant levels of NORMs, if not properly handled and disposed off appropriately may be a source of public exposure concern. This is particularly so, if these materials are discarded indiscriminately without recourse to environmental pollution concerns and consequently if the soil is used for construction or building purposes. For this reason, the hazard assessments were estimated to determine the potential health impact should these NORM contaminated soil or materials be used for building purposes.

The results of Table 5.33 presents the mean and range of radium equivalent (Ra_{eq}), external (H_{ex}) and the internal hazard (H_{in}), external gamma absorbed dose rate ($D_{\gamma r}$), and external annual effective dose ($E_{\gamma, ext}$) associated with NORM contaminated solid waste samples. The average values of the Ra_{eq}, H_{ex}, H_{in}, $D_{\gamma r}$, and $E_{\gamma, ext}$ were 119889 ± 23064 $Bq.kg^{-1}$, 324±562, 444 ± 85, 52410 ± 10114 $nGy.h^{-1}$ and 73 ± 14 $mSv.y^{-1}$ for scale; 10432 ± 9207 $Bq.kg^{-1}$, 28 ±25, 39 ± 35, 4569 ± 4035 $nGy.h^{-1}$ and 6.4 ± 5.7 $mSv.y^{-1}$for sludge; 101 ± 17 $Bq.kg^{-1}$, 0.30 ±0.05, 0.40 ± 0.07, 45 ± 8 $nGy.h^{-1}$ and 0.06 ± 0.01 $mSv.y^{-1}$for ash; 55 ± 9

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Bq.kg^{-1}, 0.15 ±0.02, 0.21 ± 0.04, 25 ± 4 nGy.h^{-1} and 0.040 ± 0.006 mSv.y^{-1}for mud; 103 ± 9207 Bq.kg^{-1}, 0.28 ±0.09, 0.39 ± 0.13, 47 ± 15 nGy.h^{-1} and 0.065 ± 0.021 mSv.y^{-1}for mud block respectively. The external annual effective dose were calculated using exposure period of 2000hrs/year for occupationally exposed worker.

Table 5.33: 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 waste samples

Samples		R_{aeq} (Bq.kg^{-1})	H_{ex}	H_{in}	$D_{\gamma r}$ (nGy.h^{-1})	$E_{\gamma, ext}$ (mSv.y^{-1})
Scale	Range	102006 - 159892	276 - 432	380 - 591	44630 - 69890	63 - 98
	mean	119889 ± 23064	324 ± 62	444 ± 85	52410 ± 10114	73 ± 14
Sludge	Range	1459 – 21968	4 – 59	6 – 83	642 – 9625	0.9 – 13.5
	mean	10432 ± 9207	28 ± 25	39 ± 35	4569 ± 4035	6.4 ± 5.7
Ash	Range	78 – 127	0.21 – 0.34	0.29 – 0.48	35 – 57	0.050 – 0.080
	mean	101 ± 17	0.30 ± 0.05	0.40 ± 0.07	45 ± 8	0.060 ± 0.010
Mud	Range	46 – 66	0.12 – 0.18	0.18 – 0.26	20 – 30	0.029 – 0.042
	mean	55 ± 9	0.15 ± 0.02	0.21 ± 0.04	25 ± 4	0.040 ± 0.006
Mud block	Range	80 – 126	0.22 – 0.34	0.30 – 0.50	36 – 57	0.051 – 0.080
	mean	103 ± 33	0.28 ± 0.09	0.39 ± 0.13	47 ± 15	0.065 ± 0.021
*RRV		370	1	1	60	

**RRV- Recommended reference value*

It is clearly seen from Table 5.33 that all hazard parameters for scale and sludge samples presented as previously explained under chapter 4 exceeded the recommended reference values for safe use and hence an indication that the Scale and sludge samples could present significant future radiological risk if not properly managed. On the other hand, the radiological hazard assessments determined for the ash, mud and mud block samples were all below the recommended reference values and thus may not pose any significant radiological radiation hazard.

The radon emanation fraction (EF) is an important radiological index used to evaluate the amount of ^{222}Rn released from the waste materials containing naturally occurring radionuclides. In this study, the assessment of EF was related only to ^{222}Rn decayed

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from its parent ^{226}Ra content in the waste. Since ^{222}Rn and its respective decay progenies (e.g. ^{210}Pb and ^{210}Po) have longer half lives than that of other radon isotopes, ^{222}Rn is considered to be more radiologically hazardous to human health than radionuclides of other radon isotopes. Table 5.34 show the values of the emanation fraction (EF) and radon mass exhalation rate (Rn_{ex}) for the NORM waste samples. The mean EF and (Rn_{ex}) were 0.560 ± 0.002 and 51647 ± 9615; 0.578 ± 0.018 and 4883 ± 4476; 0.551 ± 0.014 and 20.1± 3.0; 0.498 ± 0.009 and 12.3 ± 2.0; 0.534 ± 0.015 and 21.8 ± 4.9 for scale, sludge, ash, mud and mud block respectively.

Table 5.34: Radon emanation fraction and Radon mass exhalation rate for waste samples

Sample ID	Radon emanation fraction (EF)	Radon mass exhalation rate (Rn_{ex}) ($\mu Bq.kg^{-1}.s^{-1}$)
SC1	0.560 ± 0.011	45276 ± 2142
SC2	0.561 ± 0.012	48891 ± 2321
SC3	0.560 ± 0.012	47863 ± 2270
SC4	0.556 ± 0.010	47521 ± 2352
SC5	0.561 ± 0.011	68683 ± 3310
SLw1	0.570 ± 0.012	718 ± 25
SL2	0.563 ± 0.011	1064 ± 43
SL3	0.556 ± 0.010	1109 ± 45
SL4	0.605 ± 0.016	9402 ± 400
SL5	0.591 ± 0.015	10425 ± 478
SLw6	0.580 ± 0.014	6577 ± 258
AS1	0.564 ± 0.012	16.6 ± 0.5
AS2	0.525 ± 0.010	17.6 ± 0.6
AS3	0.547 ± 0.010	19.5 ± 0.7
AS4	0.550 ± 0.010	21.9 ± 0.7
AS5	0.561 ± 0.011	24.7 ± 0.8
AS6	0.560 ± 0.010	20.0 ± 0.7
RM1	0.510 ± 0.008	15.0 ± 0.4
RM2	0.500 ± 0.008	12.6 ± 0.4
RM3	0.489 ± 0.008	10.3 ± 0.3
RM4	0.494 ± 0.007	11.4 ± 0.3
MB1	0.523 ± 0.010	25.3 ± 0.8
MB2	0.544 ± 0.010	18.3 ± 0.6

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The comparison of Normalized (weighted fraction of their total) average values of ^{226}Ra concentration, Radon emanation fraction and Radon mass exhalation rate as well as the Correlation between ^{226}Ra with Radon emanation fraction and Radon mass exhalation rate for waste samples for waste samples are presented in Figures 5.20 and 5.21.

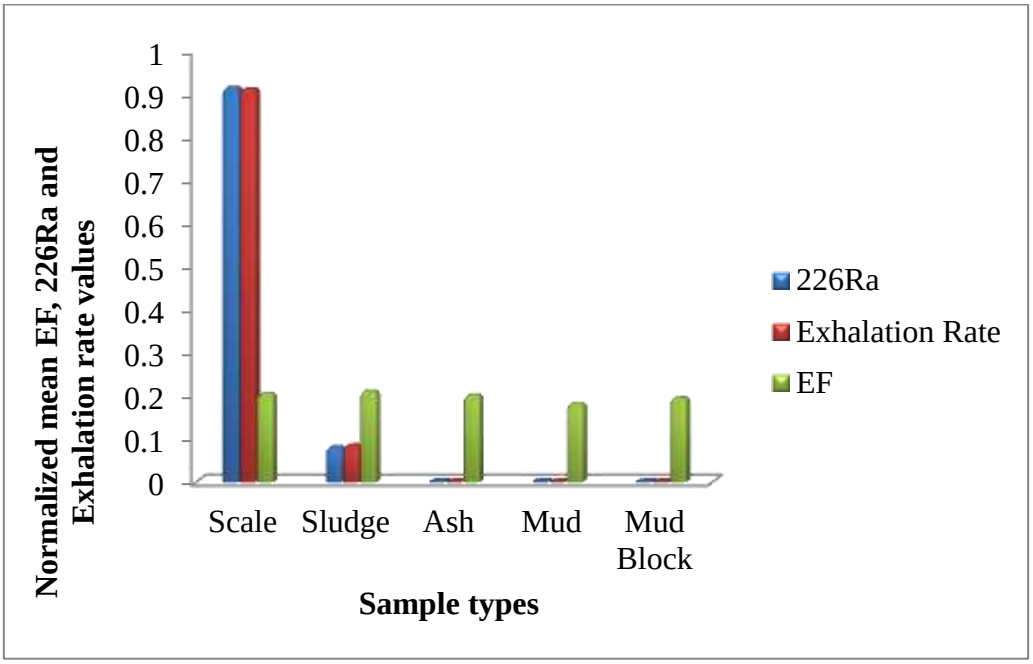

Figure 5.20: Comparison of the Normalized average values of ^{226}Ra concentration, Radon emanation fraction and Radon mass exhalation rate for waste samples

It was observed from Figures 5.20 and 5.21 that sludge samples recorded slightly higher emanation fraction values than scale samples even though scales recorded much higher ^{226}Ra activity than scales as presented earlier above. This difference is probably due primarily to the less porous structure of the pipe scale which serves to restrict the rate at which ^{222}Rn is released from the material. The Radon mass exhalation rate (production rate) on the other hand showed an increasing trend with increasing ^{226}Ra activity as well a very good linear correlation (R^2=0.999).

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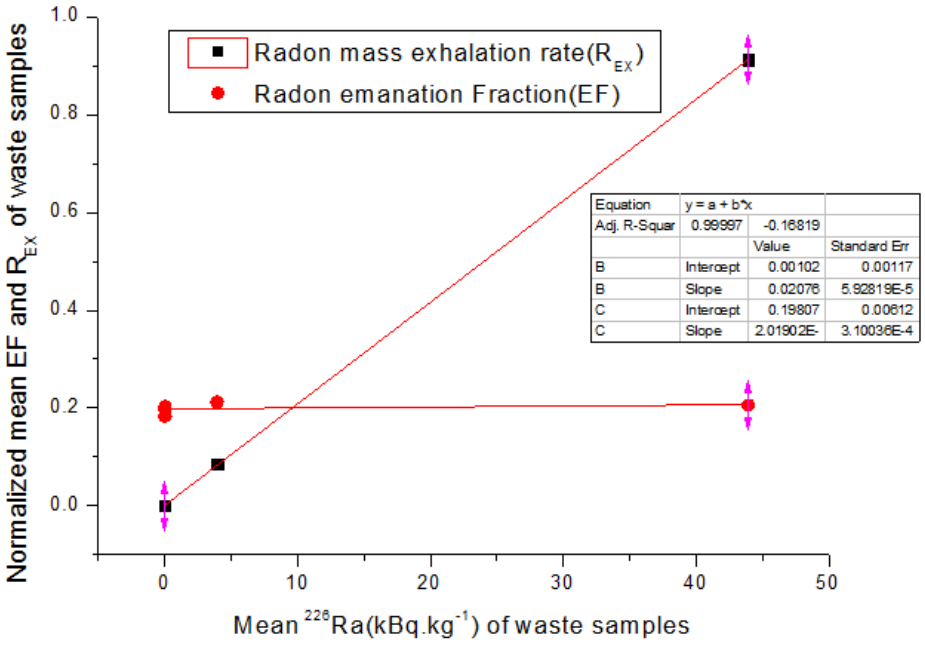

Figure 5.21: Correlation between ^{226}Ra with Radon emanation fraction and Radon mass exhalation rate for waste samples

Overall, the current study suggests that Rn release is dependent to a large degree on the physical characteristics of the medium containing the NORM radionuclides.

In order to assess the committed dose from the air borne radon likely to be inhaled or ingested directly by persons that may work closely to the scale samples, the annual effective dose was estimated from the radon concentration obtained via ambient measurements on the field from pipes at storage and maintenance facility and the results are presented in Figure 5.22 and summarized in Tables 5.35 and 5.36. The ^{222}Rn concentrations measured in air were 21 – 194 Bq.m^{-3} with average 113 ± 49 Bq.m^{-3} for outdoor and 200 – 548 Bq.m^{-3} with average 334 ± 94 Bq.m^{-3} for indoor. The corresponding annual effective doses calculated were in the range of 0.2 – 2.1 mSv.y^{-1} with an average of 1.2 ± 0.5 mSv.y^{-1} and 5.1 – 13.8 mSv.y^{-1} with an average of 8.4 ± 2.4 mSv.y^{-1} for outdoor and indoor air borne concentrations respectively.

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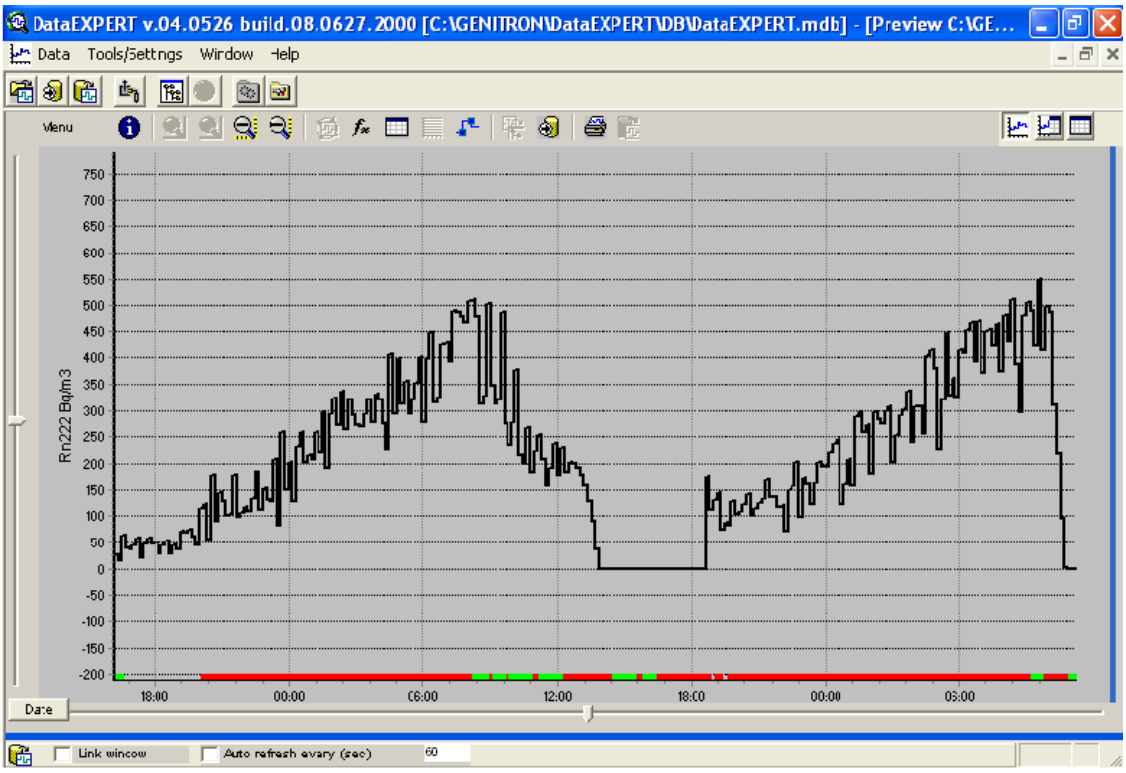

Figure 5.22: Ambient ^{222}Rn concentration measured at storage and maintenance facility for pipes embedded with scales using alpha guard

Table 5.35: Annual effective dose from inhalation of outdoor ^{222}Rn concentration for scale samples embedded in pipes and mud processing and block moulding facility

Area		^{222}Rn(Bq.m^{-3})	Effective dose(mSv.y^{-1})
Scale pipes storage & maintenance facility	Mean	113 ± 49	1.2 ± 0.5
	Range	21 - 194	0.2 – 2.1
Mud & mud block facility	Mean	8.5 ± 4.9	0.09 ± 0.05
	Range	2 - 19	0.02 – 0.20

Table 5.36: Annual effective dose from inhalation of indoor ^{222}Rn concentration for scale samples embedded in pipes

Area		^{222}Rn(Bq.m^{-3})	Effective dose(mSv.y^{-1})
Scale pipes storage & maintenance facility	Mean	334 ± 94	8.4 ± 2.4
	Range	200 - 548	5.1 – 13.8

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Similarly air borne radon measurements were carried out at the mud treatment and mud block moulding section of the onshore oil and gas waste treatment facility, Zeal Environmental Technologies limited and the results are presented in Figure 5.21 and Table 5.34. The ^{222}Rn concentrations measured in air were 2 – 19 Bq.m^{-3} with average 8.5 ± 4.9 Bq.m^{-3} and a corresponding average annual effective dose of 0.09 ± 0.05 mSv.y^{-1} in a range of 0.02 – 0.20 mSv.y^{-1}.

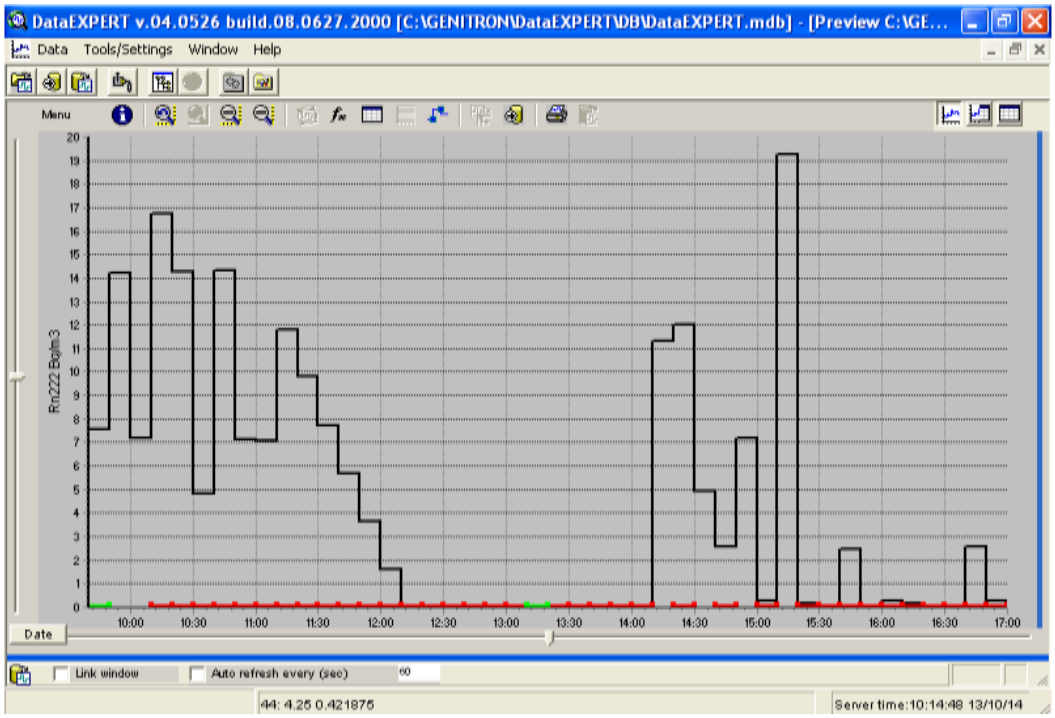

Figure 5.23: Ambient ^{222}Rn concentration measured at oily based mud treatment and block moulding facility using Alpha Guard

The airborne radon concentration measurements were made at average conditions of temperature, atmospheric pressure, and relative humidity with mean values of 34.5 ^{o}C, 100.3 kPa and 90.4 % respectively.

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By comparison of results, it is observed that indoor concentrations were about 3 times higher than that of outdoor measurements as a result of diffusion and dilution outdoor. This indicates that, one of the most effective means of reducing radon exposure is to provide proper and effective ventilation when the levels are high in an enclosed area. From Tables 5.35 and 5.36 it can be seen that, the airborne radon concentration are within the ICRP recommended value of 200-600 Bq/m^3 in dwellings and below the value of 1000 Bq/m^3 for workers (IAEA,1996).

The deposition of contaminated NORM waste particularly scales and sludge in pipes and vessels may produce significant external gamma dose rates inside and outside these components. Table 5.37 presents the annual effective dose rate measured inside and outside for pipes with embedded scales. The annual effective dose measured externally for pipes ranged from 0.6 – 1.0 mSv.y^{-1} with an average of 0.8 ± 0.3 mSv.y^{-1} while the measured internally for pipes ranged from 2.2 – 2.4 mSv.y^{-1} with an average of 2.3 ± 0.1 mSv.y^{-1}.

Table 5.37: Ambient effective dose rate measured externally and internally for scale samples embedded in pipes

	Effective dose (mSv.y^{-1}) externally measured	Effective dose (mSv.y^{-1}) internally measured
Mean	0.8 ± 0.3	2.3 ± 0.1
Range	0.6 -1.0	2.2 – 2.4

It can be seen from the results that the shielding provided by the walls of the pipes reduced the external dose rate by a factor of 3.

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Short lived progeny of the radium isotopes, in particular ^{226}Ra, emit gamma radiation capable of penetrating the walls of these components, and the high energy photon emitted by ^{208}Tl (583 keV and 2614 keV) (one of the progeny of ^{228}Th) can contribute significantly to the dose rate on outside surfaces when scale has been accumulating over a period of several months. The dose rates depend on the amount and activity concentrations of the radionuclides present inside and the shielding provided by the pipe or vessel walls. Maximum dose rates are usually in the range of up to a few microsieverts per hour. In exceptional cases, dose rates measured directly on the outside surfaces of production equipment have reached several hundred microsieverts per hour, which is about 1000 times greater than normal background values due to cosmic radiation and terrestrial radiation.

Where scales are present, opening the system for maintenance or for other purposes will increase dose rates. External exposure can be restricted only by maximizing the distance from the source, and minimizing duration of exposure within the area of concern. In practice, restrictions on access and occupancy time are found to be effective in reducing doses to workers. Deposits consisting almost exclusively of ^{210}Pb cannot be assessed by measurements outside closed plant and equipment. Neither the low energy gamma emissions of ^{210}Pb nor the beta particles emitted penetrate the steel walls. Therefore, ^{210}Pb is not considered to be an external exposure hazard but could be a very serious internal hazard if inhaled and/or ingested.

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5.3.2.1 Morphological and elemental composition of NORM waste Samples

Figures 5.24 – 5.32 present morphological and elemental compositions of particles in same sludge, scale ash, mud and mud block samples at different spots by SEM. From the figures the elements Al, Ba, Ca, Cl, Cu, Fe, K, Mg, Na, P, Pb S, Si, Sr, and Zn were identified and semi qualitatively quantified. Noticeable from the results of the SEM analysis for scale is the fact of a non- uniform distribution of elements in the particles of the scale samples as could be seen from figures with Ba and S at various spots in the same sample. This notwithstanding, Ba and S were seen all the various spot of the particles in the scale sample. The results in the figures are therefore indicative that, the composition of the scale samples is more of barium sulphate. This facilitated the co-precipitation of the radium isotopes with the barium complexes during scales formation.

Generally heavy metal concentrations increased in the order mud<mud block<Ash<sludge <scale.

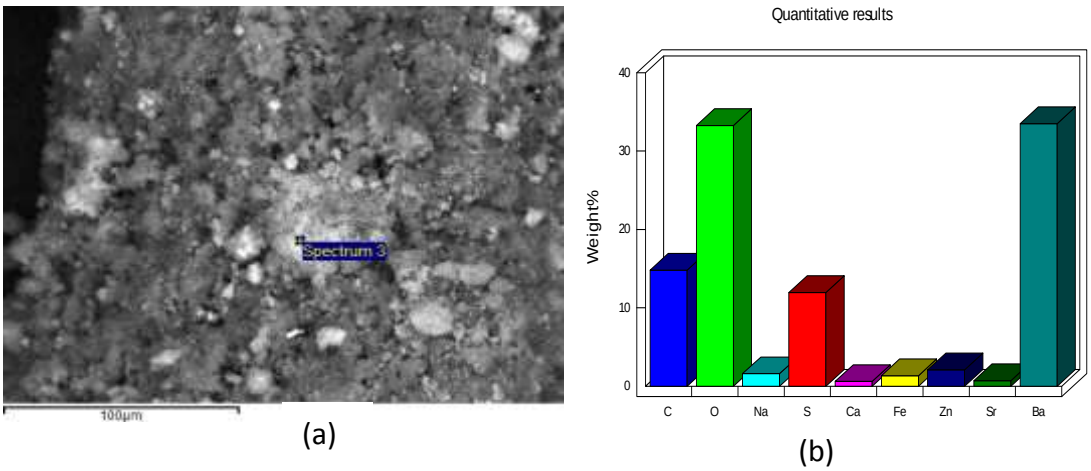

Figure 5.24: Results of SEM analysis for particles of scale (spot 1) with (a) showing grain size and (b) elemental composition

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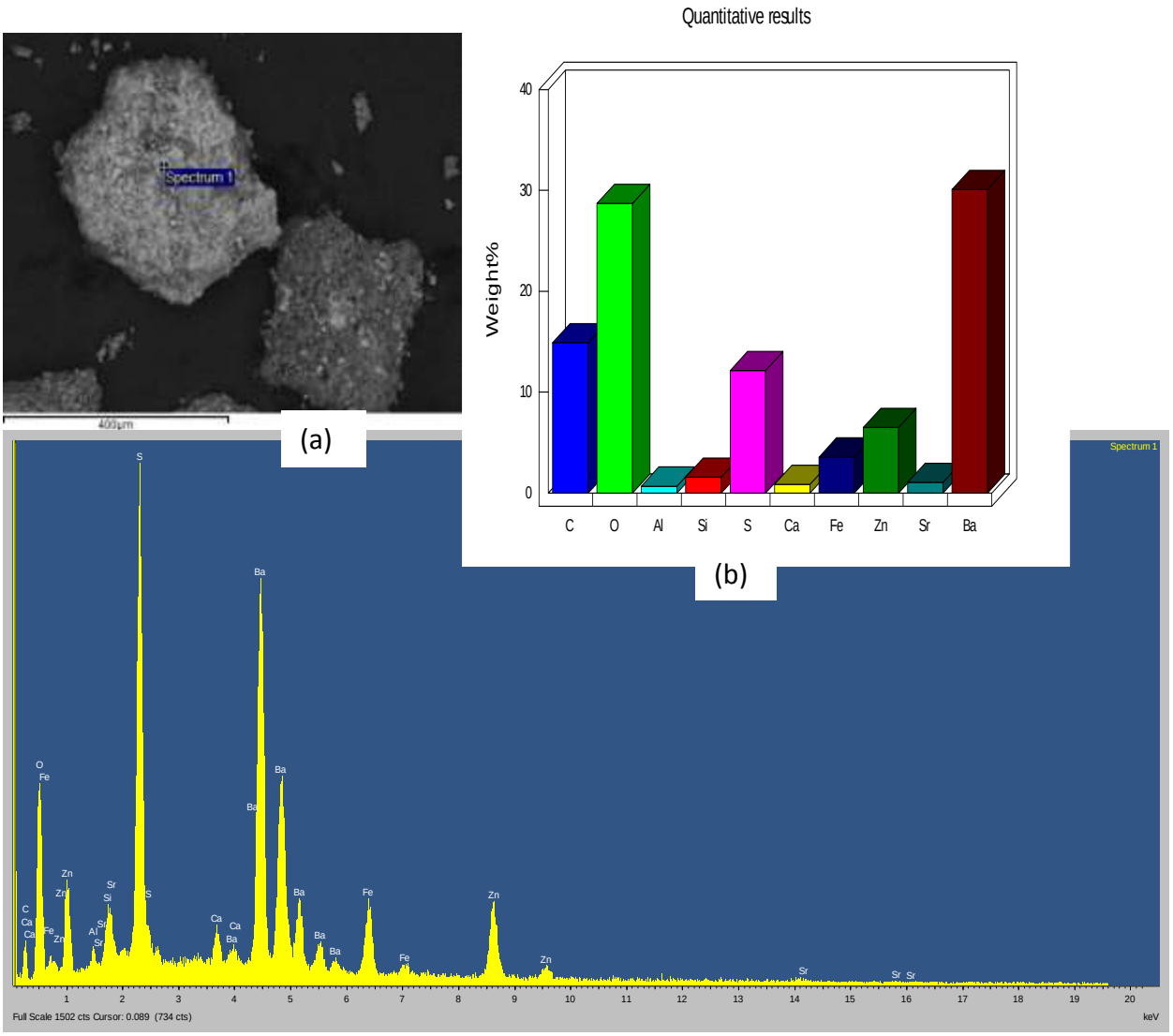

Figure 5.25: Results of SEM analysis for particles of scale (spot 2) with (a) showing grain size and (b) elemental composition

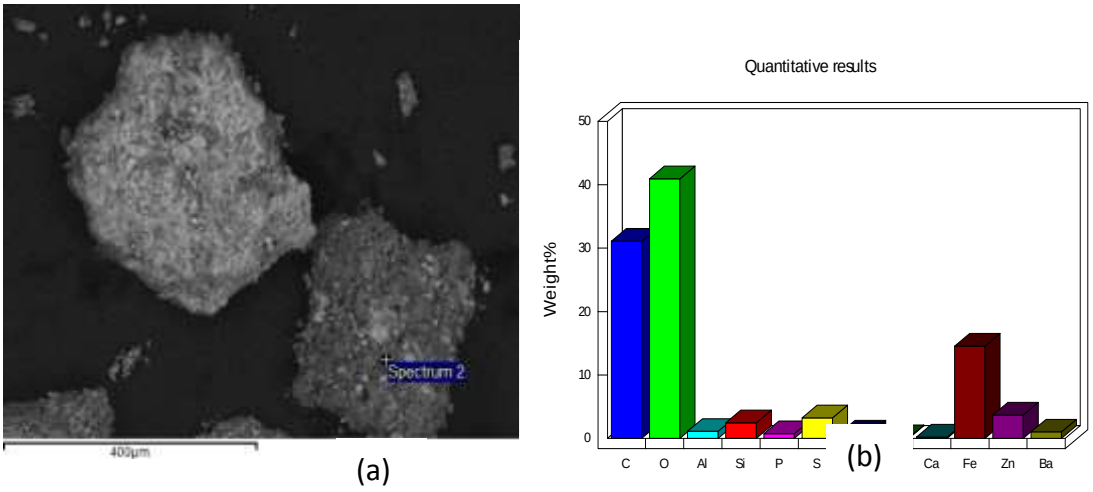

Figure 5.26: Results of SEM analysis for particles of scale (spot 3) with (a) showing grain size and (b) elemental composition

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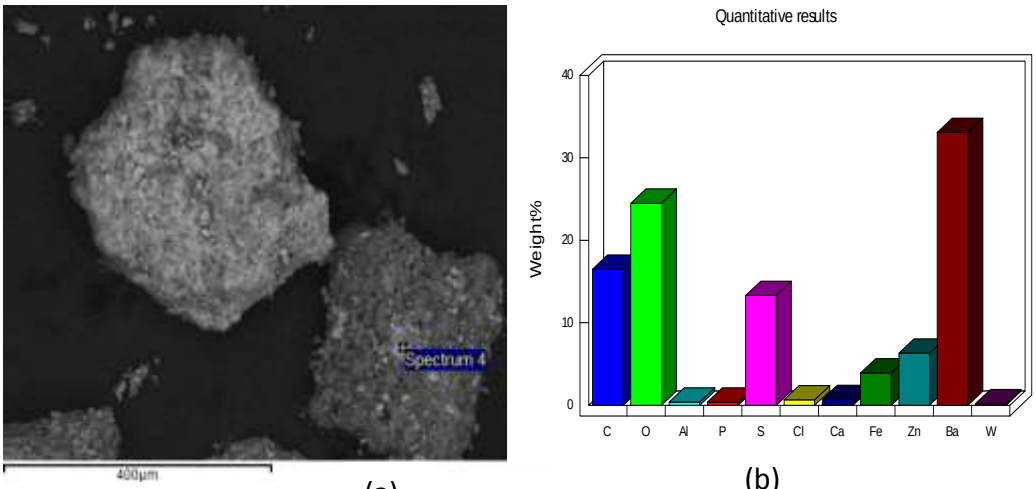
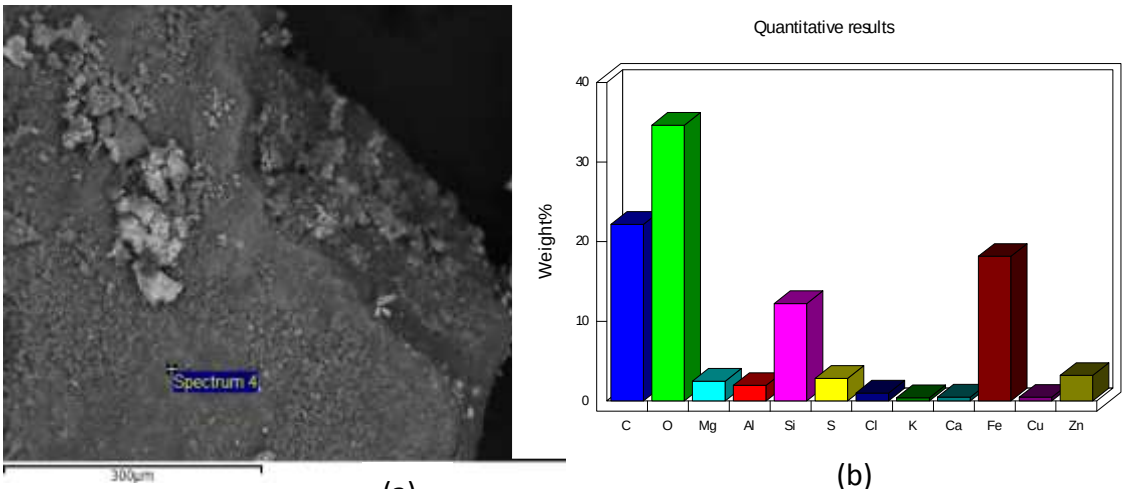


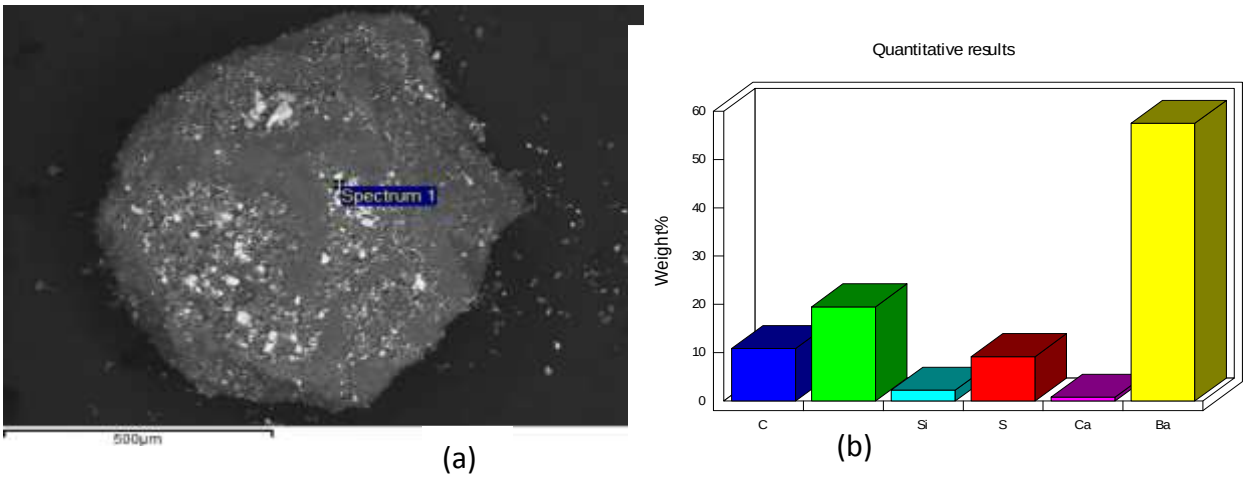
(a) (b)

Figure 5.27: Results of SEM analysis for particles of scale (spot 4) with (a) showing grain size and (b) elemental composition



(a) (b)

Figure 5.28: Results of SEM analysis for particles of sludge with (a) showing grain size and (b) elemental composition



(a) (b)

Figure 5.29: Results of SEM analysis for particles of mud block with (a) showing grain size and (b) elemental composition

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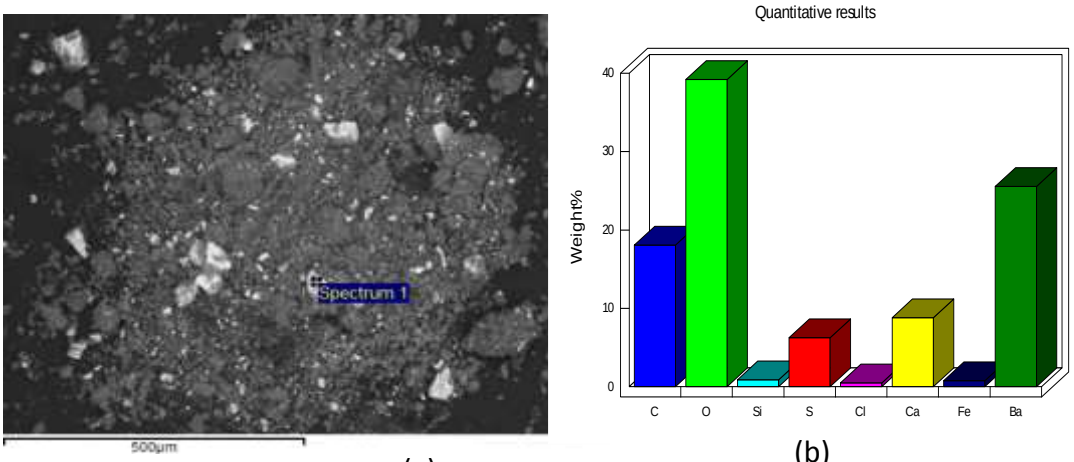
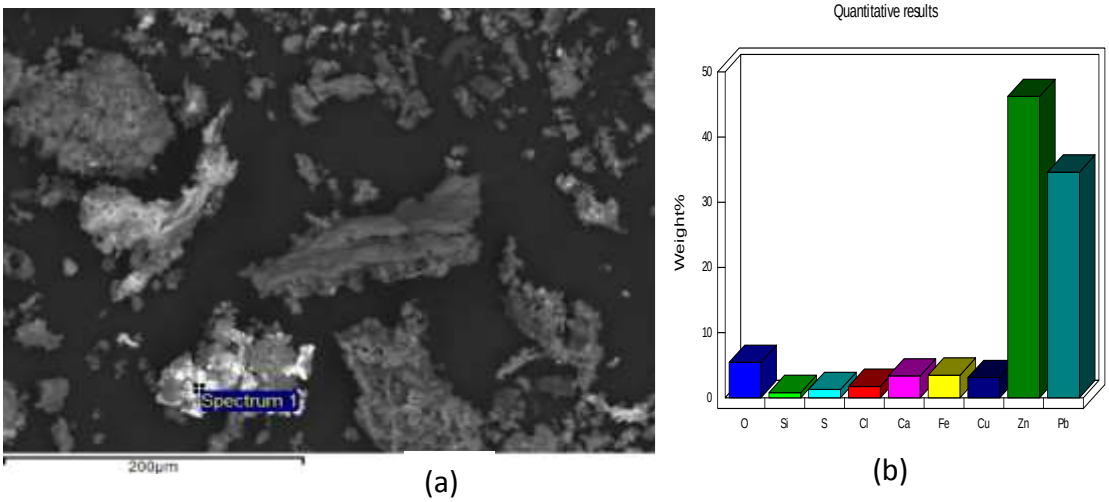


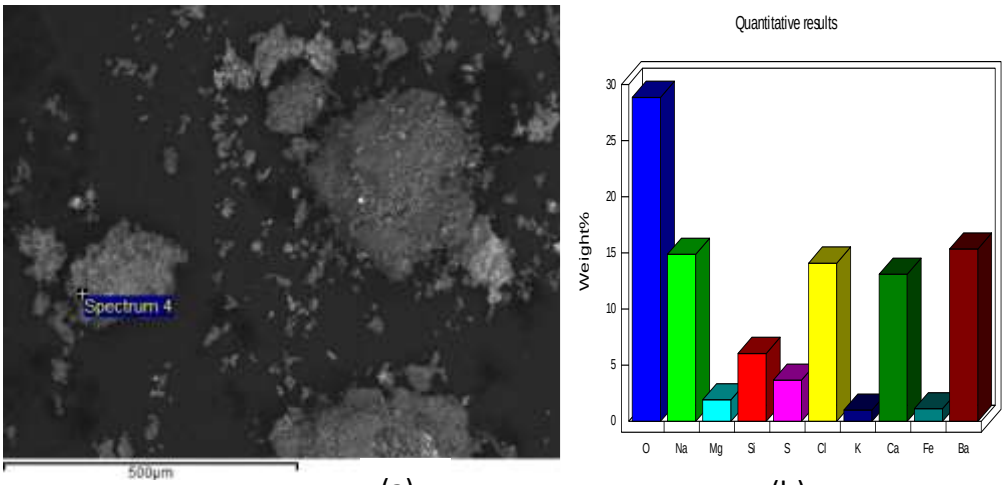
(a) (b)

Figure 5.30: Results of SEM analysis for particles of oil based mud with (a) showing grain size and (b) elemental composition



(a) (b)

Figure 5.31: Results of SEM analysis for particles of Ash (Spot1) with (a) showing grain size and (b) elemental composition



(a) (b)

Figure 5.32: Results of SEM analysis for particles of Ash (Spot2) with (a) showing grain size and (b) elemental composition

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5.4 Total annual effective dose and estimated fatality cancer risk and hereditary effects

The results of total annual effective dose and estimated fatality cancer risk and hereditary effects for public and occupational potential exposure pathways considered in this study using ICRP risk assessment methodology (ICRP, 1990; 2007) are presented in Tables 5.37 and 5.38. The total annual effective those for all exposure pathways was 0.35 mSv for the public and 80.86 for workers. From Table 5.37, it can be seen that the various components contributing to the total effective dose for the public ranged from 0.02 mSv (5.7%) in ingestion of water samples to 0.25 mSv (71.4%) in airborne radon. The contributing components to the total annual effective dose for workers as presented in Table 5.38, ranged from 0.04 mSv (0.05%) in external gamma dose of U, Th and K in mud to 73 mSv (90.3%) in in external gamma dose of U, Th and K in Scale.

The total annual effective dose of 0.35 mSv obtained for the public is also below the ICRP recommended dose limit of 1 $mSv.y^{-1}$ for members of the public. However, total annual effective dose of 80.86 mSv obtained in this study for workers clearly exceeds the ICRP recommended dose limit for an occupationally exposed worker of 20 $mSv.y^{-1}$ averaged over 5years but not exceeding 50 $mSv.y^{-1}$ in any single year.

It is important to point out however that, comparison of equivalent doses shown in Table 5.38 clearly indicate the external gamma dose due to U, Th and K in scale and sludge samples alone were 73 mSv representing 90.3% and 6.4 mSv representing 7.9% for scale and sludge respectively with both contributing 98.2% out of this total annual effective dose whiles the rest together contribute 1.8%.

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Table 5.38: Summary of annual equivalent doses, the estimated total effective dose and estimated risk components for the public exposure path ways considered

#	Exposure pathway	Average annual effective dose, mSv/year	Percentage contribution (%)	Cancer risk to population per year	Life time fatality cancer risk to population	Hereditary effects in population per year	Life time hereditary effects in population
1	External irradiation U, Th and K in Soil/ beach sand sample	0.08	22.9	4.4×10^{-6}	3.1×10^{-4}	1.6×10^{-7}	1.1×10^{-5}
2	Ingestion U, Th and K in water samples	0.02	5.7	1.1×10^{-6}	7.7×10^{-5}	4.0×10^{-8}	2.8×10^{-6}
3	Inhalation of Radon in air	0.25	71.4	1.4×10^{-5}	1.0×10^{-3}	5.0×10^{-7}	3.5×10^{-5}
	TOTAL	0.35	100	1.9×10^{-5}	1.3×10^{-3}	7.0×10^{-7}	4.9×10^{-5}

Table 5.39: Summary of annual equivalent doses, the estimated total effective dose and estimated risk components for the occupational exposure path ways considered

#	Exposure pathway	Average annual effective dose, mSv/year	Percentage contribution (%)	Fatality cancer risk to adult workers per year	Life time fatality cancer risk to adult workers	Hereditary effects in adult workers per year	Life time hereditary effects in adult workers
1	External irradiation U, Th and K in Scale	73	90.3	3.0×10^{-3}	21.0×10^{-2}	7.3×10^{-5}	5.1×10^{-3}
2	External irradiation U, Th and K in Sludge	6.4	7.9	2.6×10^{-4}	1.8×10^{-2}	6.4×10^{-6}	4.5×10^{-4}
3	External irradiation U, Th and K in Ash	0.06	0.07	2.5×10^{-6}	1.7×10^{-4}	6.0×10^{-8}	4.2×10^{-6}
4	External irradiation U, Th and K in mud	0.04	0.05	1.6×10^{-6}	1.1×10^{-4}	4.0×10^{-8}	2.8×10^{-6}
5	External irradiation U, Th and K in mud block	0.07	0.09	2.9×10^{-6}	2.0×10^{-4}	7.0×10^{-8}	4.9×10^{-6}
6	Inhalation of Radon in air Scale pipe storage	1.2	1.5	4.9×10^{-5}	3.4×10^{-3}	1.2×10^{-6}	8.4×10^{-5}
7	Inhalation of Radon in air mud and mud block facility	0.09	0.11	3.7×10^{-6}	2.6×10^{-4}	9.0×10^{-8}	6.3×10^{-6}
	TOTAL	80.86	~100	3.3×10^{-3}	23.2×10^{-2}	8.1×10^{-5}	5.7×10^{-3}

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Generally the calculated effective doses from the various samples as presented in Tables 5.38 and 5.39 are considered insignificant except those from scale and sludge which are of radiological importance and hence necessary measures needs to be put in place to avoid such potential occupational exposures in future.

The results of the lifetime fatality cancer risk to members of public were in the range of 7.7 x 10^{-5} due to ingestion of water to 1.0 x 10^{-3} due to inhalation of airborne radon. This means that approximately 8 persons out of 100, 000 people are likely to suffer from some form of cancer from ingestion of water and this risk is considered insignificant. Also in the case of 1.0 x 10^{-3} due to airborne radon , it also means that approximately 1 person out of 1,000 people are likely to suffer from cancer related diseases from irradiation due to low background radiation exposure. The estimated total lifetime fatality cancer risk and the lifetime hereditary effect were 1.3 x 10^{-3} and 4.9 x 10^{-5} respectively. This means that approximately 1 person out of 1,000 people are likely to suffer from cancer related diseases from exposure due to low background radiation. In the case of lifetime hereditary effect, approximately 5 persons out of 100, 000 is likely to suffer from some form of hereditary diseases. This means that the lifetime fatality cancer risk is slightly above the USEPA acceptable range of risks values of 1 x 10^{-6} to 1 x 10^{-4} (Federal register, 1991) for the population of the study area. The total fatality cancer risk exceeding the acceptable range 1 x 10^{-6} to 1 x 10^{-4} means that the value in this study is quite significant but however, a risk value of 1 x 10^{-6} that is 1 case of cancer out of 1 million people dying from cancer may be considered trivial.

In the case of hereditary effects, the lifetime risk factors evaluated varied in a range of 2.8 x 10^{-6} in water to 4.9 x 10^{-5} due to airborne radon with a total value of 6.3 x 10^{-5}. This means

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that approximately 6 persons out of 100,000 may suffer from some form of hereditary disorders and this can be considered insignificant.

On the other hand, the life time fatality cancer risk and life time hereditary effects associated with the total annual effective obtained in this study for occupationally exposed workers were 23.2 x 10^{-2} and 5.7 x 10^{-3} respectively. This means that approximately 23 workers out of 100 workers are likely to suffer from cancer related diseases from exposure due to low background radiation and approximately 6 persons out of 1000 may suffer from some form of hereditary disorders and this can be considered significant. Similarly as discussed above it is clear from Table 5.39 that the high risk of occupationally exposed workers to fatality cancer and hereditary effects is mainly due to the risk associated with the scale and sludge samples. In this regard, persons who may work directly with these scale and sludge samples particularly during maintenance, the transport of waste and contaminated equipment, the decontamination of equipment, and the processing and disposal of waste in the absence of suitable radiation protection measures may be prone to severe risk of fatality cancer and hereditary effects.

The predicted activity concentrations of ^{226}Ra and ^{228}Ra in fish and associated total cancer risks for edible, non-edible and whole body approach from human health risk model for produce water discharge are presented in table 5.39. The estimated mean total cancer risks were 4.42 x 10^{-9} in the range 4.17 x 10^{-9} to 4.52 x 10^{-9} for edible part approach, 1.01 x 10^{-8} in the range 9.54 x 10^{-9} to 1.03 x 10^{-8} for non-edible part approach and 1.45 x 10^{-8} in the range 1.37 x 10^{-8} to 1.50 x 10^{-8} for whole body approach. From the results in table 5.39 it can be deduced that the mean cancer risk in the whole body approach is 3.29 times the cancer risk

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in the edible part approach. However, the risks obtained in this study for all the three approaches were lower than USEPA acceptable range of risks values of 1 x 10^{-6} to 1 x 10^{-4} (Federal register, 1991) for lifetime cancer fatality. It can be deduced based on results of human health risk assessment model used in this study that, minimal effect to marine fish is expected from radium components in produced water discharged from the Saltpond field and associated human health risk is within allowable limit.

Table 5.40: Predicted ^{226}Ra and ^{228}Ra concentrations in fish and estimated associated cancer risk using human health risk assessment model

Predicted concentrations and Risk		Edible part	Non-edible part	Whole body
^{226}Ra (Bq.kg^{-1})	mean	0.23 ± 0.01	0.52 ± 0.02	0.75 ± 0.03
	range	0.21 – 0.25	0.47 – 0.56	0.70 – 0.81
^{228}Ra (Bq.kg^{-1})	mean	0.36 ± 0.02	0.84 ± 0.03	1.21 ± 0.04
	range	0.35 – 0.37	0.80 – 0.85	1.15 – 1.22
Total cancer risk	Mean	4.42 x 10^{-9}	1.01 x 10^{-8}	1.45 x 10^{-8}
	Min	4.17 x 10^{-9}	9.54 x 10^{-9}	1.37 x 10^{-8}
	Max	4.52 x 10^{-9}	1.03 x 10^{-8}	1.50 x 10^{-8}
	SD (1σ)	1.80 x 10^{-10}	4.12 x 10^{-10}	5.93 x 10^{-10}

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CHAPTER SIX

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Overview

This chapter presents the concluding remarks from the study. Recommendations have also been made to stakeholder institutions on the need for effective management and control of waste from oil and gas industries. The need for further studies has also been emphasized

6.1 Summary and Conclusions

The primary objective of this research work was to assess the radiological hazards and risks to members of the public and workers in the study area from exposure to natural sources of radiation as a result of the crude oil production activities and waste generation from the Saltpond and Jubilee oilfields of Ghana. Prior to this study, there have not been any investigations conducted to obtain data on the activity concentration levels of the natural radionuclides of ^{40}K, ^{238}U and ^{232}Th-series in crude oil and petroleum waste from the Saltpond and Jubilee oil fields, as well as, its impact on workers and critical group population. Consequently, the radiation doses and risks associated with these radionuclides have never been investigated before. High levels of these elements could pose radiological and/or chemical hazards.

The assessment of public radiation exposure in this study was conducted via three exposure pathways; external gamma-ray exposure from natural radioactivity concentrations in soil/beach sediments, internal exposure from ingestion of radionuclides in water and inhalation of radon gas whiles occupational exposure pathways considered were; external gamma-ray exposure from natural radioactivity concentrations in NORM waste (scale, sludge, oil based mud, incineration ash and mud block) and inhalation airborne radon.

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Additionally, a human health risk assessment methodology based on discharge of radium in produced water from an offshore platform was developed to predict cancer risk to humans from consumption of fish.

In order to establish data on the activity concentrations of natural radionuclides of ^{40}K, ^{238}U and ^{232}Th-series for exposure assessment in this study, methodologies for analysis were developed for alpha spectrometry after radiochemical separation and non-destructive gamma spectrometry as well as other complimentary analytical techniques.

In this study, data on the activity concentrations of ^{40}K, ^{238}U and ^{232}Th-series radionuclides in different types of samples as well as radiation doses and risks have been established. The activity concentrations of ^{234}U, ^{238}U, ^{210}Po, ^{230}Th, and ^{232}Th in different media for all the potential public and occupational exposure pathways were quantified using alpha spectrometry after radiochemical separation, whiles activities of ^{226}Ra, ^{210}Pb, ^{234}Th, ^{228}Ra, ^{228}Th, ^{224}Ra and ^{40}K were also determined by gamma spectrometry.

The average activity concentrations of ^{234}U, ^{238}U, ^{230}Th, and ^{232}Th, determined by alpha-particle spectrometry in the soil samples from the four coastal communities with Saltpond were; 7.5 ± 4.9, 7.6 ± 4.9, 6.3 ± 3.6 and 6.4 ± 3.5 $Bqkg^{-1}$, respectively, while the average activity concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K, ^{210}Pb, and ^{238}U, determined by gamma-ray spectrometry were, 22.6 ± 13.8, 17.9 ± 11.5, 19.7 ± 11.5, 156.4 ± 87.6, 67.0 ± 29.0, and 9.4 ± 7.4 $Bq.kg^{-1}$ respectively. These activity concentrations are typical of the ones found in undisturbed sandy soils, and slightly lower than the worldwide average activity concentrations present in the earth's crust. This resulted in a corresponding lower average values of Ra_{eq}, H_{ex}, and H_{in}, than the recommended acceptable values (an indication that the soils from the study might be used for building purposes).The soils do not pose any

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significant radiological radiation hazard, and can be considered safe for use as building materials. The measured average outdoor ^{222}Rn concentration was 26.5 ± 5.5 Bq.m^{-3} which was within values published for normal areas around the world with values in the range of 2-30 Bq.m^{-3} in air (UNSCEAR, 2000).

For the water samples from the same coastal communities as the soil, the gross-α and gross-β values for all of them were lower than the recommended guidance levels (WHO 2011; GSA 2005), an indication that all the water sources in the study area which are designated for drinking and domestic purposes do not have significant natural radioactivity. In fact, the average activity concentrations values of; ^{234}U, ^{238}U, ^{230}Th and ^{232}Th in the water samples determined by alpha spectrometry were; 12.5 ± 10.0, 11.2 ± 10.7, and 2.1 ± 2.6 and 1.2 ± 2.3 mBq.L^{-1}, respectively. For underground water sources, the activity concentration of ^{226}Ra, determined by liquid scintillation counting, varied from 7.0 – 18.0 mBql^{-1} with an average of 13.7± 5.9 mBq.L^{-1}.

The results of environmental samples (soil, sediments, water) in this study compared well with available global data on studies carried out in other countries and with the worldwide average activity concentrations (UNSCEAR 2008; WHO 2011), as well as, other studies carried out in communities in close vicinity of other extractive industries in Ghana (Faanu et al., 2013; Faanu et al., 2011; Darko et al., 2010; Darko et al., 2005). This indicates insignificant levels of public exposure to natural radionuclides in the study area and also by implication suggesting that, oil production activities as at now had not significantly imparted negatively in terms of radiological hazard to the coastal communities in the study area on the basis of the results obtained for the three exposure pathways.

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However, this data could serve as a reference material in future studies for subsequent evaluations of the possible future environmental contamination due to activities of the oil industry as production increases.

The measured mean concentrations of main NORM components in produced water were 15.2 ± 7.1 $Bq.L^{-1}$, 23.0 ± 13.5 $Bq.L^{-1}$, 3.8 ± 2.5 $Bq.L^{-1}$and 16.6 ± 7.9 $Bq.L^{-1}$ for ^{226}Ra, ^{228}Ra, ^{224}Ra and ^{40}K respectively. Comparison of the mean specific activities of radionuclides for the two oilfields showed that the activity concentrations for produced water from the Saltpond field were about five times higher than that of the Jubilee field, and this can be attributed to factors such as the maturity of the Saltpond field in comparison to Jubilee field, the geological characteristics of reservoir rocks, the type of hydrocarbons produced and operating conditions for the oilfields.

The average concentrations of both ^{226}Ra and ^{228}Ra, for the two oilfields obtained in this study all exceeded the aqueous Derived Release Limit (DRL) of the Canadian guideline governing liquid discharges (Health Canada, 2011). In addition, results obtained from this study indicate that produced water from the two Ghanaian oilfields are relatively high in radium concentration compared to radium concentrations for other oilfields reported from most countries including the Gulf of Mexico as reported in literature as having higher radium concentration in produced water (Vegueria et al., 2002; Meinhold et al., 1996; Chowdhury et al., 2004; Neff, 2002; Stephenson, 1992).

On the other hand, a very good linear correlation was observed for both ^{226}Ra and total Ra (^{226}Ra & ^{228}Ra), with most physico-chemical parameters considered in this study which could be used as basis in future research for estimation of other unknown parameters.

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Based on results obtained from this study for produced water, there is the need for national efforts to establish guidance levels for radionuclides prior to discharge of effluents into water bodies in order to mitigate any possible future contamination of the environment.

In relation with crude oil, it can be concluded based on data from this study that the activities in crude oil from both fields were insignificant with activities in most cases found below detection limit, however, the Saltpond field crude oil data were generally higher than that of the Jubilee field.

Activity concentrations of radionuclides for solid NORM waste in this study was highest for scale samples with averages; 43.9 ± 8.1 kBq.kg^{-1}, 0.36 ± 0.15 kBqkg-1, 30.3 ± 5.1 kBq.kg^{-1}, 11.2 ± 2.8 kBq.kg^{-1}, 1.8 ± 0.4 kBq.kg^{-1}, 11.2 ± 2.6 kBq.kg^{-1} for ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th, ^{40}K, and ^{224}Ra, respectively.

Oil based mud on the other hand, had the least activities for solid waste with mean concentrations of 19.5 ± 5.0 Bq.kg^{-1}, 16.0 ± 8.5 Bqkg^{-1}, 11.5 ± 3.5 Bq.kg^{-1}, 11.0 ± 2.8 Bq.kg^{-1}, 5.5 ± 2.1 Bqkg^{-1}, 10.0 ± 2.8 Bq.kg^{-1}, 195.0 ± 49.5 Bq.kg^{-1} for ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{228}Th, ^{234}Th, ^{224}Ra, and ^{40}K, respectively.

The specific activities of ^{226}Ra, ^{228}Ra, ^{228}Th, and ^{224}Ra for scale samples in this study exceeded the IAEA Basic Safety Standards (BSS) exemption levels which are also adopted by the RPB, GAEC and hence, needs to be handled with care by exerting regulatory control of the NORMs residues.

Sludge on the other hand, even though had mean activities of radionuclides lower than the exemption levels, showed an increasing trend in activity concentration with increasing

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production and age of oil wells. In this regard, regular monitoring of specific activity in the sludge from the oilfields may be necessary in order to proper manage the disposal of sludge in future.

Scale and sludge samples in this study exceeded the recommended reference values of the radium equivalent (Ra_{eq}), external (H_{ex}) and the internal hazard (H_{in}) indices for safe use.

It was also clear from this study that, ^{210}Po level was highest in all the solid waste samples between the alpha emitters, an indication that ^{210}Po may contribute significantly to total alpha-activity. This could be a significant source of exposure to workers via internal contamination by inhalation during maintenance, decommissioning operations and waste processing and disposal.

Mean outdoor ^{222}Rn concentrations measured for Scale pipes storage & maintenance facility, and mud processing and block moulding facility were; 113 ± 49 $Bq.m^{-3}$ and 8.5 ± 4.9 $Bq.m^{-3}$, respectively. The airborne radon concentration measured at waste storage facilities in this study were within the ICRP recommended value of 200-600 Bq/m^3 in dwellings and below the value of 1000 Bq/m^3 for workers (IAEA,1996).

Overall, this study suggests that Rn release is dependent to a large degree on the physical characteristics of the medium containing the NORM radionuclides.

Morphological and elemental analysis in particles of NORM waste samples in this study was indicative that, the composition of the scale samples is more of barium sulphate. This facilitated the co-precipitation of the radium isotopes with the barium complexes during scales formation. The elements; Al, Ba, Ca, Cl, Cu, Fe, K, Mg, Na, P, Pb S, Si, Sr, and Zn were identified and semi qualitatively quantified by Scanning Electron Microscope (SEM).

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The total annual effective dose of 0.35 mSv/yr obtained for all exposure pathways for the public in this study was below the ICRP recommended dose limit of 1 $mSv.y^{-1}$ for members of the public.

Total annual effective dose of 80.86 mSv/yr obtained in this study for workers clearly exceeds the ICRP recommended dose limit for an occupationally exposed worker of 20 $mSv.y^{-1}$ averaged over 5years but not exceeding 50 $mSv.y^{-1}$ in any single year.

It is important to point out that, comparison of equivalent doses components of total effective dose, clearly indicated that the external gamma dose due to U, Th and K in scale and sludge samples alone were 73 mSv/yr, representing 90.3%, and 6.4 mSv/yr representing 7.9% for scale, and sludge, respectively with both contributing 98.2% out of this total annual effective dose, whiles the rest together contribute 1.8%.

Generally, the calculated effective doses from the various solid NORM waste samples in this study are considered insignificant except those from scale and sludge which are of radiological importance and hence, necessarily the need to put in place measures to avoid such potential occupational exposures in future.

The risks to members of the public and workers, from exposure to naturally occurring radioactive materials (NORM) as a result of the crude oil production activities and waste generation from the Saltpond and Jubilee oilfields of Ghana was evaluated using the ICRP risk assessment methodology for fatal cancer risk and hereditary effects.

The lifetime cancer fatality risks from the public exposure pathways considered varied from 7.7×10^{-5} due to ingestion of water to 1.0×10^{-3} due to inhalation of airborne radon.

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The estimated total lifetime fatality cancer risk and the lifetime hereditary effect for the public were 1.3×10^{-3} and 4.9×10^{-5}, respectively. This means that, in terms of the lifetime cancer fatality risk approximately, 1 out of 1000, may suffer from some form of cancer fatality and for the lifetime hereditary effect approximately, 5 out of 100, 000, may suffer some hereditary effect.

The results of the lifetime cancer risks estimated in this study for public exceeded the USEPA acceptable range of risks values of 1×10^{-6} to 1×10^{-4} (i.e 1 person out of 1 million or 10,000 suffering from some form of cancer fatality).

However, it should be noted that the risk estimations are based on a conservative approach and also could be prevented especially in occupational exposure pathways if the necessary radiation protection measures are in place such as radiation safety training for core personnel, use of appropriate protective clothing and also observing the distance, time and shielding rule of protection from radiation sources.

The total life time cancer fatality risk and hereditary effects associated with the total annual effective dose obtained in this study for occupationally exposed workers were; 23.2×10^{-2} and 5.7×10^{-3}, respectively. This means that in terms of the lifetime cancer fatality risk approximately, 23 out of 100 may suffer from some form of cancer fatality and for the lifetime hereditary effect approximately 6 out of 1000 may suffer some hereditary effect.

The high risk of occupationally exposed workers to cancer fatality and hereditary effects in this study is mainly attributable to the risk associated with the scale and sludge samples. In this regard, persons who may work directly with these scale and sludge samples,

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particularly, during maintenance, the transport of waste and contaminated equipment, the decontamination of equipment, and the processing and disposal of waste in the absence of suitable radiation protection measures may be prone to severe risk of cancer fatality and hereditary effects.

In conclusion, radium concentrations obtained in this study for scale, sludge and produced water from the production oilfields of Ghana are of radiological importance and hence, there may be the need to put in place measures for future contamination concerns due to their bioavailability in the media and bioaccumulation characteristics.

The results from this study will assist in decision making for future set up of appropriate national guidelines for the management of NORM waste from the emerging oil and gas industry in Ghana.

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6.2 RECOMMENDATIONS

6.2.1 Regulatory Body

1. The radioactivity associated with the NORMs scales, sludge and produced water residues are significant, specifically with ^{226}Ra, ^{228}Ra and ^{228}Th as shown in this study with activities in scales exceeding the Exempt levels and therefore it's recommended that the RPB play the needed supervisory role in the management up to disposal of residues to ensure occupational, public and environmental protection.
2. In view of the high levels of radioactivity in the Scales residues, the RPB allied agencies like the National Radioactive Waste Management Center at GAEC should assist with technical support on effective management of the NORM waste to which some overview and technical recommendations have been presented in chapter two of this study.

6.2.2 Oil and gas companies

1. Workers who are to deal directly with scale contaminated equipment particularly during maintenance and removal of scale from pipes, the transport of waste and contaminated equipment, the decontamination of equipment, and the processing and disposal of waste **need** radiation safety training.
2. Appropriate workplace Personal Protective Equipment (PPEs) particularly against internal exposure via inhalation should be used by any staff who works directly with scale and sludge contaminated equipment.
3. Individual and Work place monitoring programme should be instituted at controlled areas as part of the overall radiation protection programme to help address the issues of exposure of radiation to workers and members of the public.

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4. There should be periodic assessment of the ambient dose rate on the offshore oilfield platforms for the following areas; water outlets, separator, wellheads and production manifolds, safety valves, and production lines. These measurements will be necessary to quantify direct occupational dose to workers on the oilfield platforms
5. Analysis for radionuclides in waste water and sludge as a result of oil and gas processing should be carried out at least once a year. This will provide vital information on the levels of radioactivity in the wells as production increases with time.
6. Care should be taken in the disposal of NORM waste samples with levels of radioactivity found below the exempt levels and are not expected to be of any significant radiological hazards in not to pollute the environment with respect to other environmental pollutants such as trace and heavy metals which were found in high concentration for some of the samples.

6.2.3 Future Research

1. Chemical speciation studies on the geochemistry of U and Th in the study area
2. The model can be applied to all the contaminants of produced water. This will provide deep understanding about the total risks from produced water: both for the environment and human health.

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Publication Lists

The following published articles and presentations were made during the course of the PhD programme related to this research are shown below:

Journal Papers

- **D.O. Kpeglo**, J. Mantero, E.O. Darko, G. Emi-Reynolds, E.H.K Akaho, A. Faanu, R. Garcia -Tenorio, 2014. Radiological Exposure Assessment from Soil, Underground and Surface Water in Communities along the coast of a Shallow Water Offshore Oilfield in Ghana. Radiation Protection Dosimetry, Advance Access Publication, doi:10.1093/rpd/ncu197, 1-12.

- **D.O. Kpeglo**, J. Mantero, E.O. Darko, G. Emi-Reynolds, A. Faanu, G.Manjón, I. Vioque, E.H.K Akaho, R. Garcia -Tenorio, 2016. Radiochemical characterization of produced water from two production offshore oilfields in Ghana. Journal of Evironmental Radioactivity 152 (2016) 35 – 45.

Conference Papers

- **D.O. Kpeglo,** J. Mantero, E.O. Darko, G. Emi-Reynolds, G.Manjón, I. Vioque, E.H.K Akaho, A. Faanu and R.García-Tenorio, 2014. NORM studies in an offshore oil production field located in the coast of Ghana. Conference Poster , EU NORM conference, Prague, 20-23June

- **D.O. Kpeglo,** J. Mantero, E.O. Darko, G. Emi-Reynolds, G.Manjón, I. Vioque, E.H.K Akaho, A. Faanu and R.García-Tenorio, 2015. Radioactive characterization of residues from an Oil Industry in Ghana. Oral Presention , ENVIRA15 conference, Thessalonika, 21-25 September 2015

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APPENDIX A: Input parameters and their characterization

Model parameters	Characterization
Q(Effluent discharge rate, m^3/s)	0.104
u(ambient current speed m/s)	LN(-3.29,0.96)
K_z(Vertical diffusion coefficient, m^2/s)	0.012
v (Horizontal diffusion velocity, m/s)	0.013
r (Horizontal length of consideration, m)	100
BCF(Whole fish bioconcentration factor)	LN(2.99,0.92)
x (Edible part of fish %)	78
y (concentration factor ratio)	LN(2.29,1.2)
FIR (Fish ingestion rate, g/day)	177
FR (Fraction of contaminated fish ingested, %)	50
EF(Exposure frequency, days/yr)	350
ED(Exposure duration, yr)	30
^{226}Ra input(Bq/l)	20.5 (mean)
	18.7 – 22.3 (range)
^{228}Ra input(Bq/l)	33.3 (mean)
	31.6 – 33.5 (range)

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APPENDIX B: Moisture and lipid content in selected species (USEPA 1996)

Species	Moisture content (%)	Total lipid content (%)	Category	Comments
Anchovy, European	73.37	4.101	Finfish	Raw
Bass, stripped	79.22	1.951	Finfish	Raw
Carp	76.31	4.842	Finfish	Raw
Haddock	79.92	0.489	Finfish	Raw
Halibut, atlantic and pacific	77.92	1.812	Finfish	Raw
Halibut ,Greenland	70.27	12.164	Finfish	Raw
Herring, atlantic &turbot	72.05	7.909	Finfish	Raw
Herring, pacific	71.52	12.552	Finfish	Raw
Mackerel, Atlantic	63.55	9.076	Finfish	Raw
Ocean perch, Atlantic	78.80	1.296	Finfish	Raw
Pike northern	78.92	0.477	Finfish	Raw
Salmon, atlantic	68.5	5.625	Finfish	Raw
Salmon ,Chinook	73.17	9.061	Finfish	Raw
Salmon, Coho	72.63	4.908	Finfish	Raw
Salmon, pink	76.35	2.845	Finfish	Raw
Sardine, Atlantic	59.61	10.545	Finfish	Canned in oil
Seatrout ,mixed species	78.09	2.618	Finfish	Raw
Trout , rainbow	71.48	2.883	Finfish	Raw
Trout, mixed species	71.42	5.901	Finfish	Raw
Crab, Alaska king	79.57	N/A	Shellfish	Raw
Lobster, northern	76.03	0.358	Shellfish	Raw
Shrimp, mixed species	52.86	10.984	shellfish	Cooked, breaded and fried
	72.56	1.421		canned
Mussel, blue	80.58	1.538	Shellfish	Raw
Oyster, eastern	85.14	1.620	Shellfish	Raw
squid	78.55	0.989	shellfish	Raw
	64.54	6.763		Cooked, fried

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APPENDIX C: Concentration factors for edible and non-edible parts in a fish (adapted from Swanson 1983; Iyengar *et al*., 1980; Hamilton *et al*. 1992; Meinhold and Hamilton 1992)

Species (1)	Radium Component(2)	CF(flesh) (3)	CF (bone, shell, skeleton) (4)	Ratio (4)/(3)
White sucker	Ra	12	1793	149.4
Lake whitefish	Ra	3	360	120
Lake trout	Ra	1	10	10
Oyster	Ra	50	500	10
Green mussel	Ra	46	419	9.1
Snail (*petalla radiate)*	Ra	44	256	5.8
sole	^{226}Ra	55	370	6.7
	^{228}Ra	21	160	7.6
Oil sardine	^{226}Ra	130	610	4.7
	^{228}Ra	44	180	4.1
Ray	^{226}Ra	60	65	1.1
	^{228}Ra	--	98	
prawn	^{226}Ra	80	360	4.5
	^{228}Ra	56	300	--
Moluscs-marine	^{226}Ra	44-63	156-500	2.5-11.4
Crustaceans-marine	^{228}Ra	35-360	230-800	0.6-22.9
Crab	^{228}Ra	35	800	22.9
Clam	Ra	--	200	--
Moluscs	Ra	2-240	--	--

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APPENDIX D: Sampling Co-ordinates for environmental samples from study area

Sample ID	Co-ordinates		Sample ID	Co-ordinates	
	Latitude	Longitude		Latitude	Longitude
S1	5°12′18.79″N	1°02′26.81″W	SD17	5°11′37.65″N	1°05′22.39″W
S2	5°12′00.74″N	1°02′45.42″W	SD18	5°11′35.73″N	1°05′26.12″W
S3	5°12′10.23″N	1°02′45.48″W	SD19	5°11′47.97″N	1°04′33.83″W
S4	5°12′15.11″N	1°02′44.80″W	SD20	5°11′49.78″N	1°04′21.74″W
S5	5°11′46.96″N	1°05′53.99″W	SD21	5°11′52.65″N	1°03′24.86″W
S6	5°12′30.18″N	1°05′24.91″W	SD22	5°11′51.88″N	1°03′14.78″W
S7	5°12′19.22″N	1°05′18.78″W	SD23	5°11′54.30″N	1°02′52.76″W
S8	5°11′44.06″N	1°05′27.18″W	SD24	5°11′55.55″N	1°02′42.32″W
S9	5°11′56.99″N	1°04′29.28″W	SD25	5°11′37.14″N	1°05′25.63″W
S10	5°12′08.11″N	1°02′1.83″W	SD26	5°11′39.20″N	1°05′26.88″W
S11	5°12′19.72″N	1°02′18.62″W	SD27	5°11′34.86″N	1°05′23.58″W
S12	5°12′38.51″N	1°05′15.90″W	SD28	5°11′45.62″N	1°05′28.91″W
S13	5°11′41.88″N	1°05′50.56″W	SD29	5°11′47.7″N	1°04′30.24″W
S14	5°11′38.03″N	1°05′32.50″W	SD30	5°11′50.22″N	1°04′35.16″W
S15	5°11′30.44″N	1°05′40.20″W	SD31	5°11′52.68″N	1°03′19.46″W
S16	5°11′51.62″N	1°05′45.26″W	SD32	5°11′53.79″N	1°03′22.71″W
W1	5°12′02.93″N	1°02′29.19″W	SD33	5°11′55.13″N	1°02′48.08″W
W2	5°11′44.59″N	1°05′29.57″W	SD34	5°11′56.70″N	1°02′40.27″W
W3	5°12′06.79″N	1°02′30.80″W			
W4	5°12′01.80″N	1°03′11.61″W			
W5	5°12′01.34″N	1°03′19.32″W			
W6	5°11′45.26″N	1°05′24.40″W			
W7	5°11′53.02″N	1°04′30.87″W			
W8	5°12′33.26″N	1°05′25.15″W			