Cape Peninsula
University of Technology

# RADIONUCLIDES AND TRACE ELEMENTS OF RED PALM OIL, WATER, AND SOIL FROM PALM PLANTATIONS.


**BY**

**OLADUNNI BOLA OLAFISOYE**

**B.Tech. (Hons) Bauchi, M.Sc. (Analytical Chemistry) Ibadan**


**Thesis submitted in fulfilment of the requirements for the Doctor of Philosophy: Chemistry**
**in the Faculty of Applied Sciences**

**At the**

**CAPE PENINSULA UNIVERSITY OF TECHNOLOGY**

| | |
|---|---|
| **Main Supervisor:** | **Doctor O.A. Osibote** |
| **Co-supervisor:** | **Professor O.O. Oguntibeju** |
| **Co-supervisor:** | **Professor O.S. Fatoki** |

**Cape Town**
**April 2021**

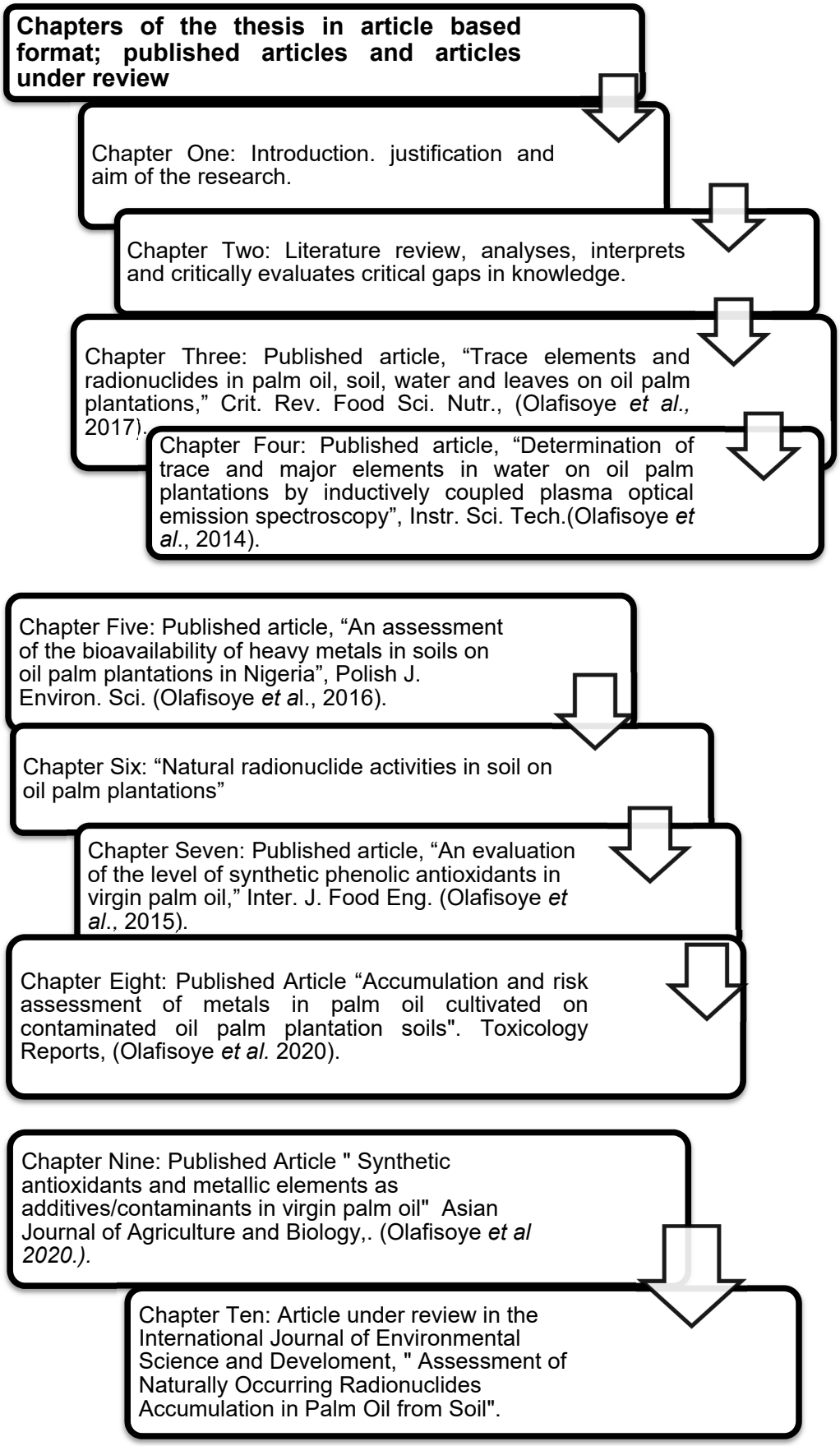
## DECLARATION

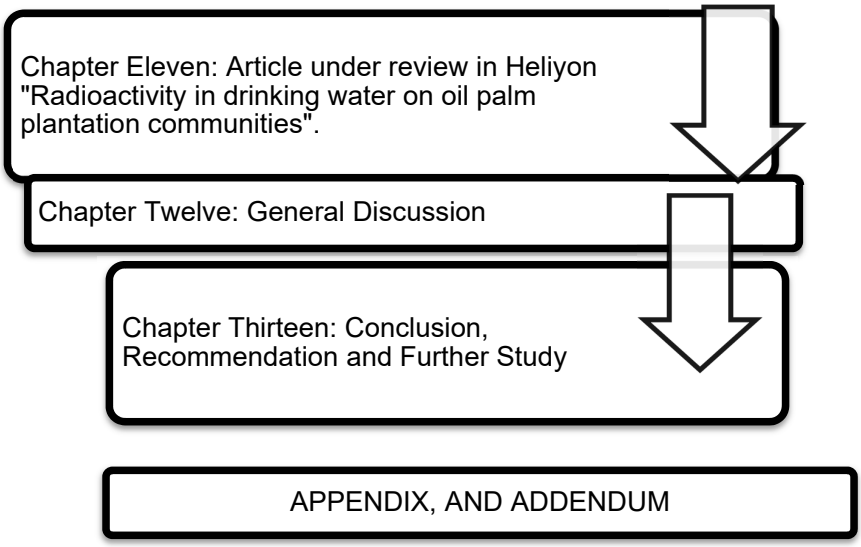
I, Oladunni Bola, Olafisoye, declare that the contents of this thesis represent my own unaided work, and that the thesis has not been previously submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

**2/03/2021**

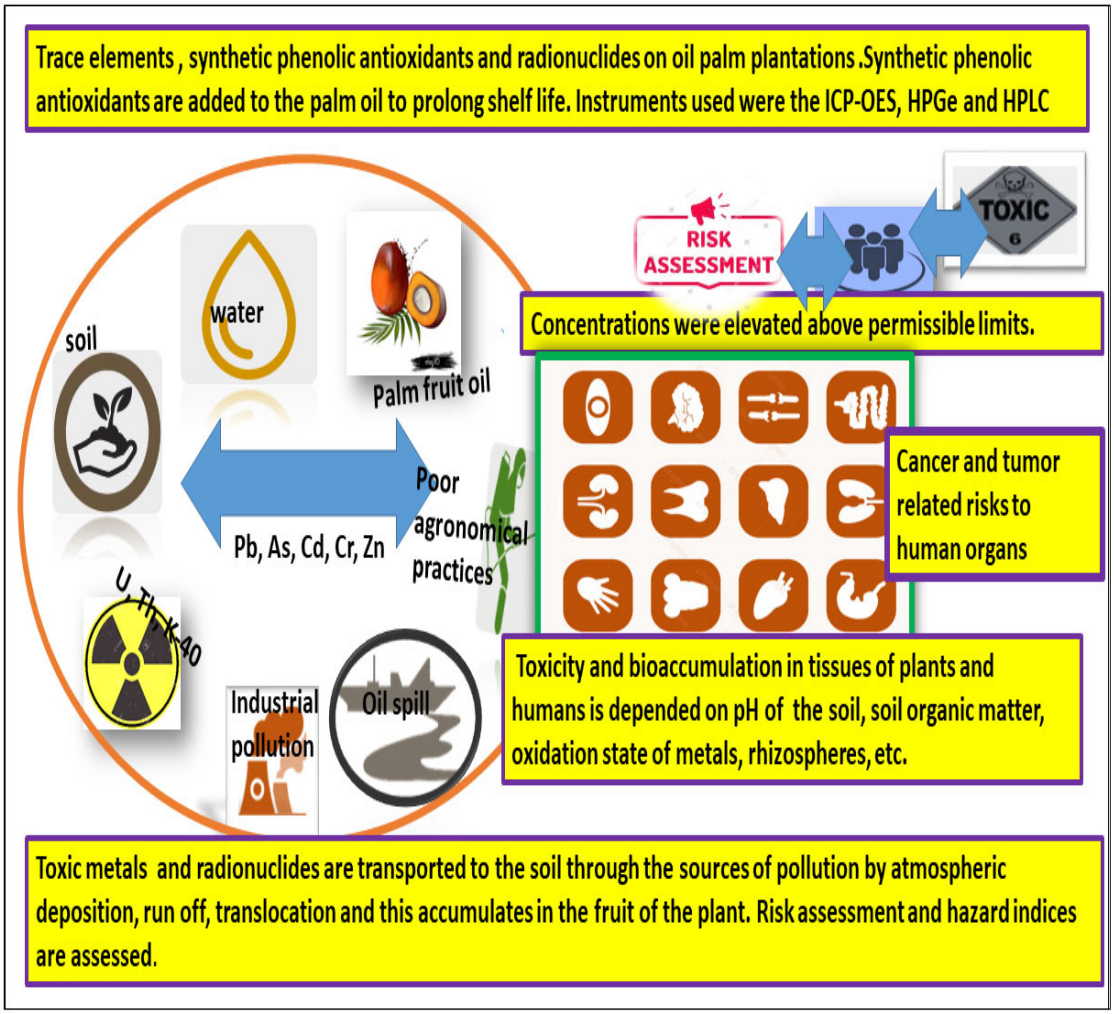
**Signed** **Date**

## CHRONOLOGY OF THE THESIS




Chapter Eleven: Article under review in Heliyon "Radioactivity in drinking water on oil palm plantation communities".
Chapter Twelve: General Discussion
Chapter Thirteen: Conclusion, Recommendation and Further Study
APPENDIX, AND ADDENDUM

## GRAPHICAL ABSTRACT



## ABSTRACT

The oil palm plantation and produce from the oil palm tree has provided employment and economic maintenance of life and existence for numerous countries all over the globe. The virgin palm oil has a good percentage of vitamin A, C and E. Having discovered that metals and radionuclides may be persistent detrimental, non-biodegradable and accumulate in the eco-system; major concerns of regulatory agencies in countries worldwide are the susceptibility of metals and radionuclides due do the deregulation of disposal of wastes and effluents in the environment. Based on this fact, the effect of the uptake of metals and radionuclides from soil, groundwater, and its translocation to the oil palm fruit was determined on fifteen independent oil palm plantations in Nigeria. Areas in the Southern part of Nigeria where oil palm is greatly cultivated include the states of Edo, Enugu, Delta, Akwa Ibom, Ondo, Ekiti, Kogi, Oyo, Osun, Ogun, and Lagos. Soil, water, and palm oil were collected from fifteen major sites from areas in Nigeria. Sampling was performed in the dry season of October 2012 to April of 2013 using random and grab sampling methods. The solutions and reagents used for all analysis were analytical grade. Reference materials were used for the validation of the analytical methods when using the instruments. The Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) equipped with radial viewed plasma was used in the research for the determination of total metal concentrations in soil, water, and palm oil and metal speciation in soil samples. The highest concentration of metals recorded was for Lead (Pb) (0.090-10.29 mg/L) and the lowest for Cadmium (Cd) (0.119-0.391 mg/L) on all the ground water sampled on the fifteen independent sampling locations. The procedure for the determination of the bioavailability and bio-accessibility of metals in soil in this study was the BCR three-step sequential extraction. The concentration of metals in palm oil and the risk assessment of metals from palm oil to soil were also evaluated. Micro emulsion technique was used as sample preparation method for the extraction of the metals in virgin palm oil from the matrix. The concentrations of metals found in the oil samples analysed on all fifteen sampling locations ranged between 0.006 mg/L in Ubiaja plantation and 161.576 mg/L in Benin City plantation respectively. Sn metal recorded high concentration in Benin City plantation and Pb metal recorded a low concentration in Ubiaja plantation. The study revealed that the Daily Intake of Metals (DIM), Health Risk Index (HRI), and Accumulation Factor (AF) values were above unity in most of the plantations and this is suggestive of risk to the food chain. The concentrations of metallic elements were rather high in most samples, hence the oil is best suitable for use as fuel or raw material for the chemical industry. Most of the palm oil analysed for metallic elements were not suitable for human consumption, and anthropogenic pollution of the soils may be identified as the source of contamination. The concentration of the metals found in the study was compared with quality standard for metals in soil, water and food set by the World Health Organization.

Other aspect of the study focused on the oxidative stability coupled with the cheap monetary cost of the virgin palm oil as one of the best cholesterol-free oils especially when blended to prolong shelf life. Virgin palm oil undergoes rancidity during storage and this affects the shelf life and aesthetics of the palm oil. Oil palm plantation farmers may add synthetic phenolic antioxidants to the palm oil during storage for preservation and for longer shelf life of the palm oil. Virgin palm oil was analysed for synthetic phenolic antioxidants by Reverse Phase-High Performance Liquid Chromatography (RP-HPLC) coupled with an Ultraviolet /Visible (UV-Vis) detector. Hexane and acetonitrile were employed as solvents for the extraction procedure. Qualitative and quantitative analysis was performed on the oil to determine the concentration of Butylatedhydroxytoluene (BHT), butylatedhydroxyanisole (BHA), propyl gallate (PG) and 2-ethylhexyl 4-methoxycinnamate (EEMC). The limits of detection for BHA, BHT, EEMC, and PG were 0.041, 0.057, 0.06, and 0.03 mg/L respectively. Limits of quantification for BHA, BHT, EEMC and PG were also 0.56, 0.49, 0.05 and 0.04 mg/L respectively. None of the synthetic antioxidants was detected in the real samples under investigation. This was an indication that local farmers probably preserved the oil samples prior to storage by traditional methods.

Soil, palm oil, and water were assessed in another aspect of the study for radionuclide activity concentrations on the fifteen sampling locations in the southeast, southwest and south south regions of Nigeria using the Hyper Pure Germanium Detector (HPGe). The radioactivity concentrations of $^{238}U$, $^{232}Th$ and $^{40}K$ were obtained from averaging the radioactivity concentrations of their respective progenies. The activity concentrations of $^{40}K$ from soil depth of (0 – 15 cm) ranged from 187.4 – 514.4 Bq/kg. The activity concentrations of $^{238}U$ from soil depth of (0 – 15) cm ranged from 2.328 - 6.571 Bq/kg and the activity concentrations of $^{232}Th$ from soil depth of (0 - 15 cm) ranged from 1.509 - 6.121 Bq/kg respectively. The activity concentration of palm oil for $^{40}K$, $^{238}U$ and $^{232}Th$ ranged from 122.3 -968.0, 1.240 - 6.651 and 1.199 - 8.061 $BqL^{-1}$ respectively. The annual effective dose and cancer risk in water polluted with Naturally Occurring Radioactive Materials (NORM) was investigated in the water as the ground water in the community is used as a source of drinking water and for domestic use. The activity concentration of $^{40}K$, $^{238}U$ and $^{232}Th$ were discussed and the annual effective dose for different age groups and cancer risk were estimated in the ground water samples. Activity concentration of $^{40}K$ (Bq/L) were least in Okitipupa plantation (171.7 ± 0.01 Bq/L) and the highest activity was recorded in Ago-Emokpae plantation (468.9 ± 0.01 Bq/L) respectively. The activity concentrations of $^{238}U$ (Bq/L) ranged between 1.611 ± 0.01 Bq/L – 5.750 ± 0.01 Bq/L and the concentrations were least in Ikire plantations and highest in Ago-Emokpae plantations respectively. Activity concentrations values (Bq/L) for $^{232}Th$ in the ground water was highest in Ikire plantation (9.619 ± 0.26 Bq/L) and lowest in Apoje plantation (1.554 ± 0.62 Bq/L) respectively. The values for the Annual Effective Dose Estimation (E) (mSv/y) for $^{40}K$, $^{238}U$ and $^{232}Th$ reveal that E for $^{40}K$ was highest in infants, children, and adults in this order; $3.51 \times 10^{-4}$, $8.21 \times 10^{-4}$, and $11.72 \times 10^{-4}$ at W4 plantation respectively. Lowest values of E (mSv/y) were

recorded in the same order at W12 plantation respectively as $1.29 \times 10^{-4}$, $3.01 \times 10^{-4}$, and $4.29 \times 10^{-4}$). EDW values (mSv/y) for $^{232}$Th were negligible at W1 and W12 plantations. Highest and lowest values were recorded as $6.49 \times 10^{-4}$ (W9); $9.76 \times 10^{-4}$ (W9) and $9.17 \times 10^{-4}$ (W2) for infants, children, and adults respectively. Lowest values of $^{232}$Th E values (mSv/y) in the sampled ground water were recorded ($1.12 \times 10^{-4}$, $1.68 \times 10^{-4}$, and $1.12 \times 10^{-4}$) for infants, children, and adults in W5 and W9 plantations respectively. The radionuclide $^{238}$U recorded E values (mSv/y) in the range of $0.77 \times 10^{-4}$ mSv/y – $11.06 \times 10^{-4}$ mSv/y, $1.04 \times 10^{-4}$ mSv/y– $16.10 \times 10^{-4}$ mSv/y and $2.25 \times 10^{-4}$ mSv/y– $8.05 \times 10^{-4}$ mSv/y for infants, children, and adults respectively. The values were generally low for infants. Radionuclide $^{232}$Th was not detected in Abak and Nsukka plantations. The calculation of cancer risks based on the radium isotopes ranges from $5.91 \times 10^{-4}$ to $21.10 \times 10^{-4}$ for $^{226}$Ra. For $^{228}$Ra, the values were from $5.87 \times 10^{-4}$ to $1.64 \times 10^{-4}$. Mean estimations were calculated as $26.25 \times 10^{-4}$ and $3.891 \times 10^{-4}$ for $^{226}$Ra and $^{228}$Ra respectively. Translocation Factor (Tf) in the all pressed virgin palm oil was greater than unity/very close to unity. The estimation of the assessed annual effective dose in drinking water for all the individual populations were below the recommended reference value of 0.1 mSv resulting from a year intake of drinking water in accordance with the WHO, IAEA and UNSCEAR regulated guideline values. The mean values for $^{226}$Ra and $^{228}$Ra obtained in this study for both isotopes were $3.891 \times 10^{-4}$ and $26.25 \times 10^{-3}$ for $^{226}$Ra and $^{228}$Ra respectively. The mean estimation of the radiological cancer risk for radium isotope for both $^{226}$Ra and $^{228}$Ra in this study is acceptable within the guideline limits of $1 \times 10^{-4}$ to $1 \times 10^{-6}$. The values obtained for soil samples were lesser than the worldwide values for soils in the region. None of the soil samples exceeded the permissible levels of 370 $Bqkg^{-1}$ for radium equivalent recommended by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). Other radiological hazards in terms of Internal and External hazard indices and Representative hazard index in the soils were determined and found to be within safe limits.

**Keywords:**

Oil palm plantation, Oil Palm Fruit, Pressed Virgin Palm Oil, Soil, Water, Bioavailability, Bio accessibility, Trace and Toxic Metals, ICP-OES, HPLC, HPGe, Environmental Pollution, Synthetic Phenolic Antioxidants, NORM, Activity, Radionuclide Concentration, , Risk and Hazard Assessment.

## ACKNOWLEDGEMENT

**I want to thank:**

- God almighty for the gift of life and the strength to successfully complete a Doctoral degree.
- My appreciation goes to my main supervisor, Dr. O.A Osibote and my co-supervisors, Prof. O.O Oguntibeju and Prof. O. S Fatoki for their various contributions to the research work.
- My earnest gratitude goes to the staff members of the Chemistry Department of Bellville and Cape Town campus. I am thankful to the Oxidation Stress Research Center, Bellville campus for the use of their laboratory during the course of my research work. My High regards goes to the Staff members of the Center for Energy Research and Development (CERD), Obafemi Awolowo University, Ile Ife, Nigeria, for the use of their laboratory and equipments.
- A heartwarming appreciation to my friends and colleagues at the Cape Peninsula University of Technology South Africa and Bowen University, Iwo, Nigeria. You are too numerous to mention. Thank you all for the contributions you made to the success of the research and completion of the Doctoral degree in one way or the other.
- My heart felt indebtedness goes to my adoring parents and siblings. I appreciate your support and prayers towards my success in life.
- I acknowledge the Cape Peninsula University of Technology, Cape Town, South Africa for the University Research Funding to undertake the research.
- I acknowledge the Bowen University Iwo, Osun state, Nigeria, for granting me the study leave and staff development fund to undertake the PhD study.

## DEDICATION

The thesis is dedicated to God, the Omniscience, Omnipresent, and Omnipotent; and to His Son Jesus Christ of Nazareth.

# TABLE OF CONTENTS

## LIST OF TABLES

# LIST OF FIGURES

# CHAPTER ONE

## 1.1 Introduction

The oil palm plantation has provided employment and economic sustenance for a vast number of countries. Products from the oil palm plantation provide raw materials and feedstock for a number of dietary products for industry (Loganathan *et al.*, 2017; Ismail *et al.*, 2018). The oil palm fruit is particularly important because it possesses many medicinal benefits. The palm oil is the dark red viscous liquid pressed from the flesh of the oil palm fruit and it is referred to as the virgin palm oil. Pressed virgin palm oil is excellent oil used for most stable food processing and is versatile in the agro-allied and chemical industries. The palm oil is used in various ways for domestic use and industry. This is the more important reason the oil palm plantation is considered an economic crop. Virgin palm oil contains various vitamins that include Vitamin, A, C, and, D (Kritchevsky, 2000; May and Nesaretnam, 2014). Virgin palm oil is compared with cholesterol-free oils and found to be best of its kind. It is also cost-effective and blends well with other oils. It has a high oxidative ability and long shelf life when stored prior to usage. Hence, for the assurance of longer shelf life for the palm oil and products made from palm oil, contaminants in the oil need investigation. Auto oxidation usually sets in when edible oils are stored prior to usage especially when metals contaminate them. This deteriorates the aesthetics of the oil. Natural antioxidants are present in the virgin palm oil. Synthetic antioxidants may be added to the virgin palm oil before the storage of the oil to prevent the unset of auto-oxidation and degradation.

A great concern to researchers and scientist in many nations is the eco-toxicological contamination of metals in the environment. Metals have the tenacity to remain in the environment long after the source of pollution in the environment is gone. Essential metals are toxic at high concentrations although in trace amounts are beneficial for the effective performance of the anatomy and physiology of plants and human systems This non-persistence and non-biodegraded nature of metals affects the ecosystem and food chain (Khandaker *et al*., 2015; Dudu *et al.,* 2018). Naturally occurring radioactive materials occur naturally in the environment, and may only become detrimental if elevated to high concentrations due to human made activities. The application of pesticides in agriculture, unwholesome farming practices, deregulation of waste, industrialization, urbanization, crude oil exploration are activities which have contributed greatly to the amount of natural and manmade isotopes of radionuclides in the environment. The usefulness of radionuclides in the human body has never been discovered albeit they are extensively used in research, medicine and agriculture and power generation (Dudu *et al*., 2018). Major concerns of regulatory agencies in countries worldwide are the susceptibility of metals and radionuclides due do the deregulation of disposal of wastes and effluents in the environment (Khander *et al*., 2015).

Major pathways of exposure to human from radionuclides may be from soil, food, or water. Sources of radiation may include fallout from reactors and activation of nuclides, which contribute to radiation exposure. Nuclear weapon testing and nuclear accidents also contribute significantly to radiation exposure especially its fission products. Metals and radionuclides are absorbed by humans from the environment and are transported to human visceral organs through the consumption of contaminated food (Szarlowicz *et al*., 2013).

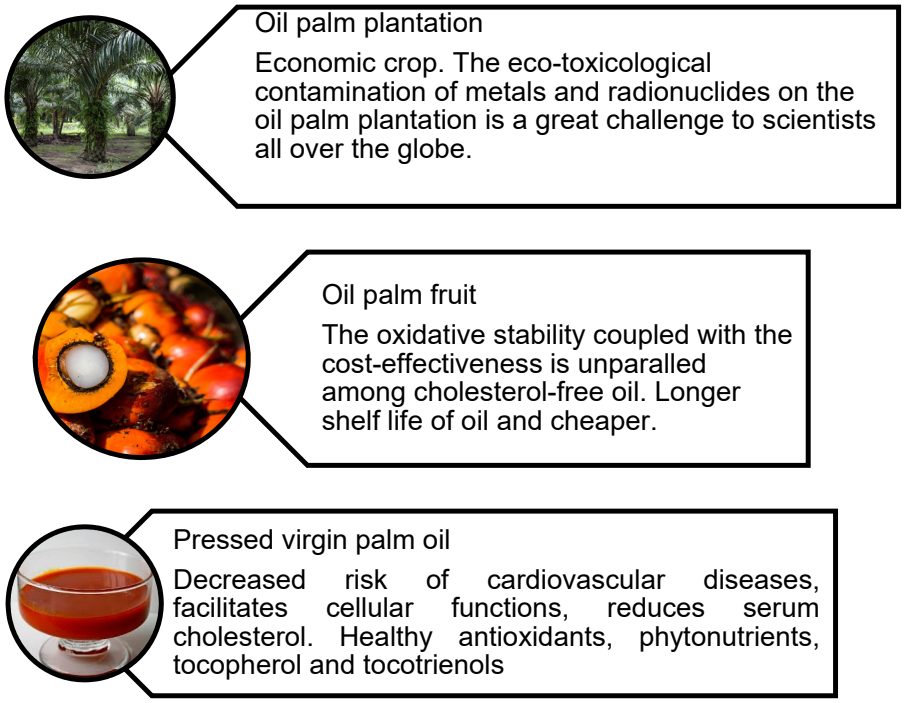



**Fig 1.1: Importance of the oil palm tree**

Oxidation usually sets in when edible oils are stored prior to usage. This can be seen as deterioration of the aesthetics of the oil (Çabuk, 2017). Synthetic antioxidants may be added to virgin palm before storage of the oil to prevent the unset of auto oxidation and degradation of the oils during storage. The oxidative stability of the palm oil coupled with the cost-effectiveness is unparalleled among cholesterol-free oils and these values are extended to blends of poly-unsaturated oils to provide long shelf life. Hence, for the assurance of longer shelf life for the palm oil and products made from palm oil, synthetic antioxidants may be added before storage to prevent the onset of auto-oxidation and oxidative degradation (Yankah *et al*., 1998; Cacho *et al*., 2016).

The toxicity of such metals and their accumulation in plant parts depends on the oxidation state in which they exist (Francis & Dodge, 1998). Biological, geological, and anthropogenic factors affect the uptake and toxicity of the concentration of metals in soils (Bradham *et al*., 2011).

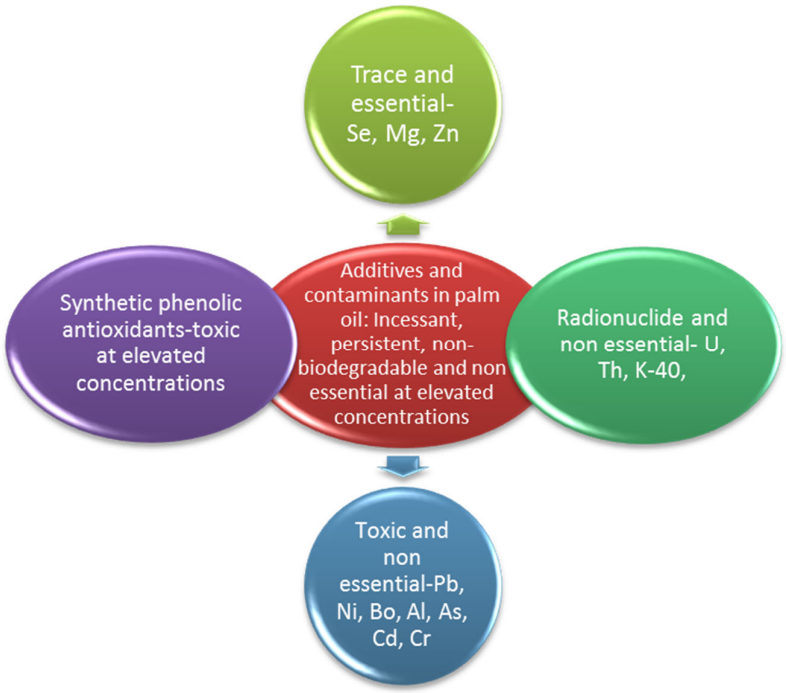



**Fig 1.2: Toxicity of elements**

The total metal concentrations when assessed, as a bioaccumulation factor in the parts of the plant does not give a true picture of the bioavailability of such elements in soil solution. Accessibility of the elements cannot be compared with the bioavailability of such elements and could be attributed to various factors such as the weathering of the parent material biological changes, surface adsorption, and nutrient uptake, which are made feasible by physical factors. These physical factors include the acidity and alkalinity, electrical conductivity and the Cation Exchange Capacity (Takáč *et al*., 2009). Geochemical and agricultural interests are considered when discussing the various implications of accumulation (Deshommes *et al.*, 2012). Tessier and colleagues extensively expatiated on the topic and classified total metal amount in soil into various segments such as the fractions that can be replaced, fractions bound to carbonates, fractions in iron/manganese oxide, fractions bound in organic forms and the remainder of the metal soil fractions (Tessier *et al*., 1979; Liu *et al*., 2017). The oxidation state in which the element exists is also a factor for consideration.

The development of a method of analysis is required with the aim of high proficiency and high sensitivity for elements present in soil water and accumulated in the fruit. Recently instrumental analyses are performed on environmental samples for metals, radionuclides, and synthetic phenolic antioxidants with simultaneous measurement of the entire spectrum of elements. This is achieved using a dual view with a multi-element technique for trace and major elements in parts per million using the Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) for metal analysis, the Hyper Pure Germanium detector (HPGe) for radionuclides measurement and the High-Performance Liquid Chromatography for the synthetic phenolic antioxidants. The instruments, ICP-OES and HPGe provided a dynamic range as low as parts per million and parts per billion ranges for quantitative and qualitative analysis (Sai Kiran, 2017; IAEA, 2014; Shasha, 2014).

Plant species significantly accumulate metals in various parts especially the fruits. This leads to bioaccumulation and bio magnifications in the food chain and the disruption of chemical and biological activities in the human body (Dudu *et al.,* 2018). The routes through which metals and radionuclides enter the food chain are via inhalation and ingestion (Cervantes-Trejo *et al.*, 2018). Although literature reveals that, some species of plants can bio accumulate metals and radionuclides more than other species when compared systematically (Jolly *et a*l., 2013). The study of metals and radionuclides in soils requires systematic assessment as a monitoring approach to eradicate the effects on the food chain (Lema *et al.*, 2014). The approach to the knowledge of risk assessment for metals has involved different mechanisms that include the Accumulation Factor, Hazard Quotient, Health Risk Index, Daily Intake of Metals, Target Hazard Quotient, Degree of Contamination, and the Uptake/Transfer Factor (Agrawal *et al.,* 2007; Jazzar, 2014; Lema *et a*l., 2014).

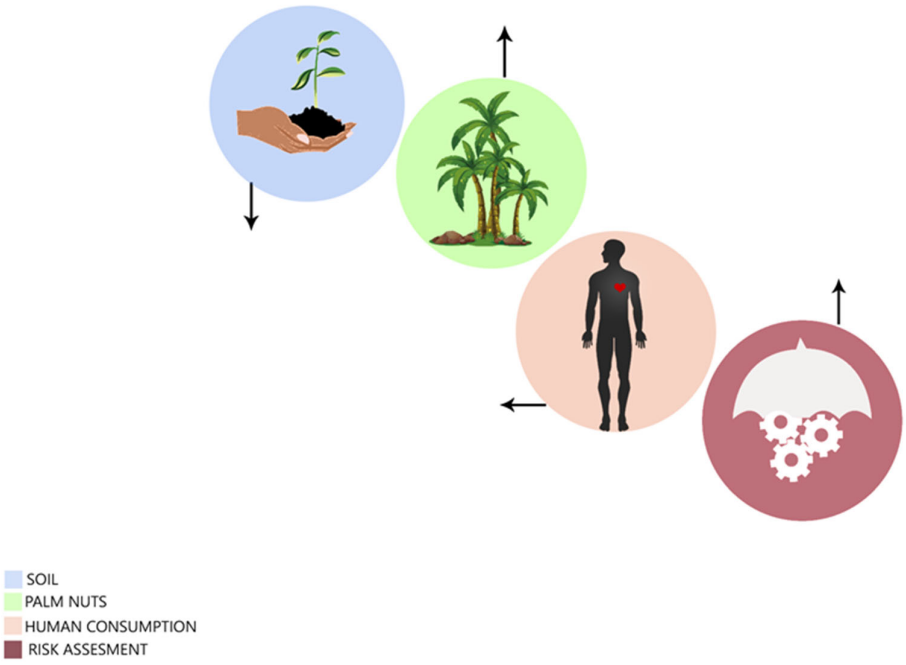



**Fig 1.3: Risk and hazard assessment**

Humans encounter four types of radiation, alpha radiation, beta radiation, gamma radiation, and x rays (Szarlowicz *et a*l., 2013). Major pathways of exposure of radionuclide to man may be from soil, food or water (Francis & Dodge, 1998). Sources of radiation may include fallout from reactors, activation and fission products, Nuclear weapon testing and nuclear accidents and these may contribute significantly to radiation exposure especially its fission products. Radionuclides are absorbed by humans from the environment and may be transported to human through the consumption of contaminated food. Radioactivity can be evaluated by calculation of Absorbed Dose Rate, Annual Effective Dose Equivalent, and Radium Equivalent and Translocation Factor (Tf). Other factors to reconsider include rhizospheres and bioavailability of NORM supported by soil factors and pore size of soils (Agrawal *et al*., 2007; Jazzar, 2014; Lema *et a*l., 2014).

The post impact assessment of the migration and bioavailability of metals, synthetic phenolic antioxidants, and radionuclides on the oil palm plantation has been put in place by several countries. This is to evaluate the risk assessment study of such contaminants from soil and water as it is transported to the oil palm fruit (Robertson et al., 2004a; Tangahu et al., 2011) The study was aimed at investigating metals, radionuclides, and synthetic phenolic antioxidants as contaminants in virgin palm oil. Hence, for the assurance of longer shelf life for

the palm oil and public health, the presence of these contaminants, their concentration and activity, bioaccumulation factors, risk assessment on humans was investigated.

### 1.1.1 Research problem

The concentration trace elements have great effects on the oil when considering the aesthetic quality, shelf life, health, and nutritional value. This can be determined from the risk assessment point of view. The transfer of metals and radionuclides from soil and water to the oil palm fruit is dependent on the bioavailability and accessibility of such metals and radionuclides and the transfer factor to the food chain. Therefore, it is necessary to conduct a research work in order to access the amount of radionuclides and metals from soil and water to palm oil. It would be worthy to assess the bioavailability and to conduct a speciation study to establish which species of metals are available in the soil. Knowledge of the toxicity of the metals and radionuclides is pertinent and the transfer factor from soil to fruit and risk assessment as it affects the food chain is of importance. The selection of an appropriate sampling and sample pre-treatment technique, method development, instrumental analysis with proper quality control is of paramount importance for achieving overall reliable results.

### 1.1.2 Justification of the research

The oil palm tree is a significant lucrative and productive tree for the food, agro allied and chemical industry. It contains various plant nutrients and antioxidants for the proper functioning of cellular systems in humans. Based on this fact, the effect of the uptake of metals and radionuclides from soil and ground water and its translocation was determined on fifteen independent oil palm plantations in Nigeria. The study furnishes information on metals and radionuclides on oil palm plantation in southern states of Nigeria. Metals in the environmental samples were investigated by the development of the method for metals analysis on environmental samples by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The bioavailability and accessibility of such metals and the species they exist in such soils was investigated. The evaluation of the presence of contaminants such as metals in the oils and the presence of phenolic antioxidants as additive was also assessed. Transfer factor and regions of hot spots for metals and radionuclides in translocation of radionuclide and metals was studied. The determination of baseline studies for the metals and antioxidants on the oil palm plantations and risk assessment was determined. Metals and radionuclides studies on oil palm plantations have not had a broad audience when it comes to research by scientist; so far, till this present time, palm oil produce has been extensively ingested in Nigeria and the remainder section is used by agro-allied industries. The determination of metals, radionuclides, synthetic phenolic antioxidants and their risk assessment in this region of the world can be

used as a baseline data in comparison with data from other regions or countries. Orisakwe and colleagues (Orisakwe et al., 2014) conducted a research update in the form of surveillance. The study was on a review on Nigerian soils and the results showed that several people die yearly in African countries because of environmental pollution of which metal and radionuclides are in the high rise. Pollution of soils may be from natural processes such as radioactive decay in soils and rocks and the geology of the rock in case of metals. Most active release of pollution comes from mining and industrial processes. Other past and ongoing researches on Nigerian soil have brought to the public view and a consensus that Nigeria soils are polluted with metals and radionuclides. Ohimain *et al*., 2012 and Ogunkunle *et al*., 2017 to reconfirm the eco-toxicological risks of polluted soils in Nigeria, orchestrated a few more studies. Soils are a sink for metals. Due to the transfer of these metals, radionuclides, and accumulation from soil to plant parts, it was pertinent to conduct a research in these areas. To my understanding and comprehension, after reviewing the available information and literature preview, no study has been carried out on this study. The study is on the assessment of contaminants (synthetic phenolic antioxidants, radionuclides and metals), transfer and soil factors, risk assessment, and the overall effect on fifteen sampling locations on oil palm plantations in the south western, south eastern and south southern states of Nigeria. These locations include the Nigeria Oil Palm Plantation sites and other locations were the oil palm tree is extensively cultivated in the south western, south eastern and south southern states of Nigeria. The locations were selected due to input from pollution sources and the oil palm plantation trees being extensively cultivated in such regions.

### 1.2. Research questions

i. What is the background concentration of metals and radionuclides on palm oil plantations from the south western, south southern and south eastern states of Nigeria?

ii. Do the amount of contaminants (synthetic phenolic antioxidants, metals and radionuclides); in the soil, water and palm oil on oil palm plantations transcend the accepted quantity and permissible levels set down by regulatory bodies?

iii. Are these sources of contamination linked to pesticides, fertilizers, oil spills, sewage water, sludge, agronomical practices and effluents from industries etc.? What are the possible sources for the metals and radionuclides on the oil palm plantations in the Southwestern, Southeastern and South southern states in Nigeria?

iv. Could the soil, palm oil or water on the oil palm plantation be a sink for the metals and radionuclides?

v. What is the potential health hazards, accumulation factor and risk assessment of elevated concentrations of metals and radionuclides in palm oil?

### 1.2.1 Aim and objectives of the research

The aim of the research is to determine contaminants (radionuclides, metals, and synthetic antioxidants) and to evaluate the accumulation and risk assessment from soil to the virgin palm oil pressed from the fleshy middle layer of the pericarp, which is the mesocarp of the oil palm fruit. The virgin palm oil differs in colour and constituency from the kernel oil derived from the edible part of the nut/seed/stone within the shell of the oil palm fruit. The concentration of metals, radionuclides, and synthetic antioxidants in soil, water, and palm oil are investigated on oil palm plantations from fifteen sampling sites in selected states in south western, south eastern and south southern states in Nigeria. The states are Abak, Acharu, Agbarho, Ago-Emokpae, Apoje, Badagry, Benin City, Igede-Ekiti, Ikire, Iresa Apa, Nsukka, Okitipupa, Onishere, Ubiaja, and Umuabi.

### 1.2.2 Specific objectives

i. To ascertain the level of contamination of metals and radionuclides on the palm oil, soil and water on the oil palm plantations in selected states in the Southwestern, Southeastern and South southern states in Nigeria.

ii. To carry out optimization studies on the materials and methods selected for the study.

iii. To ascertain the level of uptake of metals and radionuclides from soil, water and palm oil on the oil palm plantation in the South western, South eastern and South southern states in Nigeria.

iv. To access, ascertain and establish the background concentration value of metals in palm oil, water and soil on palm oil plantations in the southwestern, southeastern and south southern states in Nigeria. This will generate baseline data for radionuclides activity and metal concentrations in the region.

v. To determine the physicochemical parameters of soil and water in selected sampling points and states in Nigeria.

vi. To evaluate the sources and sinks for radionuclides and metals in palm oil, soil and water from selected sampling points and states in Nigeria.

vii. To evaluate the radiation risks of radionuclides and the effective dose rate to the ecosystem.

viii. To provide basis for the development of threshold values and environmental risk assessment for radioactive and trace contaminants on the palm oil plantation and to identify off site contamination and likely contamination sources.

ix. To determine translocation factors of metals and radionuclide from soil to water on the various sampling sites.

x. To determine the uptake and toxicity of the metals and radionuclides in soils, water and the palm oil.

### 1.3 Delineation of the research

Palm oil, soil and water from fifteen selected sampling points in states in Nigeria, was evaluated for radionuclides, phenolic antioxidants and metal contents. These sampling sites were chosen because they are from regions where palm oil is produced in commercial quantities in Nigeria and where there is exposure to contamination from radionuclides and metals. The sampling points will be areas receiving significant contamination from oil spills and gas flaring, mechanic and smelting villages, poor agricultural management practices such as bush burning, fertilizer and pesticide application, areas polluted by waste dump and possible fallout of radioactivity. Sampling regions of interest are the sub-stations of The Nigerian Institute for Oil Palm Research (NIFOR) and the southwest region of Nigeria that includes the states of Ekiti, Lagos, Ogun, Ondo, Osun and Oyo and Delta state. The metropolis is overcrowded and densely populated with small-scale, decentralized manufacturing business, which are operated and owned by small-scale owners, functioning from home. This beehive of economic activity is concerned with the processing of the raw materials in which they make their finished products. There is no laid down rule for waste generation and disposal as this is deregulated. A great deal of waste is created from point and non-point diffused pollution. Data on the radionuclides, synthetic phenolic antioxidants, and trace element levels of soil, water, and palm oil is sparse in the region and in Nigeria.

Nigeria is a tropical country characterized by a wet and dry climate at various times of the year. This is particularly beneficial for the production of the oil palm fruit. The oil palm fruit produces palm oil that is a stable ingredient in most local dishes consumed by Nigerians. Metals, radionuclides, and synthetic antioxidants may be present in the oil palm fruit due to various reasons ranging from environmental and processing processes to unwholesome agronomical methods. Contamination is usually from the cultivation of the oil palm tree and harvesting of

the oil palm fruit due to pre-planting and post-planting farming practices such as the use of fungicides and fertilizers residues. Contamination may also arise from a number of factors that includes washing of the oil palm fruit with water from lead/metal pipes or rivers. In addition, mechanical stripping of the oily flesh from the oil palm fruit, cooking and sieving of the flesh to obtain the virgin palm oil, corrosion of the processing equipment and storage in large metal vessels; are sources of metal contamination.

### 1.4 Description of study area

Table 1.1 show a list of sampling locations used in the research. Few mountains and steep terrains characterized these locations. This is usually due to their geographical disposition, with vegetation, which is mostly rain forest that supports the growth of a lot of plantation and cash crops such as the oil palm, rubber, and cocoa tree plantations, characterize the study area. Most of the terrain is flat land with rivers and various rivers and landscapes, meadows, springs, peninsulas, and islands adorn the regions. The climate is characterized into two major climates, which is the raining season and the dry season/harmattan. The raining season is between March and November and lasts for more than half of the months in the year. The soil receives a lot of rainfall all through the year and percolation of ground water into soil is to be considered in the transportation of radionuclides from water into soil. Hence, the transport of rainfall and the translocation from ground water to soil is of paramount importance.

**Table 1.1: List of sampling locations**

| Code | Location | Latitude | Longitude | Elevation above sea level (m) |
|---|---|---|---|---|
| **PP1** | Abak | 4.9833 | 7.7833 | 174 |
| **PP2** | Acharu | 7.5320 | 7.2792 | 210 |
| **PP3** | Agbarho | 5.5833 | 5.8667 | 111 |
| **PP4** | Ago-Emokpae | 7.3400 | 6.4500 | 200 |
| **PP5** | Apoje | 6.9644 | 4.1064 | 24 |
| **PP6** | Badagry | 6.4166 | 2.8833 | 36 |
| **PP7** | Benin city | 6.3176 | 5.6145 | 88 |
| **PP8** | Igede-Ekiti | 7.6667 | 5.1321 | 576 |
| **PP9** | Ikire | 7.3533 | 4.1833 | 207 |

| | | | | |
|---|---|---|---|---|
| **PP10** | Iresa-apa | 8.1504 | 4.2567 | 118 |
| **PP11** | Nsukka | 6.8667 | 7.3833 | 552 |
| **PP12** | Okitipupa | 6.5025 | 4.7795 | 305 |
| **PP13** | Onishere | 6.7150 | 5.1001 | 68 |
| **PP14** | Ubiaja | 6.6597 | 6.3822 | 255 |
| **PP15** | Umuabi | 6.17 36 | 7.2233 | 221 |

The South-western, South southern and South eastern states of Nigeria are home for rocks and sediments which encloses valleys and mountains from the south to the western regions of Nigeria. The geology of Nigeria formed in the Archean and Proterozoic eras has a province and half of the surface is igneous and metamorphic rocks with a crystalline and sedimentary basement. Massive sedimentation was under way in these basins as it returned to its terrestrial conditions within the Pan African mobile belt. The sampling sites are described as follows:

Abak is a region, which is a local government area in Akwa Ibom state in Nigeria. This was formerly part of the Cross-river state. The major economic activity in the area is palm oil and palm kernel production. Crude oil drilling is paramount in the area leading to a lot of legacy and reclaimed sites. These sites have returned to their useful purposes after mineral mining and crude oil drilling. Tailings are left on such sites that are later used for agricultural purposes.

Acharu is a local government area in Kogi state Nigeria. The oil palm plantation is the main cash crop grown by farmers of the town. Settlements are usually around the oil palm plantation as this is a major source of livelihood.

Agbarho is in Ughelli that is situated in the North local government area of Delta state, Nigeria. The town is not too far from Warri metropolis, which is a beehive of industrial and domestic activities and densely populated. Warri is also popular with crude oil drilling and industrial area for the manufacture of petroleum based products. The Urhobo people are the main tribe of the area. This area called the Niger delta is affected by oil spillages and oil leakages that are constant features of oil production and producing areas causing physical damage to lands and rending such lands unfit for agriculture and domestic use. The main economy of the Isoko/Urhobo people of the area is palm oil and palm kernel produce.

Ago-Emokpae inhabitants also farm extensively with the oil palm as a cash crop of economic interest.

Badagry is a town near the coast of the Atlantic Ocean hence a coastal town. It is also a local government region in in Lagos state of Nigeria and it is situated in Lagos near bordering towns of Porto-Novo, Benin and Seme with a lot of beehive of activities for business across the bordering towns. Badagry town is blessed with natural landscapes and lagoons extensively used for tourism. Several recreations, boat painting, and automobile engineering services are situated close to the lagoon. The town is a palm oil producing area for Egba indigenes and a major means of survival for the people. The oil palm plantation in Badagry is a distance not far from an electronic waste recycling site.

Benin City is famous for its bronzes, brass, and carved work of art. This is a significant source of industrial pollution and transport elements into the environment and the food chain. Significant deposits of copper, bronze, brass, tin and zinc is found in the area. The main occupation of the locality is oil palm production.

Igede-Ekiti is a city found in Ekiti, Nigeria. One of the cash crops of the city is palm oil. Agriculture is the main occupation of the locality that provides income and employment for 75 % of the population of Ekiti state.

Okitipupa is a region in the south west of Nigeria and a local government area. The Ikales are to the Okitipupa lineage and major occupation is farming and the cultivation of the oil palm.

Onishere is also a local government in Ondo state, which is North of Idanre and North East of Ajekunle area in the locality. Major occupation of the people is also oil palm production.

Ubiaja is located in Edo state and it is a community in Esan south East local government of the state. The red alluvial soil in Ubiaja is fertile and very adequate for oil palm plantation propagation. Inhabitants of the area are farmers cultivating cash crops, which include the oil palm, cocoa, and rubber tree.

**Fig: 1.4: Oil palm fruit bunches**

**Fig 1.5: Kernel (A); Palm oil (B)**

## 1.5 Outline of method design

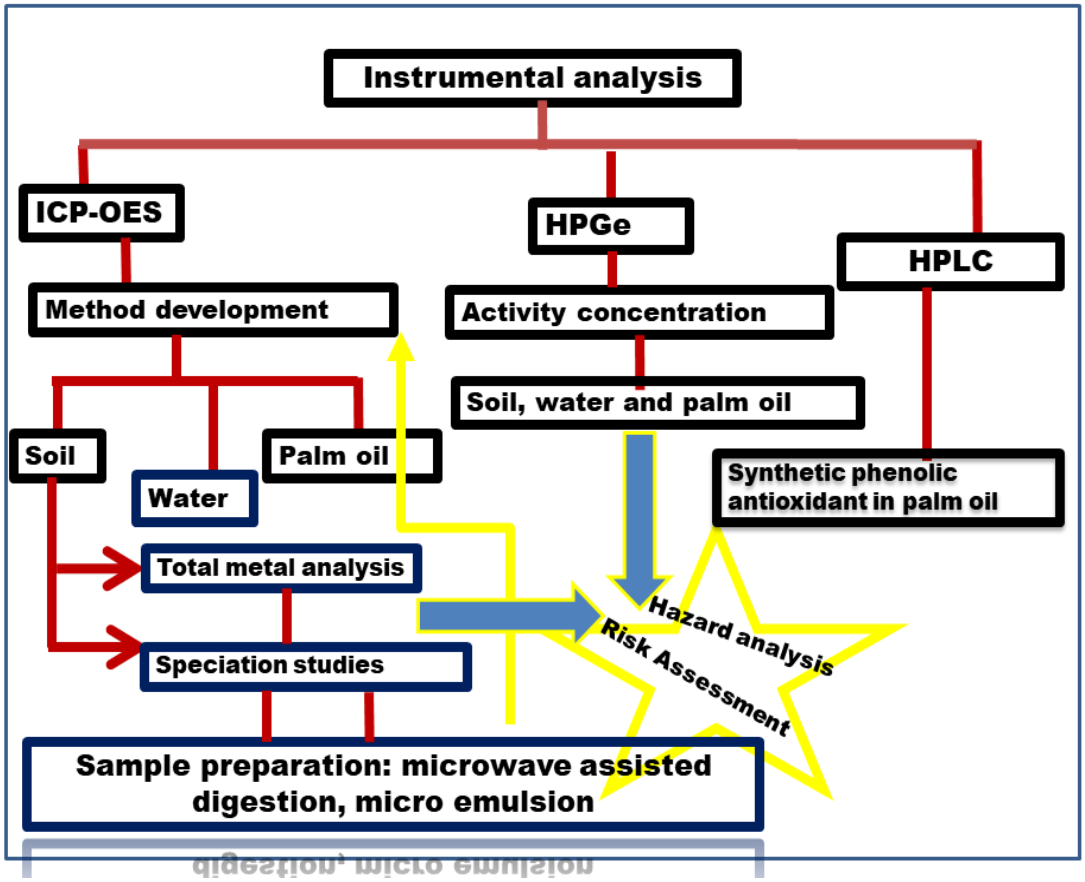



**Fig 1.6: Outline of methodology**

## 1.6 Chapters of the thesis

The thesis has been written in an article format based on the guidelines of the journal where it has been published or submitted for review consisting of thirteen chapters.

***Chapter One*** is a brief introduction on trace and toxic metals, antioxidants and radionuclides in polluted soils. Past and ongoing research has shown that soils in the region of study are polluted and hence there is a transfer of these pollutants to the edible part of plants. The oil palm tree *(Elaeis guineensis)* is the cash crop studied which is a sustainable crop for most countries and it is a useful raw material for the food, agro-allied and chemical industry. Nigeria depends on the cash crop for inclusion in the diet and use in industry. Contaminants (radionuclides, metals, and synthetic phenolic antioxidants) are transferred from soil to plant above permissible levels. Hence the need to discuss the concentration of these contaminants in the soil, water and pressed palm fruit oil. Accumulation of the contaminants in the palm oil and risk assessment to man was highlighted. A highlight instrumental analysis was taken into

consideration. The aims and the objectives of the study were included at the end of chapter one.

***Chapter Two*** introduces a detailed literature review on the study of radionuclides, metals, synthetic antioxidants and the instrumentation for their analysis. Chapter Two also analyses, interprets and critically evaluates the literature on key points of the thesis.

***Chapter Three*** is a **published** research article, which was published as the review of the literature of the title of the research work. This literature helps to synergize sources, highlight patterns, themes, conflicts, and gaps on the research concluded on similar works. It is a written overview on selected journal articles, books, government reports and provides a summary and evaluation. The published review article is entitled, "***Trace elements and radionuclides in palm oil, soil, water and leaves on oil palm plantations," a review; which was published in Critical Reviews in Food Science and Nutrition, Taylor and Francis Journal*** (O.B Olafisoye, O.O. Oguntibeju, & O.A. Osibote, 2017; 57(7), pp. 1295-1315).

***Chapter Four*** is a **published** research article on the instrumentation and method development on the use of the Inductively Coupled Plasma Optical Emission Spectrometer which was the instrument of choice for the determination of metals in the environmental samples in the study. The optimisation of the instrument was established and a published article on the analysis of metals in water. ***The research article entitled, "Determination of trace and major elements in water on oil palm plantations by Inductively Coupled Plasma Optical Emission Spectroscopy, which was published in the Instrumentation Science and Technology, Taylor, and Francis Journal*** (Olafisoye O. Bola, Fatoki O. Olalekan, Oguntibeju O. Oluwafemi, Osibote O. Adelaja, 2014. Instrumentation Science & Technology, 42(6), pp. 652).

***Chapter Five*** is a published research article on the bioavailability and accessibility of metals in the soil. This is to be considered alongside soil factors in the transfer of metals from soil, water and to the edible part of the plant. The research article is **published** and entitled, ***"An assessment of the bioavailability of heavy metals in soils on oil palm plantations in Nigeria", which has been published in the Polish Journal of Environmental Studies*** (Bola O. Olafisoye, Oluwafemi O. Oguntibeju, Otolorin A. Osibote, 2016. Polish Journal of Environmental Studies, 25(3), 1125-1140).

***Chapter Six*** is a chapter entitled, ***"Natural radionuclide activities in soil on oil palm plantations".***

***Chapter Seven*** is a research article on synthetic antioxidants. Contaminants were determined in the virgin oil (radionuclides and metals) and the synthetic antioxidant was inclusive. The

research article is a **published** research article entitled, ***"An evaluation of the level of synthetic phenolic antioxidants in virgin palm oil," which has been published in the International Journal of Food Engineering*** (Oladunni B. Olafisoye, Olalekan S. Fatoki, Omoniyi O. Oguntibeju, & Osibote O. Adelaja) 1(2), 2015).

***Chapter Eight*** is a research article entitled, "***Accumulation and risk assessment of metals in palm oil cultivated on contaminated oil palm plantation soils*****. This is an original paper accepted and published with the Elsevier Journal, Toxicology Reports** (Oladunni B. Olafisoye, Olalekan S. Fatoki, Oguntibeju O. Omoniyi, & Osibote O. Adelaja) 7

(2020), 324-334).

***Chapter Nine*** is an **original article** entitled, ***"Synthetic antioxidants and metallic elements as additives/contaminants in virgin palm oil,"*** (Oladunni B. Olafisoye, Olalekan S. Fatoki, Oguntibeju O. Omoniyi, & Osibote O. Adelaja). This is published paper in **the Asian Journal of Agriculture and Biology,** 2020; 8(2): 98-112.

***Chapter Ten*** is an original article entitled, "Assessment of Naturally Occurring Radionuclides Accumulation in Palm Oil from Soil", (OB Olafisoye, OO Oguntibeju, and OA Osibote). This is an **original paper under review in the peer review journal*: The International Journal of Environmental Science and Development.***

***Chapter Eleven*** is an original article entitled, **"*Radioactivity in drinking water on oil palm plantation communities,"*** (O.B Olafisoye, O.O Oguntibeju, and O.A Osibote). This is an original paper under review in the peer review journal: Heliyon, Cell Press, Elsevier

**Chapter Twelve** is a **General Discussion** on the key findings of the entire study.

Included in the last chapter of the thesis (***Chapter Thirteen***) is a **Recommendation** of the study and **Future Work.**

The **Appendix** and **Addendum** forms the last section of the Thesis**.**

## 1.7 References


Agrawal, S.B., Singh, A., Sharma, R.K. & Agrawal, M. 2007. Bioaccumulation of Heavy Metals in Vegetables : A Threat to Human Health. *Terrestrial and Aquatic Environmental Toxicology*, 1(2): 13–23.

Bradham, K.D., Scheckel, K.G., Nelson, C.M., Seales, P.E., Lee, G.E., Hughes, M.F., Miller, B.W., Yeow, A., Gilmore, T., Serda, S.M., Harper, S. & Thomas, D.J. 2011. Relative bioavailability and bioaccessibility and speciation of arsenic in contaminated soils. *Environmental Health Perspectives*, 119(11): 1629–1634.

Çabuk, H. (2017) 'Liquid chromatographic determination of synthetic antioxidant content of some vegetable oils produced in Turkey', *Gida / the Journal of Food*, 42(1), pp. 37–42. doi: 10.15237.

Cacho, J.I., Campillo, N., Viñas, P. & Hernández-Córdoba, M. 2016. Determination of synthetic phenolic antioxidants in edible oils using microvial insert large volume injection gas-hromatography. *Food Chemistry*, 200: 249–254. http://dx.doi.org/10.1016.

Cervantes-Trejo, A., Pinedo-Álvarez, C., Santellano-Estrada, E., Cortes-Palacios, L. & Rentería-Villalobos, M. 2018. Distribution of chemical species in the water-soil-plant (Carya illinoiensis) system near a mineralization area in Chihuahua, Mexico—health risk implications. *International Journal of Environmental Research and Public Health*, 15(7): 1-18.

Deshommes, E., Tardif, R., Edwards, M., Sauvé, S. & Prévost, M. 2012. Experimental determination of the oral bioavailability and bioaccessibility of lead particles. *Chemistry Central Journal*, 6(1): 1–31.

Dudu, V. P., Mathuthu, M. and Manjoro, M. (2018) 'Assessment of heavy metals and radionuclides in dust fallout in the West Rand mining area of South Africa', *Clean Air Journal*, 28(2), pp. 42–52. doi: 10.17159.

Francis, A. J. and Dodge, C. J. (1998) 'Remediation of soils and wastes contaminated with uranium and toxic metals', *Environmental Science and Technology*, 32(24), pp. 3993–3998. doi: 10.102.

IAEA (2014) 'Radiation protection and safety of radiation sources: international basic safety standards general safety: No GSR part 3', in *IAEA safety standards*, p. 436.

Ismail, S.R., Maarof, S.K., Ali, S.S. & Ali, A. 2018. Systematic review of palm oil consumption and the risk of cardiovascular disease. *PLoS ONE*, 13(2): 1–16

Jazzar, M. M. (2014) 'transfer of natural radionuclides from soil to plants and grass in the western north of west bank environment- Palestine', *International Journal of Environmental Monitoring and Analysis*, 2(5), p. 252. doi: 10.11648.

Jolly, Y. N., Islam, A. and Akbar, S. (2013) 'Transfer of metals from soil to vegetables and possible health risk assessment', *SpringerPlus*, 2(1), pp. 1–8. doi: 10.1186.

Khandaker, M.U., Asaduzzaman, K., Nawi, S.M., Usman, A.R., Amin, Y.M., Daar, E., Bradley, D.A., Ahmed, H. & Okhunov, A.A. 2015. Assessment of radiation and heavy metals risk due to the dietary intake of marine fishes (Rastrelliger kanagurta) from the Straits of Malacca. *PLoS ONE*, 10(6): 1–16.

Kritchevsky, D. (2000) 'Impact of red palm oil on human nutrition and health', *Food and Nutrition Bulletin*, 21(2), pp. 182–188. doi: 10.1177

Lema, M.W., Ijumba, J.N., Njau, K.N., Ndakidemi, P.A., Arusha, P.O.B.N. & Republic, U. 2014. Environmental contamination by radionuclides and heavy metals through the application of phosphate rocks during farming and mathematical modeling of their impacts to the ecosystem. *International Journal of Engineering Research and General Science*, 2(4): 852–863

Liu, B., Ai, S., Zhang, W., Huang, D. & Zhang, Y. 2017. Assessment of the bioavailability, bioaccessibility and transfer of heavy metals in the soil-grain-human systems near a mining and smelting area in NW China. *Science of the Total Environment*, 609: 822–829. doi.org/10.1016

Loganathan, R., Subramaniam, K.M., Radhakrishnan, A.K., Choo, Y.M. & Teng, K.T. 2017. Health-promoting effects of red palm oil: Evidence from animal and human studies. *Nutrition Reviews*, 75(2): 98–113.

May, C. Y. and Nesaretnam, K. (2014) 'Research advancements in palm oil nutrition', *European Journal of Lipid Science and Technology*, 116(10), pp. 1301–1315. doi: 10.1002.

Ogunkunle, C., Aniefiok, I., Adeniyi, S., Akintola, E. & Okere, U. 2017. Urban vegetable arming: Anthropic level, bioavailability, and health implication associated with bioaccumulated trace metals in selected vegetables in Ilorin, Nigeria. *Pollution*, 3(2): 285–300.

Ohimain, E.I., Seiyaboh, E.I., Izah, S.C., Oghenegueke, E. V & Perewarebo, G.T. 2012. Some selected physico-chemical and heavy metal properties of palm oil mill effluents. Greener *Journal of Physical Sciences*, 2(4): 2276–7851.

Olafisoye, O.B., Oguntibeju, O.O. & Osibote, O.A. 2017. Trace elements and radionuclides in palm oil, soil, water, and leaves from oil palm plantations*: A review. Critical Reviews in Food Science and Nutrition*, 57(7): 1295–1315.

Orisakwe, O.E., Blum, J.L., Sujak, S. & Zelikoff, J.T. 2014. Metal Pollution in Nigeria: A Biomonitoring Update. *Journal of Health and Pollution*, 4(6): 40–52.

Sai Kiran, S. 2017. A Review on Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) with a Special Emphasis on its Applications. *Der Pharmacia Lettre*, 9(10): 44–54.

Shasha, D. (2014) 'Reversed Phase HPLC-UV Quantitation of BHA, BHT and TBHQ in food items sold in Bindura supermarkets, Zimbabwe', *International Research Journal of Pure and Applied Chemistry*, 4(5), pp. 578–584. doi: 10.9734.

Szarlowicz, K., Reczynski, W., Misiak, R. & Kubica, B. 2013. Radionuclides and heavy metal

concentrations as complementary tools for studying the impact of industrialization on the environment. *Journal of Radioanalytical and Nuclear Chemistry*, 298(2): 1323–1333.

Takáč, P., Szabová, T., Kozáková, L., Benková, M. & Takáč, Peter. 2009. Heavy metals and their bioavailability from soils in the long-term polluted Central Spiš region of SR. *Plant, Soil and Environment*, 55(4): 167–172.

Tessier, A., Campbell, P. G. C. and Bisson, M. (1979) 'Sequential Extraction Procedure for the Speciation of Particulate Trace Metals', *Analytical Chemistry*, 51(7), pp. 844–851. doi: 10.1021.

Yankah, V. V., Ushio, H., Ohshima, T. & Koizumi, C. 1998. Quantitative determination of butylated hydroxyanisole, butylated hydroxytoluene, and tert-butyl hydroquinone in oils, foods, and biological fluids by high-performance liquid chromatography with fluorometric detection. *Lipids*, 33(11): 1139–1145.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Radiochemistry

Radiochemistry can be defined as the chemistry of radioactive materials or elements that can be naturally made or artificial. Scientists have created a platform of research using the principle of radiochemistry all over the world. Radiochemistry shows insights into the fundamental physical properties, which radionuclides do exhibit (Rudziński & Komosa, 2011). Applications of radioactivity are in the radiochemical industries, atomic energies, processing, and the development of new methods and ideas in chemistry and physics and the synthesis of radionuclide compounds.

## 2.2 Naturally Occurring Radioactive Materials (NORM)

NORM (naturally occurring radioactive materials) is an acronym and simply described as radioactive materials naturally found in the environment. Humans are exposed to natural radioactivity called Natural Radioactivity or NORM because of two decay series, ($^{238}$U and $^{232}$Th) and $^{40}$K in the soil. Minerals and raw materials found on earth contain radionuclides of natural origin. The most important ones, which are usually, considered when discussing health and radiation protection are the $^{238}$U and $^{232}$Th series and $^{40}$K. Most of the human activities on earth involving the use of minerals and raw materials and the level of exposure of these naturally occurring radionuclides are not greater than the normal background levels and not of much concern in radiation protection studies. There is certain human made activities, which can lead to an enhanced exposure of these naturally occurring radionuclides, and hence regulatory bodies (Blundell, 2015) must control these radionuclides. In time past, regulatory attention was focused on the mining extraction and processing of ores of uranium. This activity has an ability to enhance the concentration of the naturally occurring radionuclides. Hence, affected countries have introduced guidelines and regulations for their control. Terrestrial sources of NORM are the vast majority as they occur in the ground, earth, and mantle and human activities may increase their exposure. Most significant are Uranium and Thorium series. Another major source is Potassium 40, which has a half-life of 1.25 billion years (Blundell, 2015). This is found naturally in foods and forms about 0.012 % of natural potassium isotopes K-39 and K-41. This gives the average human being a dose of around 1 mSv per year (approximately 12 nGy/h) (Rodgerson & Reidenberg, 2012). Recently, over the few decades, several countries have initiated actions and standards to regulate the effect of exposures related to the use of some raw materials and food (Robertson *et al*., 2004a; Blundell, 2015). The International Basic Safety Standards for Protection against Radiation and for the Safety of Radiation Sources is a document which contains provisions for protection standards against

the elevated exposures of radiation in humans from natural sources of radiation (WHO, 2018; Doyi *et al.*, 2017; NCRP, 1987; L' Annunziata & Mohammed, 2003; Pattison & Hugtenburg, 2009). Rocks such as feldspar, phosphogypsum mica, and granite contain concentrations of radionuclides that occur naturally and of late the description of these radionuclides have been extended to those which are anthropogenically produced (Blundell, 2015). However, certain anthropogenic and human activities significantly increase such concentrations and the concentration of these radionuclides must be regulated (Pibida, 2012; Joyce *et al*., 2017). The radiation from naturally occurring radionuclides sources may probably cause some form of cancers but there is no sense in trying to regulate NORM. The concern is when anthropogenic activities cause the natural radioactivity to be concentrated to Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM) (Blundell, 2015; IAEA, 2014; Ishida & Yamazaki, 2017). TENORM exposures to human are that it should not be more than 1 mSv to members of the public from sources such as nuclear reactions in the applications of $^{60}$Co or $^{137}$Cs in industry or staying next to a nuclear reactor. This is radiation over and above NORM, or TENORM and adds more than 1 mSv.to the average human dose exposure. Other natural exposures that are present are radon gas from the Uranium series that can build up in houses and medical application such as X-rays and fall-out from Chernobyl and nuclear power stations in some regions of the world (L' Annunziata & Mohammed, 2003).

### 2.3 NORM in industrial areas

The uranium mining is one of the highest producing industries when it comes to the introduction of NORM to the environment. Other associated industries include the industries where coal is produced and combusted, petroleum and petroleum product industries, smelting of metal industry, the precious metal mining industry, rare earth mining industry and the phosphate fertilizer industry (Chambers, 2015).

#### 2.3.1 NORM in the coal and energy producing industry

Coal fired combustion plants emit more radioactivity into the environment when compared to other industries. This is particularly in areas where there is no deployment of emission reduction technology such as scrubbers and flue gas de-sulphurizers. Coal contains a substantial amount of Uranium, Thorium, Potassium, and their progenies. The level of radionuclides in coal is similar to those close to their geology and region such as rocks and vegetation approximately or near the coalmine (Kolo *et al.,* 2016; Olise *et al.,* 2016; Carvalho, 2017; EPA, 2008; Baxter, 1993; Dudu *et al*., 2018). Coal is used in electricity production and the coal wastes buried in landfills. Recently, fly ash is used in construction and the production of building materials. Coal mining in open pits or underground mines produces a considerable quantity of waste rocks and soils. Coal sediments discharged into wastewater and effluents

have elevated concentrations of NORM. Miners mine coal underground and this poses occupational hazards (Tchokossa *et al*., 2013; Harlow, 2017).

### 2.3.2 NORM in the metal and smelting industry

Ore tailings and smelting slag are waste produced in the metal and smelting industry. These wastes contain large quantities of NORM at elevated concentrations. Radon gases in metal mines pose risk to workers. Dusts formed during mining also contain high levels of radionuclides (Todorović *et al*., 2017).

### 2.3.3 NORM in the phosphate and fertilizer production industry

A common fertilizer is the phosphate fertilizer. Phosphate is mined in high concentrations in countries such as USA, Morocco, and China with phosphoric acid as the intermediate step in the production of phosphate from phosphate rock (Harb *et al*., 2008). The leaching of the phosphate rock with sulphuric acid produces gypsum (phosphogypsum) which contains about 80 % $^{226}$Ra, 30 % $^{232}$Th and 14 % of $^{238}$U (ARPANSA, 2008; International Atomic Energy Agency, 2007; Coenen et al., 2017; Pibida, 2012). This is a significant NORM material. In the United States of America and other countries, EPA bans the use of phosphogypsum with radium equivalent greater than 370 Bq/kg. The processing and use of phosphate fertilizer have measurable dose of radioactivity, which affects humans (Scholten & Timmermans, 1995; Harb *et al*., 2008).

## 2.4 Gamma ray interaction with matter

Gamma rays penetrate the body posing alarming radiation threat that requires shielding from dense materials like lead or concrete to reduce harm to living cells. Materials with high atomic numbers and densities (compactness) shield gamma rays by contributing to the overall stopping power. Gamma decay alters the state of a nucleus during shielding, as it possesses ionizing properties, which causes the scattering of ions and electrons. Gamma rays are ionizing causing the scattering of ions and electrons. They are emitted when radioactive atoms or isotopes decay and the daughter nuclei produced in an excited state, which consequently decays to a lower state gamma ray photon. Gamma rays strike materials producing excited atoms, which emit characteristic secondary gamma rays as described in nuclear gamma fluorescence and applied in nuclear physics and spectroscopy (Davisson, 1965).

A description of the gamma photons energy is seen by the equation

$$E = h\nu = h\frac{c}{\Lambda} \dots\dots\dots\dots\dots [1]$$

where: $h, c \; and \; \Lambda$ : are the Plank's constant, velocity of light and wavelength respectively. Gamma ray is penetrating with high ionization from radioactive decay of atomic nuclei or

isotopes of atoms. It has a short wavelength when compared to other electromagnetic radiations and possesses the highest photon energy. The physical universe is comprised of energy and matter and there is a constant interaction between these two. Health effects of gamma radiation present significant risks as they are ionizing and knock out electrons from atoms and molecules. However, less ionizing and penetrating when compared to alpha and beta radiation; they penetrate skin damaging internal organs and bone marrow. It produces and discharges electromagnetic radiation (Knoll, 1999; Ragheb, 2008). This interrelationship is demonstrated in the photoelectric effect of matter, electron positron pair production in matter, photo-fission interaction with matter, Rayleigh, Thompson, and the Compton scattering. At low to high energies in comparison to visible light, a photon can be absorbed to eject an electron from the atom in the photoelectric effect. Higher energies may strike the nucleus producing an electron and a positron in pair production Description of Compton scattering may be likened to a photon from the left direction hitting a target at rest and resulting in the production of a new photon. The target recoils by carrying a part of the incident energy away (Pattison & Hugtenburg, 2009; Davisson, 1965; Charles, 1961).

### 2.4.1 Photo-electric effect

Matter absorbs electromagnetic radiation emitting X-rays and establishing a phenomenon known as the photoelectric effect. The photoelectric effect is produced when a gamma ray hits an electron in an atom whereby all the energy of the gamma ray is absorbed by the electron, which leaves the atom with a kinetic energy equal to the energy of the gamma ray, minus its binding energy (which is usually much less than that of the gamma ray). When a solid absorbs electromagnetic radiation, there is an ejection of an electron usually from the ‘K’ shell. The photoelectric effect in radiochemistry and radiation medicine protection helps in transforming penetrating X-rays into electrons, hence protecting life from the penetrating effects of these radiations (Knoll, 1999; Ragheb, 2008). The shell structure of atoms is important in combating an electron when it exceeds the binding energy. The principle behind the study of photoelectric effect is applied quantum chemistry in the theory of the wave/particle nature of light. The photons of light beam have a particular energy, which is proportional to light frequencies. In the photoemission process, if an electron absorbs photon energy of one photon, which is greater than the electron binding energy, the electron is ejected (Bubb, 1924; Hufner, 2003; Weaver & Margaritondo, 1979; Zhang, 1996). With low photon energy, the electron is unable to escape and an increase in low frequency light will produce low-energy photons. Overtime the outer electron moves to occupy the vacancy that is created with an emission of a photon. The photoelectric effect is a principal form of interaction of gamma ray with matter and the scattering effect is caused by the interaction of X-rays or gamma rays with free electrons (Knoll,

1999) In Compton's theory light is not explained as a wave but as a particles (photons) with energy which is proportional to the frequency of light. The deflection and diffusion of a photon by a charged electron is described by a phenomenon, which results in a reduced energy of the photon or gamma ray. Transfer of energy of the photon to the electron is deflected with the help of an electron or charged particle (Bubb, 1924; Hufner, 2003; Weaver & Margaritondo, 1979; Zhang, 1996).

### 2.4.2 Compton effect/scattering

Compton scattering is a phenomenon whereby a photon has a high impact collision with a free electron. Conservation of energy and momentum is fundamental to this process as it leads to the equation for the scattered photon. It is a principal form of interaction of gamma ray with matter and the scattering effect is caused by the interaction of X-rays or gamma rays with free electrons (Knoll, 1999). In Compton's theory, light is not explained as a wave but as a particle (photons) with energy, which is proportional to the frequency of light. There is a conservation of momentum of the system when an electron and a photon interact. The electron recoils energy to the photon, which emits this energy in a different way conserving momentum of the system. The deflection and diffusion of a photon by a charged electron is described by a phenomenon, which results in a reduced energy of the photon or gamma ray. Transfer of energy of the photon to the electron is deflected with the help of an electron or charged particle (Christillin, 1986; Malcolm, 2004).

### 2.4.3 Pair production

Pair production is the creation of a sub atomic particle and its anti-particle, which is usually created close to the nucleus. The probability to find an electron in pair production of a neighbouring atom is high and the probability of this process is proportional to the square of the atomic number. For photons with high energies, the principal mode of interaction of the energy with matter is pair production (Hubbell, 2006). This is in accordance with the Einstein equation.

$$E = mc^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [2]$$

Where $m$ is the mass of the particle, $E$, the energy and $c$ the velocity of light.

The Einstein's equation shows the conversion of the photon's energy to particle mass. The photon must have more energy than the sum of the rest mass energy of the electron and the positron that are created in the process; In addition, the photon must be close to an atomic nucleus for this process to occur. When these criteria are met, the energy of a photon can then be converted into an electron–positron pair (Hufner, 2003). The near proximity of the photon

to the nucleus is to satisfy the law of conservation of momentum. This leads to pair production and the nucleus recoils. The probability of pair production is approximately proportional to the square of the atomic number of the nearest atom (Zhang, 1996; Hubbell, 2006). An opposite reaction to electron pair production is the electron positron annihilation. The reverse of this phenomenon describes as electron positron annihilation. The overall process provides an avenue where photons can lose energy as they interact with matter (Nagirner & Loskutov, 1999). It further describes the disappearing act of a photon replaced by the antimatter or opposite pair. The process of creating a subatomic particle and its antiparticle from a neutral boson is the principle behind pair production (Hubbell, 2006).

### 2.5 Radioactive decay and schemes

Radioactive decay can be defined as a process where by an unstable nucleus disintegrates and loses radiation energy. The common radioactive decay is alpha, beta, and gamma decay. Radioactivity decay occurs randomly and it is impossible to predict the time an atom will decay. Hence, for a number of identical atoms, the overall rate of decay can be denoted by decay constant or a half-life (Rodgerson & Reidenberg, 2012). For alpha and beta decay, the decaying nucleus is referred to as the parent radioisotope that produces daughter nuclides with differing number of protons or neutrons or both which creates an atom of a different element. In gamma decay, the radioactive nucleus might decays by first emitting an alpha or beta particle. A daughter nucleus is created which is left in an excited state and can decay to a lower energy state emitting gamma rays. Gamma decay are usually accompanied by other types of decay and are released shortly after such decays or at about the same time. Gamma decay is unique because of gamma decay of metastable nuclear isomers created from other forms of radioactive decay (L' Annunziata & Mohammed, 2003). The average lifetime and half-life of a large number of nuclei can be known but the time until an individual nucleus decays is unknown (Nagirner & Loskutov, 1999). Several radionuclides have been successful in medicine for the treatment of a number of diseases and disorder (Pattison & Hugtenburg, 2009; (NCRP, 1987). Though radiation could naturally be found in rocks and soils, such as some forms of mica, clay and feldspar, man's activities in the use of nuclear weapon testing, irradiation in medicine and agriculture has generated anthropogenic sources of radionuclides. Acute effects are manifested in forms of cancers and tumours. Radioactive decay nuclei, which are unstable usually, emit radiation to attain a more stable nucleus. Naturally occurring radioactive materials decay into their daughter nuclides from parent nuclide emitting alpha, beta, gamma rays, or other forms of emitters. Radionuclide decay schemes can be represented in flow diagrams or graphically to show how the transitions and atoms are related with the indication of what type of radioactive decay is involved (UNSCEAR, 2000, 2010; (Knoll,

1999; Ragheb, 2008; Joyce et al., 2017). The respiratory tract model discusses at length the routes in which radionuclide particles enter the human body (NCRP, 1987; Rodgerson & Reidenberg, 2012).

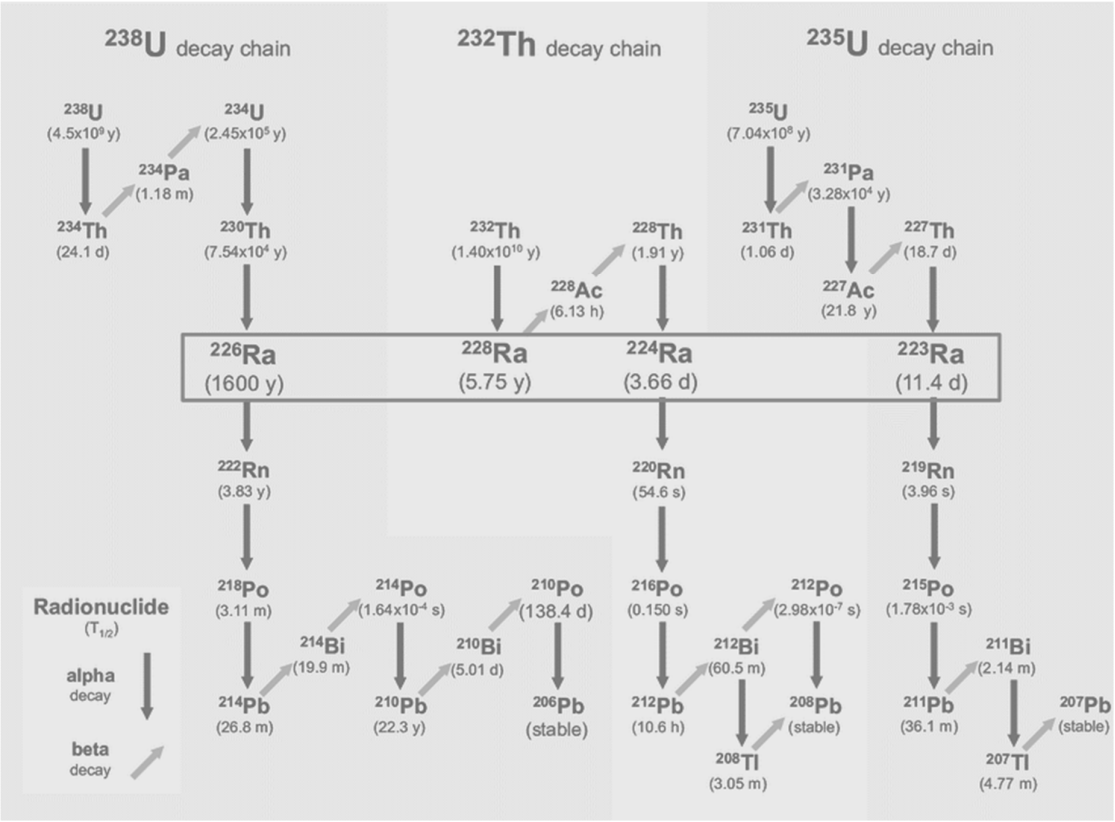



**Fig 2.1: Radioactive decay schemes (Attallah, *et al.,* 2012)**

## 2.6 Virgin pressed palm oil and the oil palm tree

Palm oil has been considered globally as one of the important vegetable oils (Oguntibeju et al., 2010; May & Nesaretnam, 2014; Zulkiply et al., 2019). The oil palm plantation is cultivated in regions of the world most especially Asia and Africa. It is one of the highest economic and productive oils when compared with other adipose fatty oils. The oil palm fruit contributes its percentage to the worlds demand for healthy vegetable oils and saturated fats (Winarso et al., 2016). Areas suitable for the production of the oil palm tree are rich in wildlife and this sector has experienced a lot of challenges recently especially when it comes to the extinction of some species of wildlife such as the Orang-utan.

Due to the expansion of the palm oil plantation and pollution, the plantation land stretches into forests and such forest are fell, demolished and razed down. Habitat destruction as farming land expands and forests are cut-down leading to the extinction of species is the main cause

of the present day extinctions (Gruca et al., 2014). The increase in agriculture especially of the oil palm plantation has caused an expanse in the rate of deforestation in Africa and Asia. Since these trees are predominantly owned by large-scale owners. Oil palm plantations have destroyed habitats and threatened the biodiversity of some species. Nevertheless, the palm oil and the palm oil products have been rated as one of the economical cash crops of most nations (Ohimain et al., 2012; Shimizu & Desrochers, 2012). Virgin pressed palm oil is a very important product for human consumption and the industry. The thick red viscous liquid reduces cholesterol levels and slows down the frequency and occurrence of heart related diseases. In addition, an antecedent support in the boost of brain health and mental function.

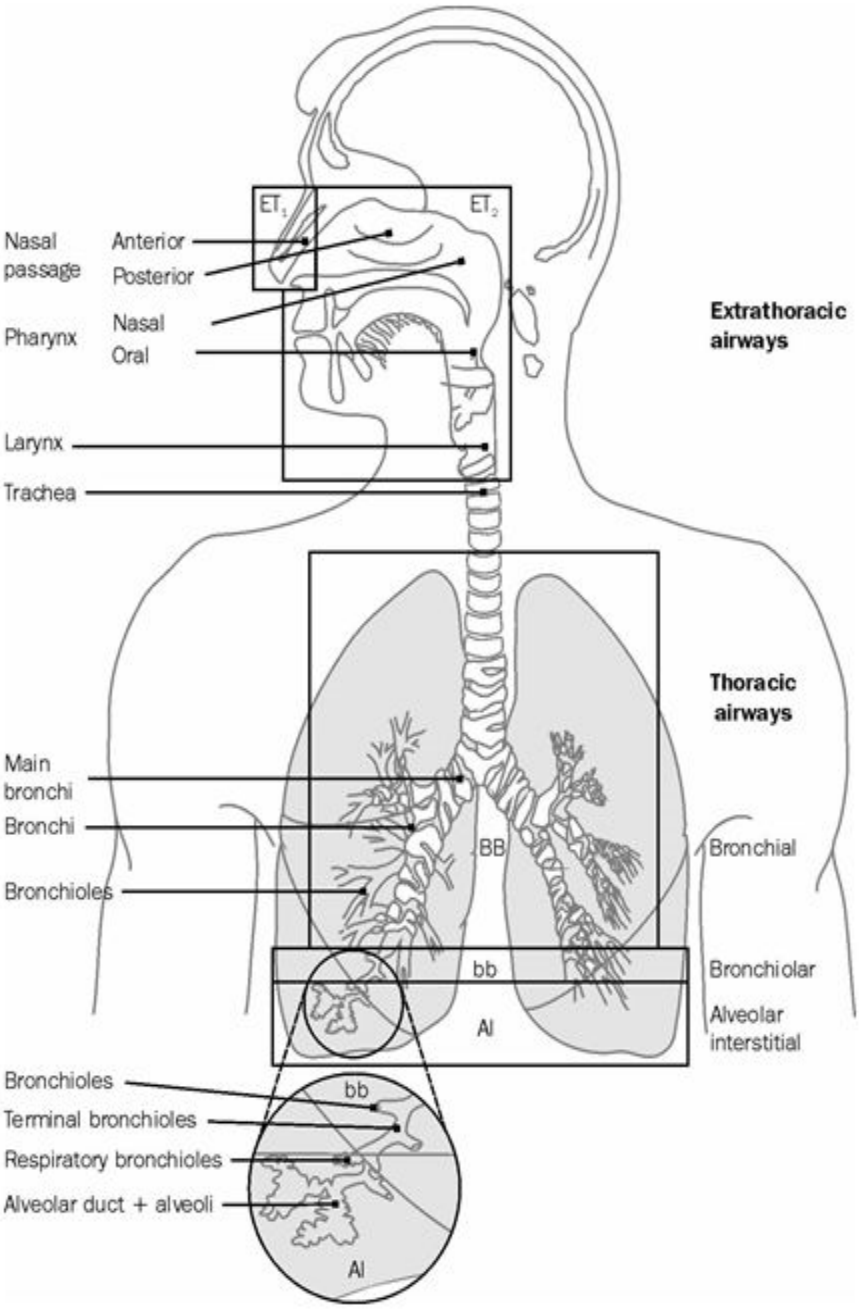



**Fig 2.2: The ICRP Human Respiratory tract model (Charles et al., 2005)**

The palm oil is packed with plant nutrients and vitamins, which helps in the alleviation of oxidative stress improving skin and hair health (Ajuwon et al., 2013; Gruca et al., 2014; Ismail et al., 2018). The oil palm tree has a lot of usefulness as all the proportions and parts of it are useful. The leaves and husks have been used in folk medicine from way back. These are effective in the treatment of cancer and tumours and for the treatment of various cardiovascular and visceral organ diseases. Rich in phytonutrients, it has also been utilized in the production of succinic acid and a good source of carbon (Taghvaei & Jafari, 2015; EPA, 2002).

### 2.7 Bioavailability and accessibility of metals in soils on oil palm plantations

Bioavailability and Speciation is explained by a few researchers as “the identification and the description of different species, forms or phases in which an element occurs. The oxidation states of metals differ in complexes (Zimmerman & Weindorf, 2010; Liu *et al.,* 2017). The bioavailability is more concerned on the harm or toxicity of a metal to plants. The world-wide goal of the remediation of soils contaminated with metals is necessary to reduce the risks associated in using such soils, restitution of damage and restore land to promote food security. It is an important tool for regulatory bodies and government and this is important as it accesses risk and hazard (Liu *et al.,* 2017). Various methods have been used to determine how bioavailable or bio accessible a metal is in soil. Several scientists have also considered the approach of steps of extraction methods. The mostly used extraction method is that which Tessier and colleagues propose, which is a three-stage extraction protocol (Tessier *et al*., 1979). This stage process involves different extraction and acid digestion steps and allows for the measurement of the metals in the soil using the Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). It is obvious that trace metals (at elevated concentration) and toxic metals have the potential of posing danger to humans and the environment. Metals are usually classified into mobile, immobile and semi mobile fractions and it is only a particular percentage of the concentration that is mobile or available for plant uptake and the accumulation in human (Takáč *et al*., 2009). Variations in different available concentrations could be explained by total metal concentration. It is pertinent that predictions would be enhanced if soil physicochemical properties were determined such as pH, electrical conductivity, soil organic matter and more. Soils of oil palm plantations are polluted generally with metals and radionuclides. Pollution sources are diverse which ranges from poor agronomical practices, industrial effluents, oil spillage, and urban domestic waste. Pollutants remain in soil for a long residence time, as they are persistent and generally non-biodegradable. Sources of pollution may generally be spread over a large area in a different manner and not concentrated (Sylvia et al., 2017). For a general and detailed assessment of risk factors from plants to humans, a combination of factors must be considered which includes

but is not limited to metal speciation, bioavailability and bioaccessibility for the assessment of permissible levels by regulatory bodies (Bradham *et al*., 2011; Deshommes *et al*., 2012; Cervantes-Trejo *et al*., 2018). Various researches and methods have been applied to access this concept but the mostly used is that proposed by Tessier and colleagues where a sequence of extraction steps with various strong acids, oxidizing and reducing agents, complexation and chelating agents have been used to extract the mobile, immobile and semi mobile metals. These extracted metals are an indication of the concentration of metals in soil available for plant uptake. Other forms of metal toxicity in humans can arise from atmospheric deposition, dust inhalation and skin contact (Ono *et al*., 2016; Yang *et al*., 2018; Tessier *et al*., 1979; Jaishankar et al., 2014; Balkhair & Ashraf, 2016).

### 2.8 Accumulation factor and risk assessment

A major pathway through which metals enter soils is by anthropogenic means. Plant species significantly accumulate metals in various parts especially the fruits thereby remediating soils. This leads to bioaccumulation and bio magnifications in the food chain and the disruption of chemical and biological activities in the human body. The routes through which metals enter the food chain are via inhalation and ingestion. Although literature reveals that, some species of plants can bio accumulate metals better than others (Balkhair & Ashraf, 2016; Jia *et al*., 2018). Anthropogenic sources of metal pollution are mostly from industries and unwholesome farming practices. Wastewaters from factories usually drain to farmlands elevating the levels of metals in soils. The populace is incessantly exposed to metals through the consumption of food grown on such soils. Numerous literatures support this fact (Jiang *et al*., 2013; Chibuike & Obiora, 2014; Wuana & Okieimen, 2014; Balkhair & Ashraf, 2016; Tesfaye & Abebaw, 2016; Jia *et al*., 2018; Yang et al., 2018; Chen *et al*., 2019; Pobi et al., 2019). The study of metals in soils requires systematic assessment as a monitoring approach to eradicate the effects on the food chain. Risk assessment has been studied using various tools such as the Accumulation Factor (AF), Hazard Quotient (HQ), Health Risk Index (HRI), Daily Intake of Metals (DIM), Target Hazard Quotient (THQ), Morbidity Status (MS), Enrichment Factor (EF), Degree of Contamination ($C_{deg}$) and the Uptake/Transfer Factor (UF) (Balkhair & Ashraf, 2016). Non-essential metals bio accumulates in plant parts. Toxicity increases overtime and this becomes a threat to humans and animals when such plant parts are consumed as food. Application of fertilizers, untreated sewage water from municipal and industrial applications, leaching from dumpsites, fertilizer application, and waste from mining have contributed significantly to the build-up of metals in soils (Gruca *et al*., 2014). The oil palm tree (*Elaies guineensis*) is a perennial crop. It is an excellent source of fatty acids, minerals, and vitamins for the food and chemical industry. Palm oil from the oil palm fruit has been proven to cure various diseases

especially cancer and heart maladies (Ajuwon *et al*., 2013; Imoisi *et al*., 2015; Pezeshk *et al*., 2015).

### 2.9 Synthetic phenolic antioxidants in oils to prolong shelf life during storage

Auto oxidation usually sets in when edible oils are stored prior to usage. This can be seen as deterioration of the aesthetics of the oil. Antioxidants may be added, either natural or synthetic to virgin palm before storage of the oil to prevent the unset of auto oxidation. Usually during storage, antioxidants both natural and synthetic are added to oil to stop the oxidative degradation of the oils during storage (Ayodele & Oluyomi, 2011; Shimizu & Desrochers, 2012; Gruca *et al*., 2014). Generally synthetic antioxidants are defined as substances added to oils to prolong the shelf life of such oils preventing the unset of auto oxidation which causes rancidity, change in colour, texture and odour of the oils. They act by inhibiting reactions that catalyse oxygen through the transfer of hydrogen and hence inhibiting the chemical reactions, which favour the production of aldehydes, ketones and peroxide radicals, major substances contributing to auto oxidation (Shasha, 2014). The applications of antioxidants range across a wide variety of products such as fruit concentrates and juices, snacks, confectionaries and meat. Usually manufacturers and local farmers may use antioxidants in the preservation of their products and this may be oblivious to the consumers. There is a possibility of synthetic antioxidants being added to farm produce. Local farmers may add these additives to prolong the shelf life of the palm oil without adequate analytical measurements or quality control (Pezeshk *et al*., 2015; Taghvaei & Jafari, 2015). Synthetic antioxidants in oils have the ability of preventing the oxidation of unsaturated fatty acids. They also help to prevent chain initiation in oils. The increased concentration of synthetic antioxidants in various analyses from various countries in foods is not strictly recognized. Synthetic antioxidants are chemically synthesized since they do not occur naturally in nature and are more harmful than beneficial to man. At low and permitted concentrations, synthetic antioxidants could be helpful in the prevention of spoilage of food in addition to possessing anti-inflammatory and antiviral properties (Pezeshk *et al*., 2015). Regulatory bodies responsible for the administration and control of synthetic antioxidants have not been very effective especially in developing countries. Generally, the guidelines for the administration and control for synthetic antioxidants vary from country to country. Invariably the administration of synthetic antioxidants depends on the interest of the manufacturer who may want to prolong the shelf life of the food above a certain limit. Most manufacturer label synthetic antioxidants as dietary supplements while others especially local farmers do not give any information on the composition of a particular food additive whether singly or in combination with other antioxidants. Synthetic antioxidants in minute concentrations may not pose a threat to human health although elevated concentrations and

long-term use in humans can lead to acute and chronic toxicity. Chronic toxicity is manifested in symptoms such as cancer, obesity, infertility, mutation, and decreased immunity. The choice of synthetic antioxidants in palm oil by the manufacturer is dependent on many factors that range across value regulation and its efficacy. Most countries have placed a ban in the use of synthetic antioxidants singly or in combination with other antioxidants, though these regulations are not enforced especially in developing countries. This is a very good reason why the use of synthetic and natural antioxidants in foods should be checked and kept under control (Shasha, 2014; Pezeshk *et al*., 2015; Ismail *et al*., 2018).

### 2.10 Analysis of metals using the ICP-OES

The concentration of trace elements is important as it promotes the uptake of essential nutrients, growth, and the production of enzyme for the optimum performance of the plant. These are required in minute quantities as elevated amounts become toxic. Trace and essential elements include and are not limited to Iron (Fe), Cobalt (Co), Molybdenum (Mo), Zinc (Zn), Copper (Cu) and Nickel (Ni). The most popular toxic metals are Lead (Pb), Mercury (Hg), Arsenic (As) and Cadmium (Cd). Several sources of anthropogenic pollution exist and these increase the concentration of the natural input of metals in the environment from natural sources such as volcanic explosion, weathering of rocks and soils, deposits from the atmosphere, tsunamis etc. (Rainbow, 1995; Nunes *et al*., 2011; Sai Kiran, 2017). In general, the concentration of metals in the environment from natural and anthropogenic sources is mostly due to underlying rock formations, industries, pre-planting and post planting operations, crude oil spillage and the burning of fossil fuels, mining and metal smelting activities, municipal effluents and much more. This threatens land and aquatic life (Rainbow, 1995; Nunes *et al*., 2011; Sai Kiran, 2017).

The analysis of metals using the Inductively Coupled Plasma, Optical Emission Spectrometer involves an analysis that is relatively cheap. It also has good sensitivity, multi-element capability and a wide dynamic range that measures elements in parts per billion and parts per million. The instrument was used for this study and it was able to measure the complete elemental spectrum for the determination of major, minor and trace elements with good precision and safety (Sai Kiran, 2017). The determination of metals in virgin palm oil is of economic importance because palm oil is a very important cash crop for the food and chemical industry. It is essential to determine the presence of metals in the oil as this determines the standard for the grade and worth of the palm oil. Metals in palm oil are deleterious because this affects the shelf life and aesthetic quality of the oil. Metals enhance the oxidation of fatty acids to esters, which affects the nutritional value and the properties of the oil. Metals in virgin palm oil samples are generally toxic at elevated concentrations. However, trace elements are

essential to man, their presence in elevated concentrations in palm oil, may not be ideal for production processes. This is particularly an issue in the production of biodiesel due to the presence of such metals that consequently affects the quality of the oil. The determination of metals in the virgin palm oil using the Atomic Absorption Spectrometer (AAS) was not adequate due to the nature of the matrix and the difficulty of the analyte to be separated from such matrix. The ICP-OES was a better option. This was also attributed to the instability of the analyte in the oil and the high organic content of the oil. The use of hazardous solvents had to be employed to destroy or dissolve the matrix as the case may be so the analyte may be free in solution. Sample separation and pre-treatment steps were long and laborious. Such sample preparation steps such as solid phase extraction, microwave assisted acid digestion and wet/dry aching, involving hazardous acids or a mixture of both was normally employed. Another disadvantage of using AAS process was the use of very expensive organometallic standards for instrument calibrations. The proposed method in the present research eradicated the use of hazardous chemicals and the use of expensive unstable organometallic standards for calibration (Nunes *et al*., 2011; Galuch *et al*., 2018). Micro emulsions were employed for the determination of metals as a sample preparation method in this analysis. The micro emulsions were stable thermodynamically when tested using a UV spectrometer after being observed for about three hours. Micro emulsions were composed of water, oil, and alcohol. In addition, the micro emulsion particles were homogenous and were actually in the order of 5-100 nm in size suspended in a phase, which is continuous. The proposed ICP-OES analysis using oil-water micro emulsion as sample preparation method was not only reproducible, accurate and reliable but also equally convenient because it provided a sample extraction capable of breaking complex matrix in virgin palm oil for metal analysis by ICP-OES (Nunes *et al*., 2011; Galuch *et al*., 2018).

### 2.11 Radioactivity in food and drinking water

The most predominantly occurring radionuclide in food is Potassium ($^{40}$K). Apart from naturally occurring radionuclides, other radionuclides such as Caesium and Strontium are found in the environment from fallout of artificial sources of radioactivity. (Tchokossa *et al.,* 2013; Hempelmann, 1965; UNSCEAR, 2000; EPA, 2002; Chad-Umoren & Umoh, 2014; Isinkaye *et al*., 2018; Galuch *et al*., 2018; Joel *et al*., 2019). Natural radioactivity includes Potassium ($^{40}$K), Thorium ($^{232}$Th), Uranium ($^{238}$U), and their daughter radionuclides. Radioactivity contributes to four-fifth of the annual effective dose of radioactivity affected by humans (UNSCEAR, 2010; Alausa *et al*., 2017). Soils may be contaminated naturally from geological materials or by human made activities. (Durusoy & Yildirim, 2017). The major route through which humans ingest radionuclide is via food (Osibote *et al,* 1999; Chad-Umoren & Umoh, 2014; Isinkaye *et*

*al*., 2018). Edible and cash crops and drinking water are susceptible to contamination from natural and artificial radioactive elements. The transfer factor is usually from soil to the consumable parts of the crop. The accessibility of radionuclide by plants has been studied to be based on and influenced by factors such as soil acidity and alkalinity Total organic content and the degree of electrical conductivity. Pre-planting and post planting activities are also key and significant points for consideration as it plays an important role in the transportation of radionuclide from soil by plants. Another major route of radionuclide from soil to consumable parts of the plants could be in the event of an uncontrolled release of fallout or the suspension of washes off from rain. Foods are prone to contamination especially during the rainy season. Plant roots absorb such radionuclide from irrigation or ground water (Chad-Umoren & Umoh, 2014). Internal exposure to man is usually from the ingestion of foods grown on such soils. The transfer of radionuclide from soil to plant is usually one of the first pathways via ingestion and the transfer of radionuclide to man. Radionuclides transported to fruits through the plant growing process are from the $^{40}K$, $^{238}U$, and $^{232}Th$ that occurs in soil. This is independent of industrialization but may be enhanced by industrialization and this has increased since independence in the southern states of Nigeria due to the discovery of crude oil and the production of cash crops such as the oil palm. Currently, comprehensively studies have been performed on the transfer factor of radionuclides for diverse foods such as rice, milk, grains, and vegetables (Adamu *et al*., 2013; Itoh *et al*., 2014; Tchokossa *et al*., 2013; Alausa *et al*., 2017; Durusoy & Yildirim, 2017; Osibote *et al*, 1999). The determination of radioactivity in environmental samples is of paramount importance to humans to prevent the translocation of such radionuclide to the food chain. The evaluation of radionuclide demands dependable and efficient techniques. Most times the support of IAEA is sought in on a vast number of environmental samples (IAEA, 2007). This will assist member states in the development of accelerated analytical procedures for the determination of radionuclide. Recently radiochemical methods have been replaced with more recent techniques that are non-destructive such as the gamma ray spectrometry. Factors to consider when analysing radionuclide may include the source of release of such radionuclide and the season of the year (UNSCEAR 2000, 2010; Adamu *et al*., 2013). About 83 % of the exposure to radionuclide and effective dose is usually from the activity of radionuclides such as $^{232}Th$, $^{238}U$ and its progenies and $^{40}K$. The remaining percentage is contributed artificially or anthropogenically. Radium is the most radiotoxic of the naturally occurring radionuclides since it has a relatively long half-life. $^{226}Ra$ is toxic because it mimics the properties of calcium, which is a macro element essential to plant and animal life. Potassium 40 has the tendency to be absorbed and assimilated into tissues of plants and animals through normal biochemical processes. The study of the radioactive elements is essential because it is bioavailable in soils in the fine clay

fraction or the Fe-oxide fraction. Radionuclide deposited in soils overtime is a precise pathway to the food chain. Several levels of radioactivity can be found in soils and rocks through natural and human made means. Radioactivity is transported to the surface of the earth through processes such as tectonic, volcanic, coal mining, crude oil spilling and processing and ground water flow. The migration of ground water to soil surface is dependent on other factors such as the solubility of radioactive substances and porosity of the soil (Chad-Umoren & Umoh, 2014; Alausa *et a*l., 2017; Isinkaye *et al*., 2018).

The global mean dose of natural radiation is estimated to be 2.4 mSv/y and from artificial or synthetic uses 0.8 mSv/y (UNSCEAR, 2000). From time immemorial, the earth has inhabited natural radioactivity with naturally occurring radionuclides in its crust (Fujii *et al*., 2014). These radionuclides are persistent as they have very long half-lives and radionuclides include $^{40}K$, $^{238}U$ and $^{232}Th$. It is pertinent to assess these naturally occurring radionuclides as a baseline or monitoring evaluation to as ascertain they do not go beyond the set limits in soil, water and cash crops. The environment consists of soils, water, local vegetation and the air surrounding. The determination of these components can assist in knowledge of the natural radioactivity of the region. The palm oil plantation is one of the cash producing crops in the south western stated of Nigeria supplying palm oil and palm kernel products for local farmers and chemical and allied industries. It is of paramount importance to have knowledge of the concentration of naturally occurring radionuclides in the soil and the way they are distributed in the environment. These radionuclides are responsible for background radiation experienced globally. On earth, natural background radiation in soils and water contain radionuclides. Geologically, naturally occurring radionuclides are formed in rocks and soils in varying concentrations. Natural radioactivity can be found in rock formations and other parts of the environment such as air, water, sand, clay, and these elements are in contact with humans daily. More than half of the exposure of radioactivity comes from natural sources. Terrestrial radiation originated from rocks, and then rocks are broken down into finer particles of sand and silt in soils and sediments. Terrestrial radiation is transferred to water bodies from sediments and to the atmosphere via atmospheric deposition. Amongst the terrestrial radionuclides is Uranium that is prevalent and persistent. Uranium decays into daughter radionuclides, which are sources of Radium ($^{226}Ra$) and ($^{222}Rn$) (Fujii *et al.,* 2014; Itoh *et al*., 2014; Durusoy & Yildirim, 2017; Todorović *et al*., 2017). In a section of the study, a survey was accomplished for the measurement of naturally occurring radioactivity and the assessment of transfer from soil water to the fruit of the oil palm plantation. This aspect of the study focused on the establishment of the radiation dose and the assessment of risk factors. Routine examinations and baseline research has been carried out in other nations for comparisons of data and possible

assessment of radioactivity in environmental samples. Research is limited in the area of environmental samples in the south west, south east and south south regions of Nigeria (Adamu *et al*., 2013; Tchokossa *et al*., 2013; Chad-Umoren & Umoh, 2014; Alausa *et al*., 2017; Isinkaye *et al.,* 2018; Joel *et al*., 2019; Osibote et al, 1999). Such studies are important for routine and baseline studies and the assessment of the possibility of health risk posed by radionuclides. The analysis of radionuclides using the Hyper Pure Germanium detector (HPGe) provided analysed values of radionuclide activity. The results were compared with standard licenced and certified limits. (UNSCEAR, 2000). Risk assessment was calculated using the model recommended by The United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR, 2000). The activity concentration and health risks measurements in different population age groups due to Uranium, Potassium, and Thorium were assessed (UNSCEAR, 2000).

## 2.12 References


Abdel Rahman, R.O., Elmesawy, M., Ashour, I. & Hung, Y.T. 2014. Remediation of NORM and TENORM contaminated sites - Review article. *Environmental Progress and Sustainable Energy*, 33(2): 588–596.

Adamu, R., Zakaria, Y.I., Ahmed, A.Y., Abubakar, S. & Vatsa, A.M. 2013. Analysis of activity concentrations due to natural radionuclides in the fish of Kainji lake. *Advances in Applied Science Research*, 4(4): 283–287.

Ajuwon, O.R., Katengua-Thamahane, E., Van Rooyen, J., Oguntibeju, O.O. & Marnewick, J.L. 2013. Protective effects of rooibos (aspalathus linearis) and/or red palm oil (elaeis guineensis) supplementation on tert -butyl hydroperoxide-induced oxidative hepatotoxicity in wistar rats. *Evidence-based Complementary and Alternative Medicine*, 2013:1-19.

Alausa, S.K., Odunaike, K. & Adeniji, I.A. 2017. Transfer factor of radionuclides from soil-to-palm oil produced from Elere palm tree plantation near Ibadan Oyo State, Nigeria, 7(1): 7–12.

ARPANSA. 2008. *Safety Guide for the Management of Naturally Occurring Radioactive Material (NORM)*.

Attallah, M.F., Awwad, N.S., and Aly, H.F. 2012. Environmental Radioactivity of TE-NORM Waste Produced from Petroleum Industry in Egypt: Review on Characterization and Treatment. In *Natural Gas - Extraction to End Use*. 77–95.

Ayodele, J.T. & Oluyomi, C.D. 2011. Grass contamination by trace metals from road traffic. *Journal of Environmental Chemistry and Ecotoxicology*, 3(3): 60–67.

Balkhair, K.S. & Ashraf, M.A. 2016. Field accumulation risks of heavy metals in soil and vegetable crop irrigated with sewage water in western region of Saudi Arabia. *Saudi Journal of Biological Sciences*, 23(1): S32–S44.doi.org/10.1016.

Baxter, M.S. 1993. Environmental radioactivity: A perspective on industrial contributions. *IAEA Bulletin*, 2: 33–38.

Blundell, M. 2015. Naturally occurring radioactive materials. *Proceedings of the American Gas Association, Operating Section*: 490–502.

Bradham, K.D., Scheckel, K.G., Nelson, C.M., Seales, P.E., Lee, G.E., Hughes, M.F., Miller, B.W., Yeow, A., Gilmore, T., Serda, S.M., Harper, S. & Thomas, D.J. 2011. Relative bioavailability and bioaccessibility and speciation of arsenic in contaminated soils. *Environmental Health Perspectives*, 119(11): 1629–1634.

Bubb, F. 1924. Direction of ejection of photo-electrons by polarized X-rays. Physical Review. 23 (2): 137–143. doi:10.1103/PhysRev.23.137.

Budidarsono, S., Susanti, A. & Zoomers, A. 2013. Oil Palm Plantations in Indonesia: The Implications for Migration, Settlement/Resettlement and Local Economic Development. *Biofuels - Economy, Environment and Sustainability*. 173-193

Carvalho, F.P. 2017. Mining industry and sustainable development: Time for change. *Food and Energy Security*, 6(2): 61–77.

Cervantes-Trejo, A., Pinedo-Álvarez, C., Santellano-Estrada, E., Cortes-Palacios, L. & Rentería-Villalobos, M. 2018. Distribution of chemical species in the water-soil-plant (Carya illinoiensis) system near a mineralization area in Chihuahua, Mexico—health risk implications. International *Journal of Environmental Research and Public Health*, 15(7): 1393.

Chad-Umoren, Y. & Umoh, I. 2014. Baseline Radionuclide Distribution Patterns in Soil and Radiation Hazard Indices for Abak, Nigeria. *Advances in Physics Theories and Applications*, 32: 69–80.

Chambers, D.B. 2015. Radiological protection in North American naturally occurring radioactive material industries. *Annals of the ICRP*, 44: 202–213.

Charles H. Ed. 1961. CRC Handbook of Chemistry and Physics, 44th Ed. USA: Chemical Rubber Co. p. 2850.

Charles, M., Harrison, J., Darley, P. & Fell, T. 2005. *Health implications of Dounreay fuel fragments: Estimates of doses and risks*.

Chawla, S., Saxena, S., Division, E.B., Sciences, A. & Road, L. 2013. Red Palm Oil - Health Benefits and Their Molecular Executors. *International Journal of Bioassays*, 2(09): 1223–1231.

Chen, L., Wang, G., Wu, S., Xia, Z., Cui, Z., Wang, C. & Zhou, S. 2019. Heavy Metals in Agricultural Soils of the Lihe River Watershed, East China: Spatial Distribution, Ecological Risk, and Pollution Source. *International journal of environmental research and public health*, 16: 2094: doi:10.3390

Chibuike, G.U. & Obiora, S.C. 2014. Heavy metal polluted soils: Effect on plants and bioremediation methods. *Applied and Environmental Soil Science*, 2014.12 pp.

Christillin, P 1986. Nuclear compton scattering. J. Phys. G: Nucl. Phys. 12 (9): 837–851. doi:10.1088/0305-4616/12/9/008.

Coenen, H.H., Gee, A.D., Adam, M., Antoni, G., Cutler, C.S., Fujibayashi, Y., Jeong, J.M., Mach, R.H., Mindt, T.L., Pike, V.W. & Windhorst, A.D. 2017. Consensus nomenclature rules for radiopharmaceutical chemistry — Setting the record straight. *Nuclear Medicine and Biology*, 55 (1):40-41. 55: doi.org/10.1016

Davisson, C. M. 1965. Interaction of gamma-radiation with matter in Kai Siegbahn (ed.). Alpha-, Beta- and Gamma-ray Spectroscopy: Volume 1. Amsterdam: North-Holland Publishing Company. pp. 37–78.

Deshommes, E., Tardif, R., Edwards, M., Sauvé, S. & Prévost, M. 2012. Experimental determination of the oral bioavailability and bioaccessibility of lead particles. Chemistry Central Journal, 6(1): 31 pp.

Doyi, I.N., Essumang, D.K., Dampare, S.B., Duah, D. & Ahwireng, A.F. 2017. *Evaluation of radionuclides and decay simulation in a terrestrial environment for health risk assessment*. Springer US. http://dx.doi.org/10.1038/s41598-017-16659-w.

Dudu, V.P., Mathuthu, M. & Manjoro, M. 2018. Assessment of heavy metals and radionuclides in dust fallout in the West Rand mining area of South Africa. Clean Air Journal, 28(2): 42–52.

Durusoy, A. & Yildirim, M. 2017. Determination of radioactivity concentrations in soil samples and dose assessment for Rize Province, Turkey. *Journal of Radiation Research and Applied Sciences*, 10(4): 348–352.

EPA. 2002. Radionuclides in Drinking Water: A Small Entity Compliance Guide. *United States Environmental Protection Agency*: 117 pp.

EPA. 2008. Technical Report on Technologically Enhanced Naturally Occurring Radioactive Materials from Uranium Mining Volume 1: Mining and Reclamation Background. U. S. Environmental Protection Agency Office of Radiation and Indoor Air Radiation Protection Divisi., 1(2006): 225 pp.

Fujii, K., Ikeda, S., Akama, A., Komatsu, M., Takahashi, M. & Kaneko, S. 2014. Vertical migration of radiocesium and clay mineral composition in five forest soils contaminated by the Fukushima nuclear accident. *Soil Science and Plant Nutrition*, 60(6): 751–764. doi.org/10.1080.

Galuch, M.B., Piccioli, A.F.B., Neto, E.S., Fier, N., Saldan, N.C. & Garcia, E.E. 2018. Micro emulsion as sample preparation for direct flame atomic absorption spectrometry (FAAS) determination of total iron in crude and refined vegetable oils. *Journal of the Brazilian Chemical Society*, 29(4): 748–756.

Griffiths, D. 1987. Introduction to elementary particles. Wiley. pp. 15, 91. ISBN 0-471-60386-4.

Gruca, M., van Andel, T.R. & Balslev, H. 2014. Ritual uses of palms in traditional medicine in sub-Saharan Africa: A review. *Journal of Ethnobiology and Ethno medicine*, 10(1). 24 pp.

Harb, S., El-mageed, A.I.A., Abbady, A. & Negm, H.H. 2008. Natural Radioactivity Measurements in Soil and Phosphate Samples from., (November): 15–19 Nasr City - Cairo, Egypt, 233-237.

Harlow, K. 2017. Naturally occurring radioactive materials and the regulatory challenges to the zircon industry. *Journal of the Southern African Institute of Mining and Metallurgy*, 117(5): 409–413.

Hempelmann, L.H. 1965. Comments on the 1964 Report of the United Nations Scientific Committee on the Effects of Atomic Radiation. *Cancer Research*, 25: 1939–1940.

Henders, S., Persson, U.M. & Kastner, T. 2015. Trading forests: Land-use change and carbon emissions embodied in production and exports of forest-risk commodities. *Environmental Research Letters*, 10(125012), 13 pp.

Hubbell, J. H. 2006. Electron positron pair production by photons: A historical overview. Radiation Physics and Chemistry. 75 (6): 614–623. doi: 10.1016/j.radphyschem.2005.10.008.

Hufner, S. 2003. Photoelectron spectroscopy: principles and applications. Springer. ISBN 3-540-41802-4.

Imoisi OB, Ilori GE, Agho I, E.J. 2015 Palm oil, its nutritional and health implications (A Review). *Journal Applied Science Environmental Management*, 19(1) 127-133.

International Atomic Energy Agency (IAEA). 2014. Remediation of Land Contaminated by Radioactive Material Residues, proceeding series.

International Atomic Energy Agency. (IAEA) 2007. Naturally Occurring Radioactive Material (NORM V). *Proceedings of the Fifth International Symposium Seville, Spain, 19-22*, (March): 549.

Ishida, M. & Yamazaki, H. 2017. Radioactive contamination in the Tokyo metropolitan area in the early stage of the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident and its fluctuation over five years. *PLoS ONE*, 12(11): 1–18.

Isinkaye, M.O., Jibiri, N.N., Bamidele, S.I. & Najam, L.A. 2018. Evaluation of radiological hazards due to natural radioactivity in bituminous soils from tar-sand belt of southwest Nigeria using HPGe-Detector. *International Journal of Radiation Research*, 16(3): 351–362.

Ismail, S.R., Maarof, S.K., Ali, S.S. & Ali, A. 2018. Systematic review of palm oil consumption and the risk of cardiovascular disease. *PLoS ONE*, 13(2): 1–16.

Itoh, S., Eguchi, T., Kato, N. & Takahashi, S. 2014. Radioactive particles in soil, plant, and dust samples after the Fukushima nuclear accident. *Soil Science and Plant Nutrition*, 60(4): 540–550.doi.org/10.1080.

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B. & Beeregowda, K.N. 2014. Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary Toxicology*, 7(2): 60–72.

Jia, Z., Li, S. & Wang, L. 2018. Assessment of soil heavy metals for eco-environment and human health in a rapidly urbanization area of the upper Yangtze Basin. *Scientific Reports*, 8(1) : 14 pp.

Jiang, M., Zeng, G., Zhang, C., Ma, X., Chen, M., Zhang, J., Lu, L., Yu, Q., Hu, L. & Liu, L. 2013. Assessment of Heavy Metal Contamination in the Surrounding Soils and Surface Sediments in Xiawangang River, Qingshuitang District. *PLoS ONE*, 8(8). doi: 10.1371. 11 pp.

Joel, E.S., Maxwell, O., Adewoyin, O.O., Olawole, O.C., Arijaje, T.E., Embong, Z. & Saeed, M.A. 2019. Investigation of natural environmental radioactivity concentration in soil of coastaline area of Ado-Odo/Ota Nigeria and its radiological implications. *Scientific Reports*, 9(1): 1–8.

Joyce, P.J., Goronovski, A., Tkaczyk, A.H. & Björklund, A. 2017. A framework for including enhanced exposure to naturally occurring radioactive materials (NORM) in LCA. *International Journal of Life Cycle Assessment*, 22(7): 1078–1095.

Knoll, G.F. 1999. Interaction of Gamma Rays. *Radiation Detection and Measurement- Third Edition*: 48–55.

Kolo, M.T., Khandaker, M.U., Amin, Y.M. & Abdullah, W.H.B. 2016. Quantification and radiological risk estimation due to the presence of natural radionuclides in Maiganga coal, Nigeria. *PLoS ONE,* 11(6): 1–13.

L'Annunziata, M., Mohammad B. 2003. Handbook of Radioactivity Analysis. Academic Press. p. 58. ISBN 0-12-436603-1.

Liu, B., Ai, S., Zhang, W., Huang, D. & Zhang, Y. 2017. Assessment of the bioavailability, bioaccessibility and transfer of heavy metals in the soil-grain-human systems near a mining and smelting area in NW China. *Science of the Total Environment*, 609: 822–829. doi.org/10.1016.

Malcolm C. 2004. X-Ray Compton Scattering. OUP Oxford. ISBN 978-0-19-850168-8.

Mancini, A., Imperlini, E., Nigro, E., Montagnese, C., Daniele, A., Orrù, S. & Buono, P. 2015. Biological and nutritional properties of palm oil and palmitic acid: Effects on health. *Molecules*, 20(9): 17339–17361.

Maria, G., Co, S.N.F. & Waste, M. 2004. *Uptake of nuclides by plants*.

May, C.Y. & Nesaretnam, K. 2014. Research advancements in palm oil nutrition. *European Journal of Lipid Science and Technology*, 116(10): 1301–1315.

Nagirner, D.I. & Loskutov, V.M. 1999. Two-photon processes of electron-positron pair production and annihilation. II. Kinetic equation for photons. *Astrophysics*, 42(2): 206–221.

Nunes, L.S., Barbosa, J.T.P., Fernandes, A.P., Lemos, V.A., Santos, W.N.L.D., Korn, M.G.A. & Teixeira, L.S.G. 2011. Multi-element determination of Cu, Fe, Ni and Zn content in vegetable oils samples by high-resolution continuum source atomic absorption spectrometry and microemulsion sample preparation. *Food Chemistry*, 127(2): 780–783. doi.org/10.1016.

Odia, O.J. 2015. Palm oil and the heart: A review. *World Journal of Cardiology,* 7(3): 144-149

Oguntibeju, O.O., Esterhuyse, A.J. & Truter, E.J. 2010. Possible role of red palm oil supplementation in reducing oxidative stress in HIV/AIDS and TB patients: A Review *Journal of Medicinal Plants Research*, 4(3): 188–196.

Ohimain, E.I., Seiyaboh, E.I., Izah, S.C., Oghenegueke, E. V & Perewarebo, G.T. 2012. Some Selected Physico-Chemical and Heavy Metal Properties of Palm Oil Mill Effluents. Greener Journal of Physical Sciences, 2(4): 2276–7851.

Olafisoye, B.O., Oguntibeju, O.O. & Osibote, O.A. 2016. An Assessment of the Bioavailability of Metals in Soils on Oil Palm Plantations in Nigeria. *Pol. J. Environ. Stud*, 25(3): 1125–1140.

Olafisoye, O.B., Oguntibeju, O.O. & Osibote, O.A. 2017. Trace elements and radionuclides in palm oil, soil, water, and leaves from oil palm plantations: A review. *Critical Reviews in Food Science and Nutrition*, 57(7). 1295-1315. doi: 10.1080/10408398.

Olise, F.S., Akinnagbe, D.M. & Olasogba, O.S. 2016. Radionuclides and radon levels in soil and ground water from solid minerals-hosted area, south-western Nigeria. *Cogent Environmental Science*, 2(1): 12 pp. doi.org/10.1080/23311843.2016.1142344.

Ono, F.B., Penido, E.S., Tappero, R., Sparks, D. & Guilherme, L.R.G. 2016. Bioaccessibility of Cd and Pb in tailings from a zinc smelting in Brazil: implications for human health. Environmental Geochemistry and Health, 38(5): 1083–1096.

Orisakwe, O.E., Blum, J.L., Sujak, S. & Zelikoff, J.T. 2014. Metal Pollution in Nigeria: A Biomonitoring Update. *Journal of Health and Pollution*, 4(6): 40–52.

Pattison, J. E., Hugtenburg, R. P., Green, S. 2009. Enhancement of natural background gamma-radiation dose around uranium microparticles in the human body. Journal of the Royal Society Interface. 7 (45): 603–611. doi:10.1098/rsif.2009.0300.

Pezeshk, S., Ojagh, S.M. & Alishahi, A. 2015. Effect of plant antioxidant and antimicrobial compounds on the shelf life of seafood - A review. *Czech Journal of Food Sciences*, 33(3): 195–203.

Pibida, L. 2012. Measurements for the development of a simulated naturally occurring radioactive material. *Journal of Research of the National Institute of Standards and Technology*, 117(1): 154–167.

Pobi, K.K., Satpati, S., Dutta, S., Nayek, S., Saha, R.N. & Gupta, S. 2019. Sources evaluation and ecological risk assessment of heavy metals accumulated within a natural stream of Durgapur industrial zone, India, by using multivariate analysis and pollution indices. *Applied Water Science*, 9(3): 1–16.

Quintana, B., Pedrosa, M.C., Vázquez-Canelas, L., Santamaría, R., Sanjuán, M.A. & Puertas, F. 2018. A method for the complete analysis of NORM building materials by γ-ray spectrometry using HPGe detectors. *Applied Radiation and Isotopes*, 134(July 2017): 470–476. doi.org/10.1016

Ragheb, M. 2008. Gamma ray's interaction with matter ©. *Energy*, (1): 1–25.

Rainbow, P.S. 1995. *Biomonitoring of Heavy Metal Availability in the Marine Environment*.

Robertson, A., Tirado, C., Lobstein, T., Jermini, M., Knai, C., Jensen, J.H., Ferro-Luzzi, A. & James, W.P. 2004a. *Food and health in Europe: a new basis for action.*

Rodgerson, D.O., Reidenberg, B.E., Harris, A. G., Pecora, A.L. 2012. Potential for a pluripotent adult stem cell treatment for acute radiation sickness. World Journal of Experimental Medicine. 2 (3): 37–44. doi:10.5493/wjem. v2. i3.37.

Rudziński, W. & Komosa, A. 2011. History and current research in the field of radiochemistry at Maria Curie-Skłodowska University. *Analytical and Bioanalytical Chemistry*, 400(6): 1593–1604.

Sai Kiran, S. 2017. A Review on Inductively Coupled Plasma Optical Emission Spectrometry (Icp-Oes) with a Special Emphasis on its Applications. *Der Pharmacia Lettre*, 9(10) : 44–54.

Scholten, L.C. & Timmermans, C.W.M. 1995. Natural radioactivity in phosphate fertilizers. *Fertilizer research*, 43(1): 103–107.

Shasha, D. 2014. Reversed Phase HPLC-UV Quantitation of BHA, BHT and TBHQ in Food Items Sold in Bindura Supermarkets, Zimbabwe. *International Research Journal of Pure and Applied Chemistry*, 4(5): 578–584.

Shaw, R. W, Young, J. P., Cooper, S. P., Webb, O. F. 1999. Spontaneous ultraviolet emission from 233uranium/229thorium samples. Physical Review Letters. 82 (6): 1109–1111. doi:10.1103/Phys. Rev. Lett. 82.1109.

Shimizu, H. & Desrochers, P. 2012. The health, envirShimizu, H., & Desrochers, P. (2012). The health, environmental and economic benefits of palm oil. IEM's Economic Note. September, 2012. 4 pp

Sylvia, G., Nikita, T.T., Michael, J.K., Fanyana, M.M., Sekomeng, J.M. & Vusumzi, E.P. 2017. Quantification of Cd, Cu, Pb and Zn from sewage sludge by modified-BCR and ultrasound assisted-modified BCR sequential extraction methods. African Journal of Pure and Applied Chemistry, 11(2): 9–18.

Taghvaei, M. & Jafari, S.M. 2015. Application and stability of natural antioxidants in edible oils in order to substitute synthetic additives. *Journal of Food Science and Technology*, 52(3): 1272–1282.

Takáč, P., Szabová, T., Kozáková, L., Benková, M. & Takáč, Peter. 2009. Heavy metals and their bioavailability from soils in the long-term polluted Central Spiš region of SR. Plant, Soil and Environment, 55(4): 167–172.

Tangahu, B.V., Sheikh Abdullah, S.R., Basri, H., Idris, M., Anuar, N. & Mukhlisin, M. 2011. A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. *International Journal of Chemical Engineering*, 2011: 1–31.

Tchokossa, P., Olomo, J.B., Balogun, F.A. & Adesanmi, C.A. 2013. Radiological study of soils in oil and gas producing areas in Delta state, Nigeria. *Radiation Protection Dosimetry*, 153(1): 121–126.

Tesfaye, B. & Abebaw, A. 2016. Physico-Chemical Characteristics and Level of Some Selected Metal in Edible Oils. Advances in Chemistry, 2016: 1–7.

Tessier, A., Campbell, P.G.C. & Bisson, M. 1979. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Analytical Chemistry*, 51(7): 8 44–851.

Todorović, N., Hansman, J., Mrđa, D., Nikolov, J., Kardos, R. & Krmar, M. 2017. Concentrations of 226Ra, 232Th and 40K in industrial kaolinized granite. *Journal of Environmental Radioactivity*, 168: 10–14.

United Nations Scientific Committee on the Effects of Atomic Radiation. 2010. *Summary of low-dose radiation effects on health. UNSCEAR 2010*.

United Nations Scientific Committee on the Effects of Atomic Radiation, 2000. *2000-Sources and Effects of Ionizing Radiation,* (2000).

US National Council on Radiation Protection and Measurements. NCRP.1987. Report 93: 53–55, Bethesda, Maryland, USA.

USGAO. 1999. *Animal Agriculture: Waste Management Practices*.

Varsha, V., Stuart, L.P., Clinton, N.J. & Sharon, J.S. 2016. The impacts of oil palm on recent deforestation and biodiversity. *PLoS ONE*, 11(7): 1–19.

Watkins, C. 2016. Development Stable: African Oil Palm Agroecologies in Bahia, Brazil, and implications for development.10(1): 9–33.

Weaver, J. H., Margaritondo, G. 1979. solid-state photoelectron spectroscopy with synchrotron radiation science. 206 (4415): 151–156. doi:10.1126/science.206.4415.151

Winarso, S., Pandutama, M.H. & Purwanto, L.D. 2016. Effectivity of humic substance extracted from palm oil compost as liquid fertilizer and heavy metal bioremediation. *Agriculture and Agricultural Science Procedia*, 9: 146–157.

World Health Organization (WHO). 2018. *Management of radioactivity in drinking-water*. http://www.who.int/water_sanitation_health/publications/management-of-radioactivity-in-drinking-water/en/.

Wuana, R.A. & Okieimen, F.E. 2014. Heavy metals in contaminated soils: A review of sources, chemistry, risks, and best available strategies for remediation. Heavy Metal Contamination of Water and Soil: Analysis, Assessment, and Remediation Strategies, 2011: 1–50.

Yang, J., Ma, S., Zhou, J., Song, Y. & Li, F. 2018. Heavy metal contamination in soils and vegetables and health risk assessment of inhabitants in Daye, China. *Journal of International Medical Research*, 46(8): 3374–3387.

Zhang, Q. 1996. Intensity dependence of the photoelectric effect induced by a circularly polarized laser beam. Physics Letters A. 216 (1–5): 125-216. doi:10.1016/0375-9601(96)00259-9.

Zimmerman, A.J. & Weindorf, D.C. 2010. Heavy metal and trace metal analysis in soil by sequential extraction: A review of procedures. *International Journal of Analytical Chemistry*, 2010: 1–7.

Zulkiply, S.H., Balasubramaniam, V., Abu Bakar, N.A., Abd Rashed, A. & Ismail, S.R. 2019. Effects of palm oil consumption on biomarkers of glucose metabolism: A systematic review. *Plos One,* 14(8): e0220877, 14pp.

# CHAPTER THREE

## Trace elements and radionuclides in palm oil, soil, water and leaves from oil palm plantations: a review

**O.B. Olafisoye[1], O.O. Oguntibeju[2], O.A. Osibote[3*]**

*[1]Department of Chemistry, Faculty of Applied Sciences, Cape Peninsula University of Technology, Cape Town, South Africa.*

*[2]Department of Biomedical Sciences, Faculty of Health and Wellness Sciences, Cape Peninsula University of Technology, Bellville, South Africa.*

*[3]Department of Mathematics and Physics, Faculty of Applied Sciences, Cape Peninsula University of Technology, Cape Town, South Africa.*

***Correspondence: osiboteA@cput.ac.za /Tel: +27733545569***

*O. B. Olafisoye, O. O. Oguntibeju & O. A. Osibote (2017) Trace elements and radionuclides in palm oil, soil, water, and leaves from oil palm plantations: A review, Critical Reviews in Food Science and Nutrition, 57:7, 1295-1315, DOI: 10.1080/10408398.2014.886032*

### Abstract

Oil palm (*Elaeis guineensis*) is one of the most productive oil producing plant in the world. Crude palm oil is composed of triglycerides supplying the world's need of edible oils and fats. Palm oil also provides essential elements and antioxidants that are potential mediators of cellular functions. Experimental studies have demonstrated the toxicity of the accumulation of significant amounts of non-essential trace elements and radionuclides in palm oil that affects the health of consumers. It has been reported that uptake of trace elements and radionuclides m the oil palm tree may be from water and soil on the palm plantations. In the present review, an attempt was made to revise and access knowledge on the presence of some selected trace elements and radionuclides in palm oil, soil, water and leaves from oil palm plantations based on the available facts and data. Existing reports show that the presence of non-essential trace elements and radionuclides in palm oil may be from natural or anthropogenic sources in the environment. However, the available literature is limited and further research need to be channeled to the investigation of trace elements and radionuclides in soil, water, leaves and palm oil from oil palm plantations around the globe.

***Key words: Oil palm, trace elements, radionuclides, antioxidants, toxicity***

## 3.1 Introduction

Palm oil is the world second most essential vegetable oil after olive oil (Ong & Goh, 2002). It is a good choice for manufacturers of food due of its nutritional resourcefulness. The oxidative stability and profitability is compared among oils, which are free of cholesterol. These values extend to blends of polyunsaturated oils to provide a longer storage life for the oil. Currently, there is a supply of genetic-modification-free palm oil, which is a cheap perennial crop with unparalleled productivity (Ong & Goh, 2002). Virgin palm oil also provides carotenes, tocotrienols and tocopherols. These are potent antioxidants and facilitators of cellular functions. Edible oils such as palm oil contain trace elements and radionuclides that known for their toxicities and affect the health of consumers (Arogunlo, 2007). The concentrations of radionuclides and trace elements affects oil qualities as regards to its freshness, storage, stability and influence on human nutrition and health (Don Pedro *et al.,* 2004). Man's activities have increased the baseline for these elements in the environment. However, baseline radionuclides and trace elements burden is not sufficient to explain the level of contamination of palm oil from various natural and antropogenic sources (Arogunlo, 2007 and UNSCEAR, 1988).

Metals and radionuclides occur naturally in soil in minute amounts and life has evolved to cope with only small exposures to these elements. Many industrial processes concentrate metals that later end up in soils and water bodies (Hendershot, 2005). The naturally occurring trace metals supplemented by releases from anthropogenic sources, some metals may exceed natural inputs. Hazardous effects to human health could arise when they enter the food chain (Manahan, 1991; Ayodele & Oluyomi, 2011; Omaka *et al.*, 2011).

Radionuclides can be dissolved in solution or complexed with soil organics. Radiosensitive elements can undergo transformation or sorption reaction that alters mobility and relative toxicity (Igwe *et al*., 2005). Radionuclides and trace elements are toxic to living organisms at excessive concentrations but some trace elements are essential for normal healthy growth and reproduction by plants and animals at low but critical concentrations and some radionuclide are used as tracers of some micronutrients (Alloway, 1995; Anyakora *et al.*, 2011). Trace elements and radionuclides studies on palm oil has not been extensively investigated, yet about 80% of palm oil production is destined for human consumption with the other percentage going to animal feed and various industries.

Trace elements may come from various industrial sources and may have a significant contribution to environmental pollution because of anthropogenic activities. Some trace elements are essential or beneficial micronutrients for plants and animals but others have no

known biological or physiological function. All trace elements at high concentrations have toxic effects and are an environmental threat (Igwe *et al*., 2005). Trace elements in palm oils are due to palm oil trees grown in highly acidic soils where trace elements are potentially more bio available for root uptake. Trace element contents of palm oil may have both beneficial and adverse effects on human health. The regular consumption of palm oil can contribute to the daily dietary requirements of some of these elements. Owing to the importance of trace elements and radionuclides, many studies were carried out to determine their levels in palm oil, palm fruit oil, leaves, water and soils. In view of the growing awareness and concerns about trace elements and radionuclides, an attempt was made to review recent scientific findings on the concentration levels of some trace elements and radionuclides on red palm oil, fruit, leaves, water and soil on palm oil plantations based on the available literatures.

### 3.1.1 The oil palm tree

The African oil palm *(Elaeis guineensis*) is indigenous to West and South West Africa and grown in countries such as Angola, Nigeria, and the Gambia. Specie is the American oil palm *Elaeis oleifera* grown in Malaysia, Central and South America. It is a tropical tree with a stem and at maturity reaches a height of about 20 meters. The fruit of the oil palm tree is a fleshy mesocarp with a kernel from which oil can be extracted (Reeves & Welhrauch, 1979). Biofuel produced from palm oil, has increased the overdependence on the oil causing a controversy on whether the oil be used for food or fuel. Developed countries and researchers now seek for alternative energy by using waste from the oil palm tree such as the fronds, husks, as a form of renewable energy, biogas and plastics. (Hilary Chiew, 2008). Consumption of palm oil is associated with the reduction of serum cholesterol, low-density lipoprotein, decreased risk of cardiovascular disease and cancer (Oguntibeju *et al.,* 2010; Oluba *et al*., 2011). Red palm oil is rich in vitamins, antioxidants, and phytonutrients responsible for good health and growth.

### 3.1.2 Trace elements

Trace elements are discharged from industries, farmlands, municipal urban runoffs into surface waters causing contamination. The pollution of the ecosystem presents serious concern. Trace elements are non-degradable and incessant in the ecosystem. Advancement in technology, population growth and anthropogenic activities has led to high levels of industrialization causing discharge of effluent bearing heavy metals into our environment (Igwe *et al*, 2005; Jimoh & Mahmud, 2012;). The sources of trace elements on oil palm plantations that are generally from natural and anthropogenic sources may have significant contribution to environmental pollution. Many sources of chemical contaminants such as lead, nickel and boron are gasoline additives that are released into the atmosphere and the soil through rain. Trace elements in palm oils are due to palm oil trees grown in highly acidic soils where trace

elements are potentially more bioavailable for root uptake. Several stages of processing in the extraction of palm oil from fresh fruits bunch are as follows, sterilization, bunch stripping, digestion, oil extraction and finally clarification and purification; each unit has its unique operations (Igwe & Onyegbado, 2007). Trace element contents of palm oil may have both beneficial and adverse effects on human health. The regular consumption of palm oil can contribute to the daily dietary requirements of some of these elements. The accumulation of aluminium in palm oil is associated with Alzheimer's disease (Judith, 2011). In a similar way, other trace elements, arsenic, cadmium, chromium, lead, manganese, and nickel contents have been investigated in many South Asian and African countries where palm oil is used as stable oil in food (Pais & O'Neill, 1990; Jones, 1997; Njoku *et al.*, 2010; Asemave *et al.,* 2011).

### 3.1.3 Radionuclides

Radionuclides occur naturally and can be produced artificially (Petrucci *et al*., 2002). Radionuclides are important in industry. They are hazardous to animal and human health. There are many radionuclides but only a few are encountered during routine testing in medicine, military and industry (USEPA, 2007). Naturally, occurring radionuclides can be classified as primordial, secondary, and cosmogenic radionuclides. Secondary radionuclides are mostly derived from the decay of primordial radionuclides but have shorter half-lives to their predecessors. Cosmogenic isotopes, such as carbon-14, are present because they are created in the atmosphere due to cosmic rays (Petrucci *et al.,* 2002). Nuclides of any element that have atomic number greater than bismuth-83 are unstable and therefore radioactive (Brandy, 1974). Americium-241, caesium-137, cobalt-60, iodine129 are some radionuclides that occur naturally; caesium for example, is an alkali metal like potassium and resembles it metabolically (Mster, 1996). Whereas potassium is an essential element for man, there is no evidence, that caesium is also an essential trace element. Stable caesium-133 is rare in the biosphere (Brandy, 1974). The radioactive isotope caesium-137 is produced in nuclear fission and is one of the most significant products (Brandy & Weil, 1999). Artificial radionuclides are produced from nuclear reactors, radionuclide generators and weapon testing (Petrucci *et al*., 2002). The extent of this widespread but generally diffused contamination has caused concern about its possible hazards on plants, animals, and human beings. Nuclear fission in connection with atomic weapons testing and power generation provides some of the sources of soil contamination (Holmgen et al., 1993; Nyle & Ray, 1996). These normal soil levels of the fission of radionuclides are not high enough to be hazardous. Even during the peak periods of weapons testing, soils did not contribute significantly to the level of these nuclides in plants. Atmospheric fallout on vegetation was the primary source of radionuclides in the food chain (Holmgen et al, 1993; Meiwether et al., 1988) Considerable research has been accomplished

on the behaviour of radionuclides in the soil and plants (Meiwether *et al*., 1988; Osibote *et al.,* 1999; Petrucci *et al*., 2002; Awodugba & Tchokossa, 2008). In addition to radionuclides added to soil because of weapons testing and accidents such as that which occurred at Chernobyl, Ukraine, soil may interact with low-level radioactive waste materials that have been buried for disposal (Iskauder, 1992; Knox *et al*., 2000). Radionuclides buried in landfills may be dissolved in soil (Brandy & Weil, 1999). Plutonium, uranium, americium, neptunium, curium, and caesium are among the elements whose nuclides occur in radioactive wastes and organic matter content (Wiler 1965; Nyle & Ray, 1996). Fruits and seeds have generally much lower of these nuclides than are leaves, suggesting that grains may be less contaminated by nuclides than forage crops and leafy vegetables (Knox *et al.*, 2000).

## 3.2 Trace elements in oil palm

### 3.2.1 Arsenic (As)

Arsenic is a deadly poison, which is persistent in the environment and capable of causing mutations, cancer infertility and tumors (WHO, 2003). A compound of arsenic known as arsenic trioxide was used to treat some forms of cancer; especially promyelocytic leukemia in the past. It has a long history of use as a homicidal agent, pesticide and a constituent of consumer product. Due to the toxicity of arsenic, its use in agriculture has drastically declined. Occupational arsenic poisoning is common among miners and smelters mining arsenic and farmers working in farms where arsenic fertilizers have been used (Pais & Jones, 1997).

Tables 3.1, 3.2 and 3.3 briefly summarizes a review of trace metals and radionuclides in food, edible oils, soil and water analyzed with various instruments in different parts of the world. A review indicates that the aim of the analysis was for safety, routine analysis and environmental impact assessment.

**Table 3.1: Trace metals & radionuclides in palm oil**

| Country of Origin | Sample analyzed | Number of samples | Purpose of investigation | Concentration range ($mgkg^{-1}$) | Instrument used | References |
|---|---|---|---|---|---|---|
| *Arsenic As* | | | | | | |
| Malaysia | Palm oil | 21 | Evaluation of trace element level | 0.005-0.027 | GFAAS | Hammid *et al.,* 2012. |
| Lagos, Nigeria | Red palm oil | 25 | Evaluation of purity and safety | 0.5µg/g-25µg/g | AAS | Adepoju-Bello *et al.*, 2012. |
| China | Edible oils, red palm oil | 3 | Development of arsenic in edible fats and oil | 0.005-0.027 | Atomic fluorescence Spectrometer | Chen *et al.*, 2001 |
| *Cadmium* | | | | | | |
| Markurdi, Nigeria | Red palm oil | 25 | Trace element analysis | 0.078 - 11.370 | AAS | Asemave *et al*., 2010 |
| *Zinc* | | | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| *Nigeria* | Palm kernel oil | 25 | extraction, composition and physicochemical characteristics | 2.82-3.40 | AAS | Atasie and colleagues (2009) |
| *Chromium* | | | | | | |
| Thailand | Edible oils | 6 | Trace element determination in edible oils | 0.01-0.02 | GFAAS/ICP-MS | Surasak, 2011 |
| *Copper* | | | | | | |
| Nigeria | Edible Oils | 4 | Routine Microelement In Edible Oils | 7-3-28.1 | Neutron Activation Analysis | Umar , 2011. |
| *Magnesium* | | | | | | |
| Nigeria | Palm oil | 4 | Physicochemical properties and dietary metal concentrations | 0.05-0.95 | Spectrophotometry, titrimetry and gravimetry | Njoku and colleagues (2010) |

**Table 3.2: Trace metals & radionuclides in soil**

| Country of Origin | Sample analysed | Depth | Purpose of investigation | Concentration range ($mgkg^{-1}$) | Instrument used | References |
|---|---|---|---|---|---|---|
| | | | | | | |
| **Cadmium Cd** | | | | | | |
| **Tarkwa, Ghana** | Soil on a palm kernel oil plantation | 0-30cm | Routine analysis | 1.23-4.63 | Atomic Absorption Spectrometer | Asante and Ntow, 2009. |
| **Zinc Zn** | | | | | | |
| **Malaysia** | Soil on a 10-20yr oil palm plantation | 0-30cm | Environmental Impact Assessment | 1.08-2.0 | Atomic Absorption Spectrometer | Singh *et al*., 2010 |
| **Aluminium Al** | | | | | | |
| **Negeri Sembilan ,Malaysia** | Soil on 5 yr. old oil palm plantation | 0-30cm | To improve soil fertility | 1.0-5.0 | Atomic Absorption Spectrometer | Manaf *et al*. (2009) |
| **Cote d'Ivoire** | 40 yr. oil palm plantation after post clearing | 0-30cm | Physical, chemical and organic matter properties | 0.35 | AAS | Yeboua and Ballo, 2000. |
| **Copper Cu** | | | | | | |
| **Benin, Nigeria** | 30 yr. old oil palm plantation | 0-20cm | Macro nutrients and micro nutrients | 0.32 | ICP-MS/AAS | Aweto and Enaruvbe, 2010. |
| **Magnesium** | | | | | | |
| | | | | | | |
| **Nigeria** | 30yr oil palm plantation | 0-30cm | Analysis of soil chemical properties | 0.23 | ICP-MS/AAS | Ogeh and Osiomwan, 2012 |
| **Nigeria** | 20 yr. oil palm plantation | 0-30cm | Exchangeable calcium and magnesium | 0.93 | ICP-MS/AAS | Uwumarongie-Ilori and colleagues, 2012. |
| **Uranium U** | | | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| **Jengka, Malaysia** | Top soil on oil palm plantation | 0 cm | Assessment of radiation dose from soils | ≤ 1 | HPGe counting system | Low *et al*., 2008 |

**Table 3.3: Trace metals & radionuclides in water**

| Country of Origin | Sample analysed | Purpose of investigation | Concentration range ($mgkg^{-1}$) | Instrument used | References |
|---|---|---|---|---|---|
| *Cadmium* | | | | | |
| Sampadi, Malaysia | River | Water and sediment quality of river | 0.05-0.66 | Atomic Absorption Spectrometer | Ling *et al*., 2011. |
| Johor, Malaysia | Drinking water | Physicochemical properties in selected palm oil estates | 0.99 ± 1.52 | Atomic Absorption Spectrometer | Farizwana *et al*., 2010 |
| *Radium* | | | | | |
| Ogoni, Porthar Court, Nigeria | Stream | Enviromental Impact Assessment | 0.05±0.01 | Co-axial type germanium detector | UNEP, 2011 |

**Table 3.4: Trace metals & radionuclides in plants**

| Country of Origin | Sample analyzed | Purpose of investigation | Concentration range ($mgkg^{-1}$) | Instrument used | References |
|---|---|---|---|---|---|
| *Zinc* | | | | | |
| United States of America | Soil, sediments, roots and leaves on oil palm plantations | Absorption of heavy metals from plants | 0.05 | Atomic Absorption Spectrometer | Anklam *et al*., 2001 |
| *Chromium* | | | | | |
| Greece | vegetables | Absorption of heavy metals from different parts of plants | 0.04-0.27 | ICP-MS/AAS | Toepfer *et al.,* 1973. |
| | vegetables | Absorption of heavy metals from plants | 0.021 to 0.28 | ICP-MS/AAS | Bratakos and Lazos, 2002. |
| *Lead* | | | | | |
| | vegetables | Absorption of heavy metals from plants | 0.02-0.51 | ICP-AES/FAAS | Finster *et al.,* 2004 |

### 3.2.2 Arsenic in soils from oil palm plantations

Sources of atmospheric arsenic may be from microorganisms or volcanoes. Anthropogenic activities such as the burning of fossil contribute to about 80 % of atmospheric arsenic pollution. Arsenic phytotoxicity in soil depends on factors such as pH and soil texture and increases especially at low pH and in sandy soils (O'Neil, 1995). The oil palm plantation is an economic crop and the waste such as the fibers and shells can be used as a source of fuel. Hamzah *et al.,* (2012), investigated the effect of the use of fiber and shell as a source of fuel on soil of an oil palm plantation. The study was carried out to determine the effect of anthropogenic activities such as fertilizer application and agronomical practices such as burning of fuel on the soil of the oil palm plantation. The soil and palm fronds of the oil palm tree were analyzed for As, Cu,

Ni, Co, V, Hg, Zn and Mn using Energy Dispersive X-ray Fluorescence (EDXRF) Technique. The concentration of elements such as Arsenic in the soil and palm fronds (leaves) was attributed to the fly ash, fertilizer and pesticide application. The plot distribution pattern of elements on the soils of the oil palm tree was established to determine hot spots for such metals (Hamzah *et al.,* 2012).

### 3.2.3 Arsenic in water from oil palm plantations

Significant amounts of toxic inorganic arsenics in water can cause some form of mutations in aqua culture, which poses health risks. Symptoms of chronic contamination are seen as diarrhea, skin cancer, abdominal pain and neurological defects. A lot of research has been conducted on arsenic in water and effluents (Wals *et al*., 1980; Hughes *et al*., 2011; Kumar *et al*., 2011; Chengbei *et al*., 2013; Tyson, 2013). Data on the studies of arsenic in water from oil palm plantation is limited.

### 3.2.4 Arsenic in plants from oil palm plantations

Plants absorb arsenic easily, so high concentrations of arsenic may be present in food. Arsenic is known to alter and disturb uptake and transport of nutrients in plants (Paivoke & Simola, 2001). Disturbance of plant mineral nutrition is the main cause of decrease in yield. Visual symptoms of phytotoxicity include leaf wilting, retardation in root and shoot growth, root discoloration, and leaf necrosis (Wool son *et al*., 1971). The phytotoxicity of arsenic is attributed to its ability to substitute for phosphate in enzyme-catalyzed, phosphorylation reactions and thus interfere with the energy status of the plant. Plant is the major uptake of arsenic to animals and humans. Determination of arsenic in seeds, fruits and some /8researchers, Kukier *et al*., 1994; Jurgen *et al*., 2000, Melendez *et al.,* 2011, Ramirez-Andreotta *et al*., 2013 have studied stem of various plants. The determination of arsenic in water from oil palm plantation is sparse.

### 3.2.5 Arsenic in palm oil

In addition to food, edible oils like palm oil may act as an important potential dietary ingestion source of toxic elements in daily life. The regular consumption of palm oil may contribute to the daily dietary requirements of several elements. Nevertheless, at the same time, some toxic elements like arsenic are ingested into the body (Han *et al*., 2005). The oil palm tree especially fruits can accumulate trace elements from soil and soil solution from the application of fertilizers and herbicides containing arsenic. Recently, this practice is gradually fading. Hammid *et al*., (2012), determined the concentration of arsenic in by products of palm oil using the microwave digestion technique and the graphite furnace atomic absorption spectrometry method. The

mean recovery of arsenic showed that the method was suitable in the determination of palm oil and palm kernel oil.

### 3.2.6 Cadmium (Cd)

Cadmium is mainly found in the earth crust and anthropogenically in industrial work places. Naturally, 25,000 tonnes of cadmium is released into the environment every year mostly in rivers through weathering of rocks, fires and volcanoes (Waalkes, 2000). Cadmium mostly occurs in combination with zinc. Hence, where zinc is suspected to be a major pollutant, the possibility of cadmium cannot be ruled out. It is the byproduct after the smelting of lead, copper and zinc in the mining industry. An overexposure occurs where trace quantities of cadmium are found because of its low permissible exposure limit. Industrial methods such as electroplating and spray-painting of materials constitute occupational hazards to workers. Cadmium is one of the most deleterious toxic trace metals to plants and to animals. It is designated as a human and a potent multi-tissue animal carcinogen (Johri *et al*., 2010). Principally the accumulation of cadmium in humans occurs in visceral organs especially the kidneys. Biologically the half-life of this could be close to 20 years. Symptoms of such accumulation are manifested as pulmonary emphysema and renal tubular damage to the renal organs. In chronic cases, osteomalacia and bone fractures are consequences of toxicity. History recorded a disease in Japan in the late 1950s and 60s of populations who ate majorly rice, which could have been contaminated with cadmium. The disease was named Itai-Itai because of the severe pain people felt in their spine and joints. Other health effects caused by cadmium in human are infertility, mental and immune system disorders, cancer and DNA damage (Johri et al., 2010).

### 3.2.7 Cadmium in soils from oil palm plantations

Soil analysis, has the advantage that it can measure the level of immediately available nutrients in the soil (nutrient intensity) and the soil ability to continue the supply of nutrients throughout crop growth. Interpretation of soil analysis allows for assessing fertilizer needs but it does not allow an evaluation of the efficiency or sufficiency of nutrient uptake to ensure optimal growth and productivity of the crop. With the development of modern industry and agriculture, cadmium has become one of the most harmful widespread pollutants in agricultural soils, mainly due to industrial emission, application of cadmium- sewage, phosphate fertilizers and metropolitan waste disposal (Gupta & Gupta 1998). It is an impurity in phosphate fertilizers pathway into the environment, which is mainly through soil, manures and pesticides. Acidification of soils enhances the mobilization of cadmium from soils into surface and ground waters. Phosphate fertilizer application is a significant contributor of trace elements, especially

for cadmium accumulation in cropped soils. Repeated application of phosphate fertilizers may lead to a gradual buildup of cadmium in agricultural soils over time. The continuous application of phosphate rock fertilizer caused a lot of concern about the increasing accumulation of Cd and Zn in soils. Aini *et al*., (2010) investigated two oil palm plantations in Malaysia. Trace metal concentrations were investigated on the plantations aged 10, 15 and 20 years. Cd and Zn isotherms were used to report the findings from the study. The results of the investigation indicated no accumulation of Cd but Zn, indicating that Cd adsorption can be suppressed by the presence of the zinc metal (Aini *et al.,* 2010).

### 3.2.8 Cadmium in water from oil palm plantations

Cadmium exposure can cause adverse health effects over long periods. It is a trace element that is non-biodegradable. Cadmium may be found in soil or water near industrial areas or hazardous waste sites. High levels of cadmium in surface waters usually result from cadmium particles settling from the air. Cadmium in water tends to sink and accumulate in bottom sediments. Oil palm agriculture and palm oil processing has the potential to pollute surface water through cadmium containing fertilizer run off and Palm Oil Mill Effluent (POME). Physicochemical and heavy metal parameters were investigated in a palm oil mill effluent selected randomly in palm oil milling sites in River state, Nigeria. Heavy metals found in the samples were Cd, Cr, Cu and Fe. Cu, Cr and Fe were significantly different while Cd had no significant difference. It was recommended that it is preferably to recycle POME rather than discharge into water bodies due to the concentration of trace elements (Ohimain *et al*., 2012).

### 3.2.9 Cadmium in plants from oil palm plantations

Trace element ions are reported as priority pollutants due to their mobility in natural ecosystems and their toxicity. Trace element uptake by plant can be useful in phytoremediation whereby plants clean up soils. The phytotoxicity of cadmium is known due to disruptions in plant ion. Increase soil cadmium content results in an enhanced uptake of cadmium by plant that is the pathway of human exposure through agricultural crops. Many studies have been conducted in order to identify plant species capable of accumulating undesirable toxic compound such as heavy/trace metals uptake by the roots and leaves of the plants (Adriano, 1986; Alloway, 1990; Cunningham & Ow, 1996). *Elaeis guineensis* was identified to remove heavy metals from soils. Monitoring of the content of heavy metals compounds in leaves/plants is necessary because of the toxicity of these metals. Aini and colleagues further investigated soils of a Malaysian oil palm plantation aged between 10, 15 and 20 years. Leave fronds of the oil palm plantation were analysed for the presence of cadmium. A correlation study revealed that that cadmium in soil and soil solutions possibly contributed to the concentration

of cadmium in oil palm fruit and leaf fronds. They reported that these might influence the uptake of Cd by the oil palm tree. Adsorption isotherms also revealed that the concentration of Cd was also suppressed by the presence of zinc (Aini *et al.,* 2012).

### 3.2.10 Cadmium in palm oil

Food is a major route for cadmium exposure in plants and animals. Plants may only contain small or moderate amounts in non-industrial areas, but high levels are found in plants cultivated on contaminated soils. Oil palm trees grown on soils contaminated with trace elements such as cadmium may influence the uptake of Cd to the fruit. A correlation study conducted by Aini *et al*., (2012) revealed that that cadmium in soil and soil solutions possibly contributed to the concentration of cadmium in oil palm fruit. Processed oil may be contaminated by trace metal from soils and soil solutions and contamination from oil processing. Asemave and colleagues collected palm oil samples from two major markets in Markurdi, Nigeria. The oil samples were analysed for Cd, Cu, Fe, Cr, Al and Pb. The concentrations of the trace elements were within the safe limits and safe for consumption. The physicochemical properties of the oil such as viscosity, saponification, and acid value were also investigated.

### 3.2.11 Zinc (Zn)

Zinc is an essential mineral that is naturally present in some foods, added to others, and available as a dietary supplement and takes part in numerous aspects of cellular metabolism. It is required for the catalytic activity of about 100 enzymes and actively takes part in immune function, protein metabolism, foetus development and the healing of wounds. It is a micronutrient that has been recognized as an essential trace element for normal healthy growth of animals and plants (Hartley, 1988). The average human body contains about 3 grams of zinc and a deficiency of this essential element results in oxidative stress, dysfunction of several enzyme systems of various metabolic activities. Zinc is involved in over one hundred different reactions in the body such as the growth and repair of DNA, tissues and systems. It has high antioxidant properties protecting the body from the action of free radicals. It is the active site for metalloenzymes required for nucleic acid synthesis. Zinc deficiency may lead to hair loss, mental apathy, reproductive, and growth disorders. Although zinc is an essential trace element, an excess in the human diet can lead to copper deficiency, immune system disorders, fatigue, and nausea (Hajo & Lothar, 2009).

### 3.2.12 Zinc in soils from oil palm plantations

A study on Zinc as it relates to crop nutrition was extensively studied by Alloway, (1990). This appreciably provides an enhanced perception of zinc complexes in soil and plants. The causes and occurrence of zinc deficiency in crops growing on different types of soil in most agricultural

regions of the world are reasonably well understood. Scientific methods are available to diagnose crop problems revealed by visible symptoms that identify soils of marginal or deficient zinc supply capacity. Therefore, the problem of wide spread zinc deficiencies can be solved if farmers are made aware of zinc deficient conditions and how to treat it. Zinc deficiency is not just a problem in developing countries; it also occurs in most developed nations. The difference in the situation is the existence of an extension agronomy service and rapid access to analytical facilities in developed countries, thus helping to reduce loss in yield brought about by zinc deficiency. Sandy, calcareous, and saline soils are usually prone to zinc deficiency. The problem of zinc deficiency is global and the most commonly encountered deficient trace element to plants. Soil analysis has the advantage that it can measure the level of immediate availability of nutrients in soil that is the soil nutrient intensity, and the soil's ability to continue the supply of such nutrients throughout crop growth. Interpretation of soil analysis allows for assessing fertilizer needs, but it does not allow evaluation of the efficiency or/of nutrient uptake to ensure optimal growth productivity of the plant. Levels of zinc in surplus of 500 ppm in soil hinder the ability of plants to absorb other essential elements especially iron and manganese. Aweto & Enaruvbe (2010) evaluated the effect of variation of soil properties on a 30-year-old oil palm plantation in south west Nigeria. Five soil samples were selected, 0-20 cm depth, segmented into upper and lower slopes. These were evaluated for exchangeable calcium and cation exchange capacity. Trace elements such as Zn, Cu, and Iron were significantly higher in the lower slopes. The significance of the study was to manage parts of the oil palm plantations on different topographic levels considering the variation in soil properties such as pH.

### 3.2.13 Zinc in water from oil palm plantations

Zinc is concerned with several aspects of cell metabolism. It is essential for the catalytic functioning of about 100 enzymes and it plays a significant role in immune function, protein synthesis, wound healing, growth and fetus development. The indiscriminate dumping of waste and mining operations leach significant amounts of zinc and cadmium into the water and sediments of the Geul River due to the production of zinc ores. About 1.1 million tons of metallic zinc and 130 thousand tons of lead were mined and smelted in the towns of Belgian of La Calamine and Plombieres between the year 1806 and 1882. Smelter slag and other residues of the process also contain significant amounts of trace elements hence polluting the Geul River (Kucha *et al*., 1996). Some research has been conducted on the determination of zinc metal in different types of water (Yilmaz, *et al.,* 2009; Arancibia, *et al.,* 2010; Braga, *et al.*, 2012; Kiran, 2012). Information on the studies of zinc in water from oil palm plantation is sparse

### 3.2.14 Zinc in plants from oil palm plantations

The importance of zinc to plants was scientifically established about 70 years ago. The latest innovation of prevalent zinc deficiency problems in plants is linked to the intensification of farming in many emerging nations. This has involved a revolution from conventional agricultural practices to the use of recent agricultural chemicals. Many of the modern crop varieties are much more prone to zinc deficiency than the traditional crops and the increased use of macronutrient fertilizers, particularly phosphorus, can intensify the deficiency of zinc in crops. The yield of many other crops can drastically decline due to zinc deficiency (Kauser *et al.,* 2001). Providentially, the sources and occurrence of zinc deficiency in many crops growing on different types of soil in agricultural regions of the world are reasonably well understood because tools are available to diagnose crop problems revealed by visible signs and symptoms. The importance of fertilizer in the production and maintenance of large and sustainable yields of palm oil fruit bunches cannot be overemphasized. Considerable efforts have been made to develop methods providing a scientific basis for estimating fertilizer requirements of oil palm and oil palm products. However, although soil and leaf test analysis may provide basis for decisions on fertilizer use, the success of the final crop is the result of the interaction of so many different factors such as plant growth factors and nutrient relationships. The normal range of zinc in most plants is between 20 to 100 ppm. Zinc is not a very mobile element in plants, and deficiency symptoms occur in newly emerging leaves. Stunted growth is a common symptom linked with zinc deficiency and concentration in leaves remains constant with a rapid increase at the end of the growth cycle (Kauser *et al.,* 2001).

### 3.2.15 Zinc in palm oil

Excessive absorption of zinc in the diet from foods such as palm kernel oil can suppress copper and iron adsorption into the blood stream. The free zinc ion in solution is highly toxic to humans, plants, and animals. Micro molar amounts of the free ion can be lethal. There is evidence of copper deficiencies at low intakes of 100-300 mg Zn. Possible symptoms of chronic toxicity of zinc have been reported as lethargy, ataxia, hemolytic anemia, liver and kidney damage, vomiting and diarrhea (Fosmire, 1990). Zinc has been determined in various vegetable oil using different instrumental methods (Sun, *et al*., 1999; Huang and Shih, 2001; Anwar, *et al.,* 2004; Pehlivan, 2008)

### 3.2.16 Aluminum (Al)

Humans and plants are exposed to high aluminium levels in the environment. These exposures originated from water in drinks and food preparation, cooking utensils as well as antacid preparation. Aluminium is the risk factor of Alzheimer's disease, dementia, osteomalacia and

encephalopathy (Chen *et al*., 2011). Toxicity of aluminium is traced to deposition in bones and the central nervous system in patients with reduced renal function. Aluminium competes with calcium for absorption in the bone marrows, thereby contributing to the reduced skeletal mineralization observed in infants with growth retardation (Ma *et al*., 2001). In high doses, aluminium causes neurotoxicity, and is associated with altered blood function. Other symptoms of high doses of aluminium in humans are dermatitis, digestive disorders, and vomiting. Studies have also shown that aluminium increases the incidences of breast cancer in humans. Although the use of aluminium cookware has not shown to lead to aluminium toxicity, excessive consumption of antacids and the use of cosmetics containing aluminium compounds provide significant exposure levels (Chen *et al*., 2011).

### 3.2.17 Aluminium in soils from oil palm plantations

Aluminium is a primary factor that reduces plant growth on acid soils but generally harmless to plant growth in pH-neutral soils. Acid soils are usually saturated with Aluminium instead of hydrogen ions. The acidity of the soil is consequently due to the hydrolysis of aluminium compounds. Aluminium is a major constituent of most soils but it can only be useful to plants in acidic soils in the form of $Al^{3+}$. Exchangeable Aluminium ($Al^{3+}$) values may be high in soils with pH below 5.5 but may occur at pH values as high as 6.0 in heavy textured soils (Brown & Johnston, 1982). The critical soil pH, at which Aluminium becomes exchangeable in toxic concentrations depends on many factors including the predominant clay minerals, organic matter level and concentrations of other cations, anions and total salts as well as the species of the plant (Brown & Johnston, 1982). Acosta & Munevar (2003) observed a strong relationship between high aluminium saturation in soils and the occurrence of bud rot disease of mature oil palm tree. Further investigation was that the addition of soil amendments could improve aluminium toxicity and enhance soil pH and fertility status.

### 3.2.18 Aluminium in water from oil palm plantations

Aluminium is the most abundant element and occurs naturally on earth in the form of silicates, oxides, and hydroxides (Farizwana, 2011). Excessive addition of Aluminium salts as coagulants in water treatment processes might produce elevated concentrations of aluminium in processed water. Aluminium salts reduce organic matter, colour, and turbidity and microorganism levels in polluted water. To acknowledge the limited knowledge of aluminium exposure among consumers and the fact that high concentration of aluminium in water is detrimental to health; researchers performed several studies (Farizwana *et al*., 2011; Warmate *et al*., 2010). Farizwana *et al*., (2011) investigated the concentration of Aluminium and the physicochemical parameters of different water in selected estates in Kota, Tinggi, Johor using

the Inductively Coupled Plasma Mass Spectrometer. The estates were situated in the oil palm plantation with public and private water supplies. The water supplies were within the safe water limits except for the private water supply which hard poor turbidity values. The study was conducted to determine if trace elements from various agronomical practices leached into the drinking water supply.

### 3.2.19 Aluminium in plants from oil palm plantations

Aluminum is the key element in the soil which complexes with oxygen and silicate. At low pH, aluminum becomes solubilized in soil and easily available for plant uptake, which immediately prevents root growth. Aluminum toxicity limits global crop production because half of the global lands have pH below five and Aluminium is solubilized easily at such pH. Thus, much research has been conducted to understand the mechanism of Aluminium toxicity and resistance that is important for stable food production in the future (Nosco *et al.*, 1988). Aluminum resistance is accelerated by exclusion from the root and by methods that make the plants capable of tolerating Aluminum. Many characteristics of Aluminium toxicity remain ambiguous and difficult to detect. In plants, the foliar symptoms are similar to those of phosphorous deficiency that presents itself as stunted growth, late maturity, leaf discoloration and reduction in root growth (Poschenrieder *et al.*, 2008). Findings on the determination of Aluminium in plants are sparse and more research needs to be focused in that area.

### 3.2.20 Aluminum in palm oil

Until recently, Aluminium was considered harmless for the human organism as it is readily excreted through urine. Nevertheless, research in environmental toxicology conducted in recent years indicated that Aluminium could be a cause of many diseases in humans, animals, and plants. Aluminum can be found in many food products and feed for animals. In this way, it enters the organism and accumulates in various tissues. Although the mechanism of toxic Aluminium actions on humans has not been elucidated yet, prophylactic action should be undertaken aimed at limiting the contact of humans with Aluminium. Most of all, it should be eliminated from food, food additives and medicines. Kitchen utensils and appliances made of Aluminium as well as Aluminium wrappings and containers should be avoided (Ma *et al.*, 2001). Trace metals such as Zn, As, Pb has been determined in various vegetable oils but findings on the determination of Aluminium in palm oil are sparse and more research needs to be focused in that area.

### 3.2.21 Chromium (Cr)

Chromium is an essential element that actively takes part in the metabolism of carbohydrates, cholesterol and cardiovascular diseases. It is linked with the inhibition of diabetes and cardiovascular diseases. The Hexavalent Chromium (VI) is more toxic, mutagenic and carcinogenic in nature when compared to Chromium III. Dietary intake is the main route by which chromium is absorbed by humans. Diets that contain foods made from whole wheat, brown sugar meat, cheese, cereals, nuts, and certain vegetable contributes to a high chromium intake. Packaging technology used in food and beverage processing can increase the natural levels of chromium in raw products, since this metal is widely used in the food industry, especially in stainless steels. The US National Research Council has concluded that a varied and balanced diet is the best way to guarantee adequate chromium intake. Chromium is essential elements that functions in the regulation of blood sugar levels by insulin and helps the body absorb energy from food (Schwarz, 1972). A high dose of the essential element above 0.05mg in the environment is harmful to living things (WHO, 2004).

### 3.2.22 Chromium in soils from oil palm plantations

Chromium occurs naturally in soil but contamination due to chromium related anthropogenic activities has been a matter of apprehension to researchers over the ages. Its complex speciation chemistry has been a major difficulty in unraveling its toxicity mechanism (Adriano, 1986). Absorption of chromium has resulted to acute effects such as stomach, blood and convulsion syndromes. An epidemiological study has related occupational exposure with chromium (VI) compounds to mortality due to lung cancer (Adriano, 1986). Soil contamination is an important factor contributing to total chromium concentration in plant tissues. Another study has revealed that plants growing on high-chromium rich soils contained higher chromium concentrations and vice versa. Studies have shown that there is sufficient evidence of respiratory carcinogenicity in humans exposed to chromium (VI) in occupational settings (Mohammed *et al*., 2012). Data on lung cancer risk in other chromium-associated occupational settings and for cancer at sites other than the lungs are considered insufficient. The epidemiological data does not concede to an assessment of the relative contributions to carcinogenic risk of metallic chromium, chromium (III) and chromium (VI) or of soluble versus insoluble chromium compounds. It appears that exposure to a mixture of hexavalent chromium compounds of different solubility results in the highest risk to humans (Iwegbue *et al*., 2011). Research has been performed extensively on the determination of chromium in soils using different extraction techniques (Jankiewic *et al*., 2005; Hanharan and Krishna, 2012; Shah *et al*., 2013). Adequate information is lacking on the determination of chromium in soils on oil palm plantations.

### 3.2.23 Chromium in water from oil palm plantations

Chromium is widely distributed in the earth's crust. Hexavalent Cr (VI) that is the most toxic form of the metal chromium is a major drinking water contaminant. In several countries, a limit of 50 µg/l has been established for the presence of chromium in potable water (Shils *et al.* 1994). Information was acquired from the U.S. Environmental Protection Agency (EPA) and the State of California and the assessment was to identify general occurrence trends of chromium, capture regional occurrence patterns and to assess the geographical coverage with the extent of impact of a potential future revision of total chromium on the nation's water utilities (USEPA, 1991; Seidal & Corwin, 2012). Analysis of chromium in various water bodies were analyzed by Nagaray *et al*., (2009); Sendil *et al.,* (2011) using recent analytical methods. Information is lacking on the analysis of chromium in water from oil palm plantations.

### 3.2.24 Chromium in plants from oil palm plantations

Chromium when compared with other toxic trace metals such as cadmium, lead, mercury and aluminum, has received little understanding concerning its toxicity mechanism in plants. The impact of Chromium contamination in the physiology of plant depends on the metal speciation, which is accountable for its mobilization, toxicity, and consequent plant uptake. Chromium toxicity in plants is manifested by reduced yield, inhibition of plant growth and mutagenesis (Becquer *et al*., 2003; Shanker, 2005). Due to its extensive industrial relevance, chromium is considered a significant environmental pollutant. Toxicity of chromium to plants depends on its valence state: Chromium (VI) is highly toxic and mobile whereas chromium (III) is less toxic. Toxic effects of chromium on plant growth and development include alterations in the germination and growth process that consequently affects total productivity and yield. Chromium toxicity in plants is exhibited by stunted growth, chlorosis, and finally the death of the plant Chromium also causes deleterious effects on plant photosynthesis. The potential of plants with the capacity to accumulate or to stabilize chromium compounds for bioremediation from chromium contamination has gained interest in recent years. Sources of chromium in the environment have also ensued from human activity such as industrial and urban effluents and sewages (Alvarez-Cabal *et al*.; 1994). Information on the determination of chromium in some plants species is available in literature (Cary and William, 2013; Hernandez-Martinez & Padron-sanz, 2013) but that of Oil palm tree (*Elaeis guineensis*) is lacking.

### 3.2.25 Chromium in palm oil

The determination of the inorganic profile of oils is important because of the metabolic role of trace elements in humans. Information on food nutritional composition is significant to ascertain

food quality concerning its regards to freshness, storability, and toxicity. Trace levels of metals like Iron, copper, calcium, magnesium, cobalt, nickel, and manganese are known to increase the rate of oil oxidation. In addition, metals like arsenic, cadmium, chromium, and selenium are identified for their harmfulness. The advancement of rapid and precise analytical methods for trace elements determination in edible oil has been a challenge to quality control and food analyst (Cordella*, et al*., 2002). Bratakos & Lazos, 2002 reported that virgin olive oil contained significantly lower levels of chromium than other vegetable oils. This variance could be attributed to chromium uptake by these vegetable oils during purifying, as well as from the material of packaging. Oils are usually packaged in plastic containers, which often contain certain chromium compounds, with chromium (VI) and chromium (III) compounds being used as additives and polymerization aids (Bratakos & Lazos, 2002). Utensils used in the preparation of food may contribute to chromium levels. Some operations such are grinding, sedimentation and/or centrifugation for oil separation may contribute to chromium uptake during processing. This may be minimized by using other processing methods like the seed oil extraction and refining.

### 3.2.26 Copper (Cu)

Copper is a reddish metal that occurs naturally in rock, soil, water, sediment, and air. Copper has many practical uses in society. It can be found in coins, electrical wiring, and water pipes. It is an essential micronutrient needed in small concentrations for proper functioning of systems for humans and plants. Copper is a component of hemoglobin and alongside vitamin C, helps in the maintenance of elasticity of the skin, blood vessels, and lungs. It has high antioxidant properties protecting the body from the action of free radicals and the only defense against free radicals is a healthy supply of a diet rich in antioxidants such as red palm oil. Free radicals deplete antioxidant nutrients and trace elements. High levels of trace elements in plants such palm oil can generate oxidative stress; thereby increasing the activity of antioxidant enzymes such as superoxide dismutase, catalase and glutathione peroxidase. Therefore, the levels of these trace elements in red palm oil on the water and soil on palm oil plantation will have a significant effect on the antioxidant activity of the red palm oil. Copper is toxic at high concentrations and adverse health effects of copper toxicity in humans include vomiting and diarrhea. It has also been linked with liver damage and kidney disease. Copper levels in water and food must be regulated on a daily basis. Copper II ion is water-soluble and functions at low concentration as antiseptics, fungicides, and wood preservatives. Chronic copper toxicity does not normally occur in humans due to transport systems, which regulate absorption and excretion. Small quantities of various copper salts have been used in suicide attempts that produced acute copper toxicity. The toxicity is due to red-ox cycling and the generation of

reactive oxygen species that damage DNA cells. Recessive autosomal mutations in copper transport proteins can disable such systems leading to Wilson's disease. Copper accumulation is responsible for cirrhosis of the liver in persons who have inherited defective genes (Fry *et al.*, 2012).

### 3.2.27 Copper in soils from oil palm plantations

The amount of copper in soil available to plants varies. Available copper ranges from 1 to 200 ppm in both mineral and organic soils and this are a function of soil pH and soil texture. Fine textured mineral soils generally contain the highest amounts of copper. The lowest concentrations are associated with organic or peat soils (Aweto & Enaruvbe, 2010). Neutron activation analysis was used for the determination of trace elements of soil samples in two oil palm plantation towns in Ghana. The Assin North Central town's soils were analysed for soil fertility. The acidity of the soil decreased with depth so was the concentration of Cu, Ca and Zn.

### 3.2.28 Copper in water from oil palm plantations

Copper can be found in many wastewaters of electronic and metallurgical industries. Although the judicious use of copper fungicides may not cause any problem to human health and environmental contamination, its indiscriminate use may lead to the presence of undesirable levels of copper content in water (Zhang & Gao, 1999). Cu has been determined in wastewaters and effluents (Zhang *et al.,* 1999; Brun *et al*., 2001; Iwegbue *et al*., 2011). Limited research is available on the determination of Cu on oil palm plantations.

### 3.2.29 Copper in plants from oil palm plantations

Copper is an essential nutrient for plant growth especially for seed, chlorophyll formation and proper enzyme activity. It is an important components of proteins found in enzymes of plants that regulate biochemical reactions. Plants require the presence of these specific enzymes for growth. Deficiency symptoms of copper in plants are depicted by leaf discoloration and stunted growth, which finally leads to death. The majority of Bud Rot Disease (BRD) cases in the oil palm tree initiate the deficiency of copper in the tree amongst other trace elements. Affected plants, however, may require four months to three years to recuperate. During this time, plant production drastically declines. A typical symptom of copper deficiency in plants is the yellowing of young leaves during the months of high rainfall and humidity. Infected leaf tissue eventually becomes necrotic and withers as the disease progresses. The disease is most severe when growing palm tips are infected and the fungal pathogen allowed extending deep into plant tissues. Palms can recover from BRD if the infection is superficial. However, if

enough plant tissue is damaged, measures such as the implementation of extreme measures such as heavy pruning may fail to save the tree (Acosta & Munevar, 2003).

### 3.2.30 Copper in palm oil

Trace elements are significant in the diet of humans; however, trace elements such as mercury, lead, cadmium and arsenic have detrimental effects on health. Copper is an essential component of enzymes that plays an important role in Fe transport. The harmful effect induced by copper only occurs when taken in high concentrations. High levels of Cu in the body is known to cause blood and kidney disorders. In plants, toxicity is manifests in stunted growth and low yield Trace elements have been determined in oil due to its importance to animal and man. Trace elements are toxic and are available in edible oils from fertilizer applications, soil and anthropogenic activities. Significant research has been conducted quantitatively and qualitatively on the concentration of metals in oil (Obi *et al*., 2001; Anwar *et al.,* 2004; Asemave *et al*., 2011; Adepoju-Bello *et al.,* 2012). Limited research is available on the level of copper in palm oil.

### 3.2.31 Selenium (Se)

Selenium in its pure form is metallic grey in color and referred to as elemental selenium or selenium dust. It is rare in the environment in its elemental form, but usually combined with ores of other elements. Selenium is a naturally occurring solid substance widely but unevenly distributed in the earth's crust in rocks and soils. It finds its way into the environment through weathering of rocks and soils, volcanic eruptions, burning of fossil fuels and waste dumps. Sources of selenium toxicity may also be from crops grown on soils contaminated with selenium (ATSDR, 2003). Elemental Selenium is produced primarily as a by-product of copper refining. The utmost function of Selenium compounds is in the manufacture of electronics, industrial, medical and therapeutic agents. Selenium is an essential trace element needed by the body. It has a strong antioxidant activity and is a thyroid hormone producer. It is very antagonistic to toxic metals like lead, mercury, cadmium and aluminium. It works with Vitamin C and E in preventing free radical damage to cell membranes, proteins, and DNA. Adequate Selenium in the diet reduces the risk of cancer and cardiovascular diseases and slows the progression of HIV/AIDS. Selenium relieves symptoms of osteoarthritis, rheumatism, mood disorders, and cataracts. Though selenium is, an essential trace element acute concentration in the body is related to symptoms such dizziness, tiredness, inflammation of mucous membranes and chronic bronchitis (ATSDR, 2003).

### 3.2.32 Selenium in soils from oil palm plantations

The main threats to soils are urbanization, industrial revolution, erosion, acidification, poor agronomical farm practices and pollution. This leads to, organic matter loss and deteriorating soil structure (Aweto & Ekuigbo, 1994). Soil contamination by heavy metals can originate from a number of sources included above. Contaminants usually sink and are persistent. Land use pattern has also had a significant impact on the quality of the soil in a typical environment. The maintenance of natural systems or soil fertility in tropical forest ecosystems is achieved by high and rapid circulation of nutrients through decomposition of leaves (Ola-Adams & Egunjobi, 1992; Oliveira & Lacerola, 1993; Regina *et al.,* 1999). The regrettable occurrence of so many immune diseases in Africa is because of depleted soils. China has a low rate of colon cancer, probably because of the nation's low fat diet. Cases of cancer have been reported in China where soil is devoid of Selenium. A study in China showed that Foods containing significantly high levels of Selenium are usually foods grown on Selenium rich soils. The Selenium drained regions were known as illness belts. The amount of selenium in plant proteins depended upon the Selenium content of the soil on which the plants are grown. Brazil nuts grown in Selenium-rich soil may supply 100-microgram mores of Selenium. However, those grown in soil that had poor selenium content may provide 10 times less selenium. Selenium has been determined in soils of various depths but is lacking on soils of the oil palm (Levesque & Vendette, 1971; Garcia *et al*., 1996; Vinceti *et al*., 2001; Nazemi *et al*., 2012). Research needs to be intensified in the area of the oil palm.

### 3.2.33 Selenium in water from oil palm plantations

The forms of Selenium absorbed from the digestive tract are inorganic Sodium Selenate and Sodium Selenite. People who eat food especially edible oils-containing excess selenium typically encounter hair and nail losses, numbness, and circulatory system disorders. Major sources of Selenium in drinking water are from discharges of petroleum, mining, and metal refining industries (ATSDR, 2003). Various researches have been determined on the levels of Selenium in vegetable oils (Wallschlager & Roehi, 2001; Tyburska *et al*., 2010; Jiang, *et al.,* 2013).

### 3.2.34 Selenium in plants from oil palm plantations

Despite selenium’s status as a toxic heavy metal when taking in high concentrations, the element is vital to good human health. Selenium is an important part of a molecule in the body that protects blood cells from certain radicals. Vitamin E and selenium helps the immune system produce antibodies, which keeps the pancreas and heart working properly. A deficiency of selenium is related to the development of leukemia, arthritis, and heart diseases.

Researchers have also found that the low concentrations of selenium in the blood stream have led to higher risks of cancer. Fish, grains and Brazil nuts are considered good dietary sources. Nevertheless, in the current global marketplace it is difficult to know whether the food you eat comes from selenium-rich or selenium-poor growing areas (Goldhaber, 2003). The antioxidant property of selenium has been extensively determined in various plants and seeds (Levesque & Vendette, 1971; Xu *et al*., 2003; Cartes, *et al*., 2005; Cartes *et al*., 2011) but information is lacking on the oil palm tree.

### 3.2.35 Selenium in palm oil

Selenium forms part of proteins known as selenoproteins, which help prevent cellular damage from free radicals. These vital antioxidant enzymes assist in controlling thyroid function that is important in immune system functioning (Goldhaber, 2003). Tiahou and colleagues, 2004 studied the lack of oxidative stress in a selenium deficient area in Ivory Coast due to the potential nutritional antioxidant role of crude red palm oil. The study involved 57 subjects aged 15 to 69 in the Glanle and Boudou regions who consume a vegetarian and crude oil diet. The absence of oxidative stress damage in the subjects provided evidence of a selenium independent protection against oxidative stress (Tiahou *et al.*, 2004).

### 3.2.36 Lead (Pb)

Lead is highly poisonous to plants and animals and affects almost every organ and system in the body. Long-term exposure to lead or its salts can result in decreased performance of the nervous system, high blood pressure, particularly in middle-aged and older people and anaemia. Exposure to high lead levels can severely damage the brain and kidneys and eventually cause death. Acute concentrations may cause miscarriage and reduce fertility. Lead in the environment, has been identified as a health threat. It leads to mental retardation and learning disabilities in children even at very low levels. Lead pathway into the environment may be from the inhalation of airborne lead particulates, consumption of water, food, or dust contaminated by lead. Several studies have indicated that young children have an increased risk of lead poisoning (Francek, 1994; Rabinowitz & Bellinger, 1988; Staudinger & Roth, 1988).

### 3.2.37 Lead in soils from oil palm plantations

Environmental levels of lead have been increasing for hundreds of years, and may just start declining in response to greater awareness of its harmful effects. Today, much of the lead in the environment is from the use of lead-acid batteries. Common industrial sources of lead pollution include mining, primary, and secondary metal smelting, steel and iron production, car battery recycling, and the production of pigments (Ogunseitan *et al*., 2009 Chen *et al*., 2011).

The application of fertilizer and animal manure may over time contaminate oil palm plantations with heavy and trace metals. This may pose risk to plants and animals and their environment. Uwumanrongie *et al*., (2012) investigated the effect of Pb and Cr in soil from Nigeria Institute for Oil Palm Plantations in Nigeria. The physicochemical parameters of the soil were also investigated. Fractionation studies revealed that the concentration of Pb and Cr were bound to different fractions especially the residual fractions after planting. The researchers concluded that cow dung could be used to immobilise heavy metals found on contaminated soils on oil palm plantations.

### 3.2.38 Lead in water from oil palm plantations

Aquaculture is an important industry in Malaysia due to water availability. Recent commercial development in the Sampadi river watershed may have an impact on the water quality of the river. Ling and colleagues conducted a study to determine the water and sediment of the river along a shrimp culture farm and a palm oil plantation. Results show that oxygen demand, nitrogen and phosphorus concentrations at both stations were lower at low tides than high tides. The station along the palm oil plantations showed the lowest pH and dissolved oxygen and the highest in lead and calcium (Ling *et al*., 2011).

### 3.2.39 Lead in plants from oil palm plantations

Plants take up lead from soil and under certain conditions; high levels of lead accumulate in the leaves and other edible parts of the plant. For instance, the oil palm tree can take lead from the soils and inevitably, transported to the leaves. Plants grown in lead contaminated soils can accumulate into plant tissue. Research on the translocation of lead contaminated from the soil and roots into leaves on palm oil plantation is limited.

### 3.2.40 Lead in palm oil

Palm oil is an edible substance with anti-inflammatory and antioxidant properties. Nwokocha & colleagues (2012) examined the prospective effect of red palm oil against lead and calcium in the liver. Wister rats exposed to cadmium (200 ppm) and lead (100ppm) in drinking water at different feeding regimes fed with rat chow mixed with 12 % w/w of palm oil. The heavy metal accumulation in the liver of the rats was determined using Atomic Absorption Spectrophotometry. Weight loses induced by the metal accumulation were significantly reduced due to the ingestion of red palm oil. The studies show that red palm oil is beneficial in reducing heavy metal accumulation in the liver (Nwokocha *et al*., 2012).

### 3.2.41 Magnesium

Magnesium is an essential element in biological systems. Magnesium occurs typically as the $Mg^{2+}$ ion. Its ions are essential to all living cells, where they play a major role in biological compounds like ATP, DNA, and RNA. The main source of energy in cells, ATP, must be bound to a magnesium ion in order to be biologically active. Over 300 enzymes need the presence of magnesium ions for their catalytic action, as well as all enzymes using or synthesizing ATP, nucleotides, DNA and RNA. Magnesium compounds are used medically as laxatives, antacids, in the stabilization of abnormal nerve excitation and blood vessel spasm. Cell types may regulate the concentrations of magnesium in different ways based on their unique metabolic needs. Magnesium is an important ion that activates and mediates many biochemical reactions (Marschner, 1995). An example of this is the fixation of carbon in the chloroplasts during photosynthesis. Magnesium has many functions in the metabolism of the oil palm tree. It aids in photosynthesis, being the central atom of the chlorophyll molecule that captures light energy required for photosynthesis. It acts as a co-enzyme in carbon dioxide synthesis for the production of macromolecules such as starch, carbohydrates, and some vitamins. The significance of magnesium to proper cellular function cannot be overemphasized. Deficiency of magnesium results in disease in animals and plants. These are seen as stress responses in plants and a decrease in photosynthesis. In humans, signs and symptoms are seen as muscle spasms, heart, kidney and bone dysfunction, diarrhoea, diabetes, anxiety and migraines (Euser & Cipolla, 2009). Dietary sources of magnesium are, grains, lean meat, dairy products, vegetables, and dark chocolates. Over 50 % of total magnesium in the body is found in the bone and the remaining percentage is distributed between the tissues, organs and the blood. Magnesium essentially allows the body control insulin levels in the blood. (Broschat, 1997; Uza *et al*. 1987; Saris *et al*. 2000; Bo *et al*. 2008; Cunha *et al*. 2012). Magnesium is practically used in the manufacturing industry as filler and fire retardant, in agriculture as a component of fertilizers, a flocculent in wastewater treatment and a laxative in medicine.

### 3.2.42 Magnesium in soils from oil palm plantations

Though the oil palm is a use economic tree, the expansion of the oil palm industry has resulted to some environmental impacts. One of such is the loss of wild life such as the orangutan and a decline in soil fertility. Ogeh & Osiomwan (2012) evaluated the effects of the oil palm tree on the properties of Mg in the soil in a field of over 15 years. The results of the study revealed the variation in some nutrients such as Mg could be attributed to the soil management properties and emphasizes on maintenance of the soil properties is of paramount importance.

### 3.2.43 Magnesium in water from oil palm plantations

The provision of water for use is one of the most intractable problems in society today. Access to water is essential to health, food and sustainable development. Contamination of surface and ground water from industrial, agricultural and municipal wastes is immense. The infiltration of rainfall into landfill and waste produces leachate, high in trace elements that seep into ground and surface water. Trace elements such as Mg have been determined in water and sediments of rivers (Chapman, 1986). Data on the studies of magnesium in water from oil palm plantation is limited.

### 3.2.44 Magnesium in palm leaves from oil palm plantations

Soil analysis is not particularly useful for diagnosing palm nutrient deficiencies, since palm nutrient symptoms often bears little resemblance to soil nutrient profiles (Broschat, 1997). Magnesium has many functions in the metabolism of the oil palm tree. It aids in photosynthesis, being the central atom of the chlorophyll molecule that captures light energy required for photosynthesis. It acts as a co-enzyme in carbon dioxide synthesis for the production of macromolecules such as starch, carbohydrates and some vitamins. Magnesium deficiency appears on the oldest leaves of palms as broad chlorotic (yellow) bands along the margins with the central portion of the leaves remaining distinctly green. In severe cases, only the leaflets remain green on the oldest leaves, but younger leaves show necrosis. For instance, in *Elaeis guineensis*, leaflet tips on the oldest leaves may be necrotic, but this necrosis is due to potassium deficiency superimposed on deficient leaves of magnesium. Where the two deficiencies occur on the same palm, the oldest leaves will show characteristic potassium deficiency signs, while magnesium deficiency signs will be seen on the mid-canopy leaves. Deficient Mg and the imbalance between the ion and other cations may cause magnesium deficiency symptoms. Magnesium deficiency is often detected in very high rainfall areas (greater than 3,500 mm/year). This is likely when the amount of soil exchangeable ion is less than 0.3 mg/kg. Inadequate application of magnesium to high yielding palms or to palms on magnesium, deficient soils may cause magnesium deficiency (Rankine & Fairhurst, 1999).

### 3.2.45 Magnesium in palm oil

The determination of trace elements in vegetable oil is one of the criteria for the assessment of quality of oil. Trace metals in vegetable oils are known to have an effect on the rate of oil oxidation and storage capabilities. Njoku and colleagues (2010) in Nigeria investigated the physio-chemical characteristics and dietary metal concentrations of oil from Elaeis guineensis species. Physiochemical and dietary metal components were analyzed using standard test methods such as Spectrophotometry, Titrimetry and Gravimetry. The three species of *Elaeis*

*guineensis* studied were *Elaeis pisifera, Elaeis dura* and *Elaeis tenera.* The physicochemical parameters determined were acid values, saponification values, iodine values and antioxidant content. The dietary metal concentrations for the *Pisifera, Dura and Tenera* were 0.95, 1.13 and 0.37 mg/kg for dietary magnesium and 0.08, 0.24 and 0.05 mg/kg for dietary zinc respectively (Njoku *et al,* 2010).

### 3.3 Radionuclides in oil palm

#### 3.3.1 Radium (Ra)

Radium is a radionuclide formed when isotopes of uranium and thorium decay in the environment. It is a naturally occurring radioactive metal with common isotopes $^{226}$Ra, $^{224}$Ra, and $^{228}$Ra. It occurs at low levels in virtually all rock, soil, water, plants, and animals. Radium was discovered in the 1900's and its potential health hazards were unknown by then. Its characteristics as a luminescence material made it popular in consumer goods. The use of radium declined due to health and safety reasons (Douglas *et al*, 1990). Radium is a radiation source in some industrial radiography devices and an early radiation source for cancer treatment. Safer, more effective radiation sources, for instance cobalt-60 have substituted it. Radium is highly radioactive and hence carcinogenic and microscopic quantities in the environment can lead to some accumulation in bone tissues. Radium, like calcium, is a group II element and our bodies treat it in a similar way. It is present in tiny amounts in all uranium ores and at very low concentrations in seawater, surface, and well water. Exposure to radium can be from the burning of fossil fuels. Certain occupations such as working in uranium mines or ore processing plant can lead to high exposures. Phosphate rocks typically contain relatively high levels of both uranium and radium (Douglas *et a*l, 1990).

#### 3.3.2 Radium in soil from palm plantations

Naturally occurring and anthropogenic radionuclides depends on geological and geographical conditions in the soils of each region in the world (UNSCEAR, 2000). It is well known, for instance, that higher radiation levels are associated with igneous rock and lower levels with sedimentary rocks. There are some concessions, though, as a number of shale and phosphate rocks have comparatively high content of radionuclides (UNSCEAR, 2000; Tzortzis *et al.*, 2004; Alias *et al*, 2008). Human beings are exposed to natural radiations from their surroundings. Transfer of long-lived radionuclides such as radium and cesium were analyzed in contaminated soils after the Chernobyl accident in Japan (Muramatsu *et al*., 1987; UNSCEAR, 2000). Much research has been conducted on radium in different soil types, mines, agricultural lands and phosphate fertilizers (Muramatsu *et al*., 1987; Banzi *et al*., 2000).

Adequate research has not been conducted on the analysis of Uranium on soils from palm oil plantations.

### 3.3.3 Radium in water from oil palm plantations

Radionuclides have always been present in the earth's crust but usually brought to the surface by oil and gas production and processing operations. Occurrence of radionuclides in ground water depends on the presence and solubility of the parent element. Oil and gas exploration causes radionuclides to accumulate at elevated concentrations in streams. Radium has a similar chemical behavior to other alkaline earth metals. Therefore, in aquifers with limited sorption or ion exchange sites, radium solubility can be improved by the common-ion effect when other cations are abundantly present. Recently, high concentrations of radium were associated with ground water affected by poor agricultural practices (Kraemer & Reid, 1984; Zapecza & Szabo; 1987 Focazio *et al.,* 2001). An environmental impact assessment of the coastal plain and freshwater zone vegetated by forest tree species and oil palm in crude oil exploration regions was conducted in Ogoni land Port Harcourt, Nigeria by UNEP, 2011. Radium as one of the naturally occurring radionuclides is usually encountered in oil and gas exploration in the region. Radionuclides have always been present in the earth's crust but usually brought to the surface by oil and gas production and processing operations. Occurrence of radionuclides in ground water depends on the presence and solubility of the parent element. Oil and gas exploration causes radionuclides to accumulate at elevated concentrations in streams. Radium has a similar chemical behavior to other alkaline earth metals. Therefore, in aquifers with limited sorption or ion exchange sites, radium solubility can be improved by the common-ion effect when other cations are abundantly present. Recently, high concentrations of radium were associated with ground water affected by poor agricultural practices (Kraemer & Reid, 1984; Zapecza & Szabo; 1987 Focazio et al., 2001). An environmental impact assessment of the coastal plain and freshwater zone vegetated by forest tree species and oil palm in crude oil exploration regions was conducted in Ogoni land Port Harcourt, Nigeria by UNEP, 2011. Radium as one of the naturally occurring radionuclides is usually encountered in oil and gas exploration in the region. The study conducted by UNEP, 2011 revealed high concentrations of radium in the streams nearby oil palm plantations. The UNEP team recommended that restoring the livelihoods and well-being of future Ogoni generations is within reach but timing is critical. Given the dynamic nature of oil pollution and the extent of contamination revealed in UNEP's study, failure to address crucial civic health concerns and commencing a cleanup will only exacerbate and unnecessarily prolong the Ogoni people's suffering. A transition phase was recommended to begin detailed planning in the intervening period between the release of UNEP's environmental assessment and the

commencement of a clean-up operation guided by an Ogoni land environmental restoration authority (UNEP, 2011). Ambient dose rates were investigated on all sites. The values were found to be within the normal levels of radioactivity guidelines of 80±40 nanosievert per hour (nSv/h). The studies included sites that had fresh spillage of crude oil and the levels of radionuclides on such sites were still within the save limits. A measurement of NORM was also performed on sites and the concentrations in Ogoni crude oil were recorded with no additional radioactivity contribution to the ambient dose rate within acceptable measurement uncertainties. An ambient dose rate of the range 100 nSv/h does not pose a radiological hazard since the annual dose limit guideline which is above the background limit for humans is 1,000,000 nSv per year. Ogoni crude oil sites were measured for surface contamination measurements and all the sites recorded natural background radioactivity level of 3±2 counts per second (cps).

### 3.3.4 Radium in palm leaves from oil palm plantations

Analysis of radionuclides uptake from contaminated soils by plants is important for remediation. Accumulation of radium has been studied in some plants like *Dicranopteris linearis* (Chao & Chuang, 2011), *Dicranopteris dichotoma* (Simon & Deming, 1986), vegetables and fruits (Tracy *et al.,* 1983) and in wheat grass, yellow clover and rye (Rumble & Bjugstad, 1985). Extensive research and literature has not been done on the investigation of radium in palm leaves from oil palm plantations.

### 3.3.5 Radium in palm oil

Radionuclide can be released into the environment through accidents, poor waste disposals and other means. Some level of radiation is naturally present in surface and ground water but other degrees of radiation exposure come from rocks and soil that have been contaminated by artificially produced radionuclides. Some major pathways to commonly encountered hazardous radionuclides are food contamination and occupational exposure at mining and processing sites. Studies on acute toxicity of radionuclides have been conducted on radionuclide content in food, water, waste dumps, feed materials, environmental matrices and crude oil (Osibote *et al.,* 1999; Strouble *et al.,* 1985; Olomo *et al*., 1990; Przylibski *et al.,* 2002; Awodugba & Tchokossa, 2008). Faweya & Babalola (2010) carried out gamma spectroscopic assays of radionuclide and heavy metals from waste dumpsites in southwestern Nigeria. The activity concentration level due to $^{40}K$, $^{226}Ra$, $^{226}Th$, $^{137}Cs$, $^{109}Cd$, $^{210}Pb$, $^{214}Bi$ and $^{208}Tl$ in the samples were determined using coaxial-type Ge detector. Faweya & Babalola recorded maximum concentrations of $^{40}K$, $^{226}Ra$, $^{228}Th$ and $^{137}Cs$ as 357±12, 68±7, 132±10 and 0.96 $Bqkg^{-1}$ at Ado, Abeokuta, Lagos and Ibadan; while the minimum concentrations were 180±6,

40±5, 22±2 and 0.19 $Bqkg^{-1}$ at Akure, Ado, Oshogbo and Abeokuta respectively. The highest concentrations of heavy metals $^{208}Ti$, $^{210}Pb$, $^{214}Bi$ and $^{109}Cd$ are 35±1, 46±5, 40±1 $Bqkg^{-1}$ were at Lagos, Ibadan and Ado, while the minimum concentrations were 5±0.24, 20±3, 17±2 and 40±1 $Bqkg^{-1}$ were at Ado and Ibadan respectively (Faweya & Babalola, 2010). Analysis of radium in palm oil is sparse.

### 3.3.6 Uranium (U)

Uranium is an abundant naturally occurring element that can be found in low levels in rock, soil, and water. It occurs in combination with other elements. Significant concentrations of uranium occur naturally in phosphate rock deposits, lignite, and uranium-rich ores. In nature, uranium (VI) forms highly soluble carbonate complexes at alkaline pH. Uranium is produced from anthropogenic activities such as uranium mining, fossil fuels, phosphate fertilizers, and nuclear power production (Zaini *et al*., 2010). The primary health concern of uranium mining is exposure to cancer-causing radiation. In addition to causing cancer, radiation, uranium may cause genetic damage, disrupt hormone levels, and reduce blood cell counts. One of the most troublesome aspects of radiation exposure is that symptoms of diseases may not arise until decades after exposure. Exposure to uranium increases the chances of developing cancer. A review of literature revealed that uranium workers' risk of developing lung cancer is 2-5 times greater than average. Close proximity to uranium-contaminated sites have been known to cause an increase in negative health effects. Uranium is known to cause kidney, brain, heart, and reproductive disorders (Miah & Roy, 1998).

### 3.3.7 Uranium in soil from oil palm plantations

Information of distribution pattern of radionuclides in soils is necessary in controlling radiation exposure levels and sources (Miah & Roy, 1998). The natural radioactivity of soil and sediment depends on chemical and biological formation and transport processes (Tenniseen, 1994). Much research has been conducted on uranium in different soil types and in mines (Laure et al., 2011) agricultural lands and phosphate fertilizers (Muramatsu *et al*., 1987; Banzi *et al*., 2000). Zaini *et al.,* 2011, in a study focused on the presence of natural uranium isotopes using its progenies in soils in the river basin of the granitic region of Kuala Krai district, Malaysia. Granitic characteristics of these regions were believed to produce significant concentrations of natural radionuclide such as uranium and thorium. Therefore, the assessment of radiation dose from soils on oil palm plantations is of particular importance, though limited research has been conducted.

### 3.3.8 Uranium in water from oil palm plantations

Higher rates of uranium intake have been reported for some populations who consume foods grown in areas with elevated concentrations of uranium in the soil and drinking water. Occurrence of radionuclides in ground water depends on the presence and solubility of the parent material. Kris (1991), following a survey on ground water monitoring project in southwestern North Dakota in the United States of America, determined uranium in reclaimed abandoned mines. One hundred and fifty-eight water samples were collected from wells and springs of which twenty-six exceeded the USEPA maximum contaminant level for uranium (Kris, 1991). Some researchers (Brunskill & Wilkinson, 1987; UNSCEAR, 1988) have studied the effects of uranium in wells, surface waters, shallow aquifers, old mines and hazardous wastes. Information on the uranium on water from palm oil plantation is sparse.

### 3.3.9 Uranium in palm leaves from oil palm plantations

The accumulation of radionuclides by plants acting as a monitoring system in the environment may occur by foliar absorption through the leaves and shoots of the plants or by uptake from the roots. Accumulation of radionuclide in plants can be obtained from tracer or fusion studies. Fission track technique has been widely used for the determination of uranium in environmental samples such as leaves and soils. Leave samples were collected from Dumka, Jhark land state in India and analyzed for uranium concentrations using fission track techniques. The fission track and Lexan plastic technique was also used as the external detector for uranium that varies in the different parts of the plant. The plant species used for the study were *Helianthus sativus, Lycopersicon escculentum*, *Hibiscus esculentus* and *Capsicum annum* (Singh *et al*., 2008). Uranium has been analyzed in the leaves of cypress trees at the uranium processing facility in France (Giere *et al*., 2012). The transport of uranium was also analyzed on *Andropogon elliotti* grown on sediments from a former radiological settling pond (Punshon *et al.,* 2004). Some wild plant such as *Lagonychium farctum* native to Iraqi's desert were also polluted with uranium from the desert of Iraqi's nuclear centers of research (Riyad *et al.*, 2012). Information on the analysis of uranium on *Elaeis guineensis* tree plant is sparse.

### 3.3.10 Uranium in palm oil

Radionuclides are released into the environment through accidents, poor waste disposals and other means. Some level of radiation is naturally present in surface are contaminated by artificially produced radionuclides. Some major pathways to commonly encountered hazardous radionuclides are food contamination and occupational exposure at mining and processing sites (Ahmad *et al.*, 2011). Uranium undergoes oxidation-reduction reactions in the

environment and microbial reactions to form complexes with organic matter (Premuzie *et al*., 1995). Uranium can only be removed from the environment by radioactive decay. Arogunjo (2007), using a 7.6 by 7.6 cm NaI (Tl) detector, carried out gamma radiation levels due to primeval radionuclide in surface soils in some southwestern cities in Nigeria. The mean absorbed dose rate and annual effective dose were evaluated from the measurement of $^{40}K$, $^{238}U$, $^{232}Th$. The absorbed dose rate values ranged from 18.6 to 68.4 with a mean (±SD) value of 44.2±15.9 $nGyh^{-1}$ in Lagos area; 26.8 to 145.6 within a mean value of 72.9±35.6 $nGyh^{-1}$ in Ibadan area and 30.9 to 98.9 with a mean value of 64.2±26.5 $nGyh^{-1}$ in Akure area. The mean effective dose for these locations is 56.5, 93.3, and 82.2 μSv $year^{-1}$, respectively. The average value for the region is 0.8 mSv $year^{-1}$ endorsed for normal environment (Arogunjo, 2007). Awodugba, (2008), determined the level of radionuclide concentration in water from boreholes in selected areas of Ogbomoso land. Concentration of $^{228}U$, $^{232}Th$ and $^{40}K$ was determined for the water samples from eight boreholes in Ogbomoso land by y-ray spectrometry; with a high purity germanium (HPGe) detector connected to a multichannel analyser. All the water samples from these boreholes were found to contain acceptable levels of radionuclide with mean activity values of 3.98±0.26, 11.0±2.58, and 17.73±5.04 Bql *for* $^{40}K$, $^{232}Th$, and $^{238}U$ respectively. This shows that the mean activity of $^{238}U$ for all the samples is the highest when compared to those of $^{40}K$ and $^{232}Th$. Therefore, the activity of uranium remains essentially unchanged over thousands of years. Analysis of uranium in palm oil is sparse.

### 3.4 The oil palm tree in remediation technology

The palm oil tree is a cost effective alternative solution to phytoremediation. Nowadays, many types of treatment methods are available as tools to reduce water and soil contamination by trace/heavy metals. However, these treatment methods have several disadvantages such as high cost and maintenance. Over the past decades, there has been an increasing interest for the development of plant-based remediation technologies which have the potential to be cheap and environmentally friendly (Cunningham & Ow, 1996). There are several mechanisms used by plants, which allow cleanup of surface water, groundwater, soils, sediments, and sludge contaminated by trace/heavy metals. Phytoextraction is the use of metal-accumulating plants that can transport and concentrate metals, from soil/water through roots to other parts of the plants. This ability of the plant is used to extract toxic metals from the environment and provides an interesting tool for the remediation of metal contaminated sites (Baker *et al*., 1994). Most plants in the ecosystem have great variation in the way they concentrate trace/heavy metals (Freedman & Hutchinson). The oil palm tree (*Elaeis guineensis*) has been investigated by various scientists as being able to absorb different concentrations of trace/heavy metals at various parts of the plants. Roots of *Elaeis guineensis* showed highest uptake of zinc metals

(1.2810 mg/L) compared to the leaf (0.9298) mg/L and sediment (0.5924 mg/L). The results show that *Elaeis guineensis* is able to accumulate Zinc metals more in the roots than other parts of the tree. Lead trace element accumulation was in the order of 0.3297 mg/L, 0.3267 mg/L, and 0.2529 mg/L for sediments, roots and leaves respectively. This is in agreement with Koeppe (1977), Adriano *et al.,* (1986), and Alloway (1990), who stated that the amount of metal uptake from the soils is influenced by soil factors such as pH, redox potential, organic matter content, fertilizer application, plant age and species. Chromium uptake of trace/heavy metal was highest in the shoots and lowest in sediments. Furthermore, the concentration of copper showed lowest concentrations (0.0095 mg/L) for the roots while the leaf showed the highest uptake of Copper (0.217 mg/L). From the research, cadmium had the lowest metal uptake by *Elaeis guineensis*. The mean trace/heavy metal concentration uptake values showed that the root has the highest value of metal adsorption (0.0118 mg/L) followed by leaves (0.0111 mg/L) and then sediments (0.0110 mg/L). The conclusion agrees with Adriano *et al.* (1986) who discussed the relevance of phytoremediation technology where tree parts can vary in their ability to accumulate certain types and concentrations of trace/ heavy metals due to differentiation in their solubility in soil, availability for plant uptake and their ability to undergo translocation.

## 3.5 Conclusion

Palm oil is an important dietary oil component of food, beverages and snacks. Findings from the present literature present strong evidence that essential and non-essential trace elements and radionuclide can be ingested from palm oil. Nevertheless, it also provides vitamins and carotenes that are powerful mediators for cellular functions and cure for several ailments. However, it is still difficult to find out the adverse human health effect of palm oil as related to trace elements and radionuclide and at the same time, it is difficult to translate diverse scientific findings into public health messages and setting a health standard for trace elements and radionuclides. The concentration of the trace elements and radionuclides in red palm oil could be from natural and anthropogenic sources on the soil, water and leaves/fruit of the palm oil tree on palm plantations. Despite significant research efforts, adequate research is lacking on the concentration levels of trace elements on water, soil, fruits and leaves on palm oil plantations. Research is required to comprehend the science of accumulation of trace elements and radionuclides by oil palm plants, its specification of uptake and effects on human health by regular consumption of palm oil and palm oil products.

## 3.6 References


Acosta, A., Munevar, F., 2003. Bud rot on oil palm plantations: Link to soil physical properties and nutrient status. Better Crops International 17(2), 22-25.

Adepoju-Bello, A.A., Osagiede, S.A., Oguntibeju, O.O., 2012. Evaluation of the concentration of some Ahmad, S., toxic metals in dietary red palm oil. J. Bioanal Biomed 4(50), 92-95.

Adriano, D. C., 1986. Trace elements in the terrestrial environment, 105-123.

Ahmad, S., Zaini, H., Hamimah, J., Husna, M.M., 2011. Assessment of outdoor radiation hazard of natural radionuclide in tourism beach areas. Proceeding of 3rd international symposium & exhibition in sustainable energy & environment, Melaka, Malaysia, 123-127.

Aini, A.A., Fauziah, C.I., Samsuri, A.W., 2010. Cadmium and Zinc concentrations in the soil of the oil palm plantations from long-term application of phosphate rock. World Congress of Soil Science: Soil solutions for the changing world, Brisbane, Australia, 19.

Alloway B.J., 1990. Heavy metals in soils. John Wiley and Sons Inc. NewYork.

Alloway, B.J., 1995. Heavy metals in soils. Blackie and Sons Ltd, Glasgow, London.

Alloway B.J., 2008. Zinc in soils and crop nutrition. International Fertilizer Industry Association. 2nd edition. Brussels. Belgium. 139 pages.

Alvarez-Cabal, E., Wrobel, K., Marchante, J. M., Sanz-Medel, A.,1994. Determination of chromium in biological fluids by electro thermal atomic absorption spectrometry using wall, platform and probe atomization from different graphite surfaces. J. Anal. At. Spectrom. 9, 117-123.

Alvaro, J.C.R., Hanafi, M.M., Syed Omar, S.R, Rafii, Y.M., 2009. Chemical characteristics of representative high aluminium saturation soil as affected by addition of soil amendments in a closed in a closed incubation system. Mal. J. of Soil Sci. 13, 13-28.

Anklam, E., Battaglia, R., 2001. Food analysis and consumer protection. Trends Food Sci. Technol. 12, 197-202.

Anwar, F., Kazi, T.G., Saleem, R., Bhanga, M., 2004. Rapid determination of some trace metals in several oils and fats. 55(2), 160-168.

Arancibia, V., Zuniga, M.J., Zuniga, M.C., Segura, R., Esteban, M., 2010. Optimization of experimental parameters in the determination of zinc in sea water by adsorptive stripping voltammetry. J. Braz.Chem.Soc. 21(2), 255-261.

Arogunjo, A.M., 2007.Terrestrial gamma radiation and the radiological implication in Southwestern Nigeria, J. of Appl. Sci. 7(11), 1534-1537.

Asante K.A., Ntow, W.J., 2009. Status of environmental contamination in Ghana; the perspective of a research scientist. Environ. Res. Asia, 253-260.

Asemave, K., Ubwa, S.T., Anhwange, B.A., Gbaamende, A.G., 2011. Comparative evaluation of some metals in palm oil. Intern. J. of Mod. Chem. 1(1), 28-35.

Atasie, V.N., Akinhanmi, T.F., 2009. Extraction, compositional studies and physicochemical characteristics of palm kernel oil. Pak. J. of Nutr. 8(6), 800-803.

ATSDR, Agency for Toxic Substances and Disease Registry, 2003. Toxicology profile for selenium. US Department of Health and Human Services. Atlanta, Georgia.

Aweto, A.O., Ekuigbo U.E., 1994. Effects of oil palm plantations on tropical forest soils in southwestern Nigeria. The Indonesia J. of Geog. 26, 51-59.

Aweto, A.O., Enaruvbe, G.O., 2010. Catenary properties of soil properties under oil palm plantations in southwestern Nigeria. Ethiopian J. of Environ. Studies and Manag. 3(1), 1-7.

Awodugba, A.O., Tchokossa, P., 2008. Assessment of radionuclide concentration in water supply from boreholes in Ogbomosoland. Indoor and Built Enviromental, 71(2), 183-186.

Ayakora, C., Nwaeze, K., Ayodele, O., Chinwe, N.C., Arbabi, M., Herbert, C.H, 2011. Concentrations of heavy metals in some pharmaceutical effluents in Lagos, Nigeria, J. Environ. Chem. Ecotoxicol. 3(2), 25-31.

Ayodele, J.T., Oluyomi, C.D., 2011. Gas contamination by trace metals from road traffic. J. Environ. Chem. Ecotoxicology, 3(3), 60-67

Azura, A.A., Fauziah, C.J., Samsuri, A.W., 2012. Cadmium and Zinc concentrations in the soil of the oil palm plantations from long-term application of phosphate rock fertilizers. Soil and Sediment Contamination: An International Journal. 21 (5).586-603.

Baker, A.J., Reeves R.D., McGrath S.P., 1991. In situ decontamination of heavy metal polluted soils using crops of metal accumulating plants: a feasibility study. Heinemann, Boston.

Banzi, F.P., Kifanga, L.D., Bundala, F.M., 2000. Natural radioactivity and radiation exposure at the Minjingu phosphate mine in Tanzania. J. Radiol. Prot. 20(1), 41-51.

Becquer, T., Quantin, C., Sicot, M., Boudot, J.P., 2003. Chromium availability in ultramarine c soils from New Caledonia. Sci. Total Environ. 301, 251-261.

Ben, C., John, C., 2006. Impacts of oil palm activities in the Kokonda and Popondetta catchments. An initial environmental Examination. CELCOR. 1-25.

Bo, S., Pisu, E., 2008.Role of dietary magnesium in cardiovascular disease prevention, insulin sensitivity and diabetes. Current opinion in lipidology.19 (1), 50-56.

Brady, C.N., Weil, R.R., 1999. The nature and properties of soil. Twelfth ed. Prentice Hall, New Jersey.

Bratakos, M.S., Lazos, E., 2002. Chromium content of selected Greek foods. Total Environ., 290, 47-58.

Brown, A.J, Johnston, J.A., (1982). Exchangeable aluminum in Victorian soils: In trace element review papers. Agricultural services Library, Department of Agriculture, Victoria.

Brun L.A., Maillet J., Hinsinger P., Pepin M., 2001. Evaluation of copper availability to plants in copper-contaminated vineyard soils. Environ. Pollut. 111, 293-302.

Brunskill, G.J., Wilkinson. P.,1987. Annual supply of $^{238}U$, $^{234}U$, $^{230}Th$, $^{226}Ra$, $^{210}Pb$, $^{210}Po$, and $^{232}Th$ from terrestrial and atmospheric sources. Can. J. Fish. Aquat. Sci. 44, 215-230.

Cartes, P., Gianfreda, L., Paredes, C., Mora, M.L., 2011. Selenium uptake and its antioxidant role in ryegrass cultivars as affected by selenite seed pelletization. Journal of Soil Science and Plant Nutrition.11 (4), 1-14.

Cartes, P., Giarfreda, L., Mora, M.L., 2005. Uptake of selenium and its antioxidant activity in rye grass when supplied as selenate and selenite forms. Plant and Soil. 276, 359-367.

Cary, E. E., Kubota, J., 1990. Chromium concentration in plants: effects of soil chromium concentration and tissue contamination by soil. J. Agric. Food Chem. 38, 108-114.

Chao, J.H., Chuang, C.Y., 2011.Accumulation of radium in relation to some chemical analogues in Dicranopteris linearis.. Appl. Radiat. Isot. 69(1), 261-267.

Chapman, D., 1996.Water quality assessments: A guide touse of biota sediments and water in environmental monitoring., second ed. UNESCO/WHO/UNEP. Cambridge, London.

Chen, S.S., Lee, B.Y., Cheng, C.C., 2001.Determination of arsenic in edible fats and oils by direct Graphite Furnace Atomic Absorption Spectrophotometry. Journal of Food and Drug analysis.9 (2), 121-125.

Chen, Y., Yu, M., Xu, J., Chen, X., Shi, J., 2011. Differentiation of eight teas (Camellia sinensis) cultivars in China by elemental fingerprint of their leaves. J. of the Sc. of Food and Agric. 89, 2350-2355.

Chengbei, L.I., Aydan Elc, B., Julian, F.T., 2013. Determination of inorganic arsenic in water by quartz crystal microbalance. Analytical methods. 22(5), 6286-6291.

Chong, Y.H., Ng, T.K.W., 1991. Effects of palm oil on cardiovascular risk. Med. J. Malaysia. 46(1), 41-50.

Cordella, C., Moussa, I., Martel, A.C., Sbirrazzuoli, N., Lizzani-Cuvelier, L., 2002. J. Agric. Food Chem. 50, 1746-1751.

Cunha, A., Umbelino, B., Margarida, L., Mario, F.N., 2012.International J. of Hypertension.1-7

Cunningham, S.D., Ow, D.W., 1996. Promises and prospects of phytoremediation. Plant physiology, 110(3),715-719.

De Meus, C., Eduljee, G.H., Hutton, M., 2002. Assessment and management risks arising from exposure to cadmium in fertilizers. Sci. Tot. Environ. 291(3), 167-187.

Don-Pedro, K.N., Oyewo, E.O., Oitoloju, A.A., 2004. Trend of heavy metal concentration in Lagos lagoon ecosystem, Nigeria, West Africa, J. Appl. Ecol. 5, 103-114

Douglas, G.M., George, W.M., Charles, C., 1990. Radioactive hazard of portable water in Virginia and Maryland. Bull. Env. Contam. Toxicol. 44, 508-513.

Euser A.G., Cipolla, M.J., 2009. Magnesium sulphate for the treatment of Eclampsia. Abrief Review. Stroke. 40(4), 1169-1175.

Farizwana, M.R., Mazrura, A., Fasha, Z.A., Rohi, A.G. 2011. Determination of aluminium and physicochemical parameters in the palm oil estates water at Johor. Malaysia, J. of Environ.l and Public Health, 2010. 1-7.

Faure, G., 1986. Principle of Isotope Geology. Geological magazine, second ed. John Wiley and Sons. New York.

Faweya, E.B., Babalola, A.I., 2010. Radionuclide safety assessment and occurrence of heavy metals in soil from designated waste dump sites used for building and compositing in south-western Nigeria. The Arabian Journal for Science and Engineering. 35(2A), 219-225.

Finster, M.E., Gray, K.A., Binns, H.J., 2004. Lead levels of edibles grown in contaminated residential soils, a field survey. Sci. Tot. Env. 2(3), 245-257.

Focazio, M.J., Scabo, Z., Kraemer, T.F., Mulin, A.H., Barringer, T.H., DePaul, V.T., 1988.Occurence of selected radionuclides in ground water used for drinking water in the United States: A reconnaissance survey. US Geo. Surv. Report 00-4273. Virginia.

Fosmire, G. J., 1990. Zinc toxicity. Amer. J. of Clin. Nutri. 51 (2): 225-227.

Francek, M.A., Makimaa, B., Pan, V., Hanko J.H., 1994. Small town lead levels: A case study from the homes of Pre-Schooler in MT-Pleasant, Michigan. Environ. Pollut. 159-167

Freedman, B., Hutchinson, T.C., 1980. Pollutant inputs from the atmosphere andaccumulations in soils and vegetation near a nickel-copper smelter at Sudbury, Ontario, Canada. Can. J. Bot. 58, 108-132.

Fry, R.S., Ashwell, M.S., Lloyd, K.E., O'Nan, A.T., Flowers, W.L., Stewart, K.R., Spears, J.W., 2012. Amount and source of dietary copper affects small intestine morphology, duodenal lipid peroxidation, hepatic oxidative stress and MRNA expression ofhepatic copper regulatory proteins in weanling pigs. J. Anim. Sci. 90(90, 3112-3119.

Garcia, I.L., Merlos, M.S., Cordoba, M.H., 1996. Rapid determination of seleninicum in soils and sediments using slurry sampling electro thermal atomic absorption spectrometry. J. Anal. At. Spectum (11), 1003-1006.

Giere, R., Kaltenmeier, R., Pourcelot, L., 2012. Uranium oxide and other airborne particles deposited on cypress leaves close to a nuclear facility. J. of Environ. Monitoring. 14, (4) 1264-1274

Goldhaber, S.B., 2003. Trace element risk assessment: essentiality vs. toxicity. Regulatory Toxicol and Pharmacol. 38, 232-242.

Golow, A.A., Agyemang, O., Ackah, M., 2010. Soil fertility analysis in two oil palm plantation towns in Assin, north district of the central region of Ghana. Australian J of Basic and Applied Sciences. 4(7), 1650-1655.

Gupta, U.C., Gupta, S.C., 1998. Trace element toxicity relationships to crop production, livestock and human health: Implications for management. Commun. Soil Sci. Plant Anal. 29, 1491-1522.

Hajo, H., Lothar, R., 2009. The immune system and the impact of zinc during aging. Immunity and Aging. 6(9), 1-17.

Hammid, A.A., Kuntom, A., Ismail, R., Pardi, N., (2013). Arsenic in palm kernel expeller using microwave digestion andgraphite furnace atomic absorption spectrometry method. International Journal of Basic and Applied Sciences. 1(3), 2013. 641-649.

Hamzah, Z., Darus, A., Saat, A., Tajuddin, Z., (2012). Heavy metals and arsenic deposition around a palm oil mill-using palm waste as energy source. International plantion conference, 19-21, Dec. Bogun, Indonesia.

Han, W.Y., Shi, Y.Z., Ma, L.F., Ruan, J.Y., 2005. Arsenic, cadmium, chromium, cobalt and copper in different types of Chinese tea, Bulletin of Environmental Contamination and Toxicology, 75. 272-277.

Hariharan, A.V., Krishna, D.M., 2012. Extraction of chromium (VI) from soils by tri-n- octyl amine oxide. International Journal of Analytical and Bioanalytical Chemistry. 2(4) 201-203.

Hartley, C.N., 1988. The Oil palm, first ed. Longman Scientific Technical, UK.

Hendershot, W., 2005. Digging up the dirt. The Reporter, McGraw Grill. 27(9) 37-38.

Hernandez-Martinez A.M., Padron-Sanz, C., 2013. Determination of Ni, Cr, Cu, Pb and Cd on the Mediterranean endemic plant Posidonia oceania using the green extraction method “microwave assisted micellar extraction” and GFAAS. Analytical Methods. 22(5), 6473-6479.

Hilary Chiew.The star online. http://the star.com.my/lifestyle/story.asp?file=/2008/1/1.

Holmgen, G.G., Meyer, M.W., Chaney, R.L., Daniels, R.B., 1993. Cadmium, lead, copper and nickel in agricultural soils. Agricultural soil in the United States of America, first ed. 22, 335-348.

Hughes, M.F., Beck, B.D., Chen, Y., Lewis, A.S., Thomas, D.J., 2011. Arsenic exposure and toxicology: A historical perspective. Toxicological Sciences. 123(2), 305-302.

Igwe, J.C., Onyegbado, C.C., 2005. A review of palm oil mill effluent water treatment. Global J. of Environ. Res. 1(2), 54-62.

Iskandar, I.K., 1992. Restoration of metals contaminated soil. Environmental restoration of metals contaminated soil. Lewis publishers.

Iwegbue, C.M.A., Aromoro, F.O., Iwegbue, C.E., Eguavoen, O., 2011. Levels of Cd, Cu, Cr, Ni, Zn, Pb and Mn in some species from Orogodo river, Nigeria. J. of the Chem. Soc. Of Nig. 36(1), 37-41.

Jankiewic, B., Pta, S., Zynski, B., 2005. Determination of chromium in soils of Lodz gardens. Polish Journal of Environmental Studies. 14(6), 869-875.

Jiang, S., Lu, p., Huang, M., 2013. Determination of trace arsenic and selenium in water samples by inductively coupled plasma mass spectrometry. Journal of the Chinese Chemical Society.41 (3), 139-144.

Jibiri, N.N., Okusanya, A.A., 2008.Radionuclide contents in food products from domestic and imported sources in Nigeria. Journal of Radiological Protection. 28(3), 405.

Jimoh, O.L.W., and Mahmud, I.M., A., 2012. Assessment of cadmium and lead in soils and tomatoes grown in irrigated farmland of the Kaduna metropolis, Nigeria. Research Journal of Enviromental and Earth Sciences. 4(1): 55-59.

Judth, M., 2011. Alzheimers disease- a neurospirochetosis. Analysis of the evidence following Koch's and Hill's criteria. J. Neuroinflammation. 8(90), 13-16.

Jurgen, M., Wennrich, R., Schmidt, A., Reisser, W., Fresenius, J. 2000. Determination of arsenic species in water, soils and plants. J. Anal Chem, 366, 200-203.

Kauser, M.A., Hussain, F., Ali, S., Iqbal, M.M., 2001. Zinc and copper nutrition of two wheat varieties on a calcareous soil. Pakist. J. of Soil Sc. 20, 21-26.

Kiran, K., 2012. A novel extractive spectrophotometric method for the determination of chromium in water samples. Journal of Applied Chemistry. 1(2), 45-49.

Kiran, K., 2012. Spectrophotometric determination of zinc in water samples using 3-hydroxybenzylaminobenzoic acid. Chem. Sci. Trans.1 (3), 669-673.

Klein, E.A., Thompson Jr. I.M., Tangen, C.M.A., Crowley, J.J., Lucia, M.S., Goodman, P.J., 2009. Vitamin E and the risk of prostate cancers and other cancers: the selenium and vitamin E cancer prevention trial. JAMA, 301, 39-51.

Knox, A.S., Seamans, J.C., Mench, M.J., Vangronseveld, J., 2000. Remediation of metals and radionuclides. Contaminated soil using insitu stabilization techniques. Macmillan Publishers, New York, 21-26.

Koeppe, D.E., 1977. Sci. Tot. Envir. 7, 197-206.

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

Kris, D.R.,1991. A survey of naturally occurring Uranium in ground water in south-western North Dakota. North Dakota Department of Health. North Dakota.

Kucha, H., Martins, A., Ottenburgs, R., 1996.Primary minerals of Zn-Pb mining and metallurgical dumps and their environmental behavior at Pllombiers, Belgium. Eur. J. of Mineralogy. 8(1), 93-102.

Kukier, U., Summer, M.E., Miller, W.P., 1994.Determination of arsenic in plant tissue using a slurry sampling graphite furnace. International Symposium on Soil Testing and Plant Analysis: Nutrient Management Part I. 25(7-8),1149-1159.

Levesque, M., Vendette, E.D., 1971. Selenium determination in soils and plant materials. Canadian Journal of Soil Science. 51(1), 85-93.

Ling, T.Y., Eklip, M., Nyanti, L., Mordi, B., 2011. Impacts of land use on water and sediment quality of Sampadi River, Malaysia. World Appl. Sc. J. 13(6), 1465-1470.

Ma, J.F., Ryan, P.R., Delhaize, E., 2001. Aluminum tolerance in plants and the complexing role of organic acids. Trends Plant Sci. 6, 273-278.

Manahan, S.E., 1991. Environmental Chemistry, fifth ed. Lewis Publishers, 10-565.

Marshener, H.,1995. Mineral nutrition in academic plants. San Diego.Academic Press.

Meiwether, J.R., Beck, J.N., Keeley D.F., Langley, M.P., Thompson, R.N., Young, O.N., 1988. Radionuclides in Louisiana soil. Foludex Press, Ibadan, 562-568.

Melendez, L.B., Silva-Filho, E.V., Mickeley, N., Vieira, F.A., Sella, S.M., 2011. Determination of arsenic species in *P. Calomelanos and N. biserrata.* Journal of the Brazillian Chemical Society. 22(10),1968-1978.

Miah, F.K., Roy, S., Touhiduzzaman, M., Alam, B., 1998. Distribution of radionuclide in soil sample in and around Dhaka City. Appl. Rad. & Isotopes. 49, 133-137.

Mohammed, S.S., Batu, M.A., Mohammed, M.B., 2012.Analysis of chromium in dumpsite samples using AAS and EDXRF techniques. Res. J. of Chem. Sci. 2(12), 65-68.

Mster, G.M.A., 1996. Soil introduction to environmental engineering and science, Prentice-Hall Inc. New York.

Muramatsu, T., Sumiya, M., Ohmono, Y., 1987.Iodine-131 and other radionuclides in environmental samples collected from Japan after the Chenobyl accident. Sci. Total Environ. 67(3), 149-158.

Nagaraj, P., Aradhana, M., Anantharaman, S., Shrestha, A.K., Gowda, A.K., 2009. Spectrophotometric method for the determination of chromium (IV) in water samples. Enviromental Monitoring Assessment. 157, 575-582.

Nazemi, LNazmara, S., Selenium status in soil water and essential crops of Iran. Iranian Journal of Environmental Health Sciences & Engineering 2012, 9:11

Nazmara, S., Eshraghyan, M.R., Nasseri, S., Djarfarian, K., Yunesian, M., Sereshti, H., Moameni, A., Shahtaheri, J., 2012.Selenium status in soil, water and essential crops of Iran. Iranian Journal of Enviromental Health Science and Engineering. 9(11), 1735-2746.

Njoku, D.N., Afuape, S.O., Ebeniro, C.N., 2010. Growth and yield of cassava as influenced by grain cowpea population density in southeastern Nigeria. Afr. J. of Agric. Res. 5(20), 2778-2781.

Norhayati, I., Yaakob, C.M., Chin, P.T., Idris, N.A., 2005. Monitoring peroxide value in oxidised emulsions by Fourier transform infrared spectroscopy. Eur. J. Lipid Sci. Technol.107, 886-895.

Nosco, P., Brassard P., Kramer J.R., Kershaw K.A., 1988. The effect of aluminium on seed germination and early seedling establishment growth and respiration of white spruce (Picea glauca). Can. J. Bot. 66, 2305- 2310.

Nwokocha, C.R., Nwokocha, M., Owu, D.U., Obi, J., Olatunde, B., Ebe, C., Nwangwu, O., Iwuala, M.O., 2012.Comparative analysis of the effect of palm oil in reducing cadmium and lead accumulation in liver of Wister rats. Pharmocognosy research 4(4), 214-218.

Nyle, C.B., Ray R.W., 1996. Radionuclides in soil. The natural properties of soil. Prentice Hall Inc. New Jersey. 753-754.

Obi A.L., Jonah, S.A., Umar, J., 2001 Determination of trace elements in some Nigerian based oils by neutron activation analysis. J. Radioanal. Nuc. Chem. 249, 669-671.

Ogeh, J.S., Osiomwan, G.E., 2012. Evaluation of the effect of oil palm on the physical and chemical properties of *Rhondic Paleudults*. Nigerian J. Of Basic and Appl. Sc. 20(1), 75-82.

Ogunseitan, O.A., Schoenung J.M., Saphores J.D., Shapiro A.A., 2009. The electronics revolution: from e-wonderland to e-wasteland. Sci. 326 (5953), 670-671.

Oguntibeju, O. O., Esterhuyse, A. J., Truter, E. J., 2010. The role of red palm oil supplementation in reducing oxidative stress in HIV/AIDS and TB patients; a review. Journal of Medicinal Plants Research, 4(2), 188-196.

Ohimain, E.I., Seiyaboh, E.J., Izah, S.C., Oghenegueke, E.G., Perewarebo, G.T., 2012. Some selected physic-chemical and heavy metal properties of palm oil mill effluents. Green Journal of Physical Sciences. 2(4), 131-137.

Ola-Adams, B. A., Egunjobi J. K., 1992. Effects of spacing on litter fall and nutrient content in stands of Tectona grandis Linn. F. and Terminalia superba Engl. and Diels. Afr. J. Ecol. 30:18–32.

Oliveira, R., Lacerda, L. D., 1993. Producao e compsicao quimica da serapilheira na Floresta da Tijuca (RJ). Revta Brasil Bot. 16, 93–99.

Olomo, J.B., Akinloye, M.K., Balogun, F.A., 1994. Distribution of gamma-emitting radionuclides in soils and water around nuclear researches establishments, Ile-Ife Nigeria. Nucl. Instrum. Meth. Phys. Res. 3(5A), 557- 553.

Oluba, O.M., Eidongbe, G.O., Ogieh, G.C., Idonije, B.O., 2011.Palm and egusi melon oils lower serum and liver lipid profile and improve antioxidant activity in rats fed a high fat diet. Int. J. of Med. and Med. Sci. 3(2), 47-51.

Omaka, N.O., Igidi, J.O., Iyke, F. N, Itumoh, E.J., 2011.The impacts of oil spill and soil factors on trace metals in sediments (soils) of Abakaliki and Afikpo, Nigeria.Journal of Emerging Trends in Engineering and Applied Sciences (JETEAS).2(4): 648-657.

Ong A.S.H., and Goh, S.H. 2002. Palm oil: A healthy and cost- effective diet. Food Nutrition Bulletin 23(1):11-22.

Osibote, O.A., Olomo, J. B., Tchokossa, P., Balogun, F.A., 1999. Radioactivity in milk consumed in Nigeria ten years after the Chernobyl reactor accident. Nuclear Instruments and Methods of Physics Research, 422, (3), 778-783.

Pais, I., Jones, J. B., Jr. 1997. The handbook of trace elements. Boca Raton, Fl, St. Lucie.

Paivoke, A.E.A., Simola, L.K. (2001) Arsenate toxicity toPisum sativum: Mineral nutrients, chlorophyll content, and phytase activity. Ecotoxicol Environ. Safety (Environ Res.

Pehlivan, E., Arsian, G., Gode, F., Altun, T., Ozcan, M.M., 2008. Determination of some inorganic metals in edible vegetable oils by inductively coupled plasma atomic emission spectroscopy. Grasas Y Aceites, 59(3), 239-244.

Petrucci, R.H., Harwood, W.S., Herring, F.G., 2002. General Chemistry eight, ed., Prentice-Hall, 1025-1026.

Poschenrieder, C., Gunse, B., Corrales, I., Barcelo, J., 2008. A glance into aluminum toxicity and resistance in plants: A review. Sci Total Environ. 1(3), 356-358.

Przylibski, T.A., Zebrowski, A., 1999. Origin of radon in medicinal waters of Ladek Zdrof. Journal of Environmental Radioactivity. 46(1), 21-129.

Punshon, T., Jackson, B.P., Lanzirotti, A., Hopkins, W.A., Bertsch, P.M., Burger, J., 2004. Application of synchrotron X-ray microbeam spectroscopy to the determination of metal distribution and speciation in biological tissues. Spectroscopy Letters. 38, 343-363.

Rabinowitz, M.B., Bellinger, D.C., 1993. Soil lead blood lead relationship among Boston children. Bull. Environ. Contam. Toxicol. Springer-Verlag New York.

Ramirez-Andreotta, M., Brusseau, M.L., Artiola, J.F., Maier, R.M., 2013.A green house and field based study to determine the accumulation of arsenic in common home grown vegetables grown in mining affected soils. Science of the total environment. 443, 299-306.

Rankine, I., Fairhurst, T.H., 1999.Management of phosphorus, potassium and magnesium in oil palm. Better Crops International.13(1), 3-15.

Raskin, I., Ensley, B.D., 2000. Phytoremediation of toxic metals: using plants to clean- up the environment. New York. John Wiley & Sons, Inc. 3-12.

Reeves, J.B. and Welhrauch, J.L. (1979). Composition of Foods, Fats ansd Oil.Consumer and Foods Economic Institute: Food and Agricultural Organization.

Regina, M., Wetrington B.D., Vana stru, F.F., 1999. Litter and nutrient content in two Brazilian tropical Forest. Revta Brasil. Bot. 22, 6-8.

Rice, A.L., Burns, J.B., 2012. Moving from efficiency to effectiveness: red palm oils role in preserving vitamin A deficiency. J. Am. Coll. Nutr.29(30, 1-13.

Riyad, A.F., Doug, G., Hana, A.A., 2012. The accumulation of uranium in wild plant *Lagonychium farctum* in Ninevah. Paper presented at the first winter summit at the University of Ataturk, Turkey.

Russal, M.B., 1957. Physical properties in soil. US Agricultural Year Book, Washington DC. 31-38.

Saris, N.E., Mervaala, E., Karppanen, H., Khawaja, J.A., Lewenstam, A. (2000). Magnesium: an update on physiological, clinical and analytical aspects. Clin Chim Acta. 294,1-26.

Sarmani, S., Abdullahi, P.M., Pauzi, B., Baba, I., Majid, A.A., 1992 Inventory of heavy metals and organic pollutants in an urban water ccatchment drainage basin. Hydrobiologia. 235-236(1), 669-674.

Schiller, A.M., Boyle, E.A., 1987. Variability of dissolved trace metals in the Missisipi river. Geochim. Cosmochim. Acta. 51,3273–3277.

Schwarz, K., 1972. Elements newly identified as essential for animals, International Atomic Energy, fifth ed. Vienna.

Seidal, J.C., Corwin, C.J. Total chromium and hexavalent chromium occurrence analysis. Wat. Res. Found. USEPA. Denver.

Sendil, O., Mohammed, N., Somer, G., 2011. Simultaneous determination of Cr(III) and Cr((VI) using differential pulse polarography and application to Gerede River. Turk. J. Chem. 36(2012), 335-346.

Shah, A., Niaz, A., Ullah, N., Rahman, A., Aklaq, M., Khan, M., 2013. Comparative study of heavy metals in soil and selected medicinal plants. Journal of Chemistry. 2013(2013). 1-5.

Shanker, A.K., Cewantes, C., Herminia, T.L., Avudainayagam, S., 2005. Chromium toxicity in plants: A review. Env. Int. 31, 739-753.

Shazia, Q., Mohammad, Z. H., Taibur, R., Hossain U.S., 2012. Correlation of oxidative stress with serum trace element levels and antioxidant enzyme status in Beta Thalassemia: A Review.Anemia, 2012, 1-7.

Sheil, D., 2009. The impacts and opportunities of oil palm in Southeast Asia. CIFOR, Occasional Paper, 51.

Shils, M.E., Olson, J.A., Shike, M. 1994. Modern nutrition in health and disease. Lea and Febiger, Malvern.

Singh, B.P., Pandit, B., Rau, S.P., Bhardway, V.N., Kumar, R., 2008. Trace element analysis of uranium in some leaf samples of Dumka region, Jharkhand state using fission track technique. Radiation Measurement, 43, 512-514.

Souza, A.R., Braya, E.S., Bertotti, M., Braz, J., 2012. Onsite stripping voltammetric determination of Zn(II), Cd(II), and Pb(II) in water samples of the Cananeia-Iguape Estuarine-Lagoon complex in SaoPaulo state, Brazil. J. Braz. Chem. Soc. 23(7),1320-1326.

Staudinger, K.C., Roth V.S., 1998. Occupational lead poisoning. Am Fam Physician. 57 (4), 719–726.

Strouble Jr. W.B., Jelinek, C.F., Baratta, E.J., 1985. Health Physics. 49, 731.

Sue-Jean H., Shieh-Jen J., 2001. Determination of Zn, Cd and Pb in vegetable oil by electro thermal vaporization inductively coupled plasma mass spectrometry. Journal of Analytical Atomic Spectroscopy. 16, 664-668.

Sun J., Yang, L., Zhang, D., Fang, J., Sun N, H., 1999. Determination of zinc in vegetable oils by FAAS with trace injectiom method. Guang Pu Xue Yu Guang Pu FenXi. 19(3)404-405.

Surasak, M., 2011.Trace metals in edible oils by graphite furnace atomic absorption spectrometry. Atomic Absorption.Perkin Helmer. USA.

Szabo, Z., dePaul, V.T., 1998. Radium-226 and Radium-228 in shallow ground water, southern New Jersey. U.S. Geological Survey Fact Sheet FS-062-98.

Tenniseen, A.C., 1994. Nature of earth materials. Prentice Hall, NJ, 333-334.

Tiahou, G., 2004. Lack of oxidative stress in a selenium deficient area in Ivory Coast: potential nutritional antioxidant role of crude palm oil. European J. of Nut. 43 (6), 367-74.

Toepfer, E. W., Mertz, W., Roginski, E. E., Polansky, M. M., 1973.Chromium in foods in relation to biological activity. J. Agric.Food Chem. 1973, 21, 69-73.

Tracy B.L., Pranti, F.A., Quinn, J.M., 1983.Transfer of $^{226}Ra$, $^{210}Pb$, and Uranium from soil to garden; producer assessment risk, Health Physics. 44(5), 469-471.

Tyburska, A., Jankowski, K., Ramsza, A., Roeszka, E., Strzekc, M., Andrzejczuk, A., 2010. Feasibility study of the determination of selenium, antimony and arsenic in drinking water and mineral water by ICP-OES using dual-flow ultrasonic nebulizer and direct hydride generation. J. Anal. At. Spectrom. 25, 210-214.

Tzortzis, M., Svoukis, E., Tsertos, H., 2004. A comprehensive study of natural gamma radioactivity levels and associated dose rates from surface soils jn Cyprus. Protection Dosimetry. 109, 217-224.

UNEP, 2011. Environmental assessment of Ogoni land. Background to Environmental Degradation in Ogoni land. UNEP.

UNSCEAR, United Nations Scientific Committee on the Effects of Atomic Radiations, 1988. Sources, Effects and Risk of Ionizing Radiations, United Nations, New York.

USEPA, 2007. Treatment technologies for site cleanup: annual status report, twelfth ed. Washington, DC, USA.

Usoro, E.J., 1974. The Nigerian Oil Palm Industry, first ed. Ibadan University Press.

Uwumarongie-Ilori, E.G., Sulaiman-Ilobu, B.B., Ederion, O., Imogie, A., Imoisi, B.O., Garuba, N., Ugbah, M., 2012. Vegetative growth performance of oil palm (Elaeis guineensis) seedlings in response to inorganic and organic fertilizers. Greener J. of Agric. Sc.2 (2), 26-30.

Uwumarongie-Ilori, E.G., Aisueni, N.O., Sulaiman-Ilobu, B.B., Ekhator, F., Eneje, R.C., Efetie, Ose, A., 2012. Immobilization Effect of Cow dung on Lead and Chromium in soil cultivated with Oil palm. Bulletin of Enviroment, Pharmacology and Life sciences. 1(9), 74-80.

Uza, G., Pavel, O., Uza, D., Valaicu, R.,1987. Hypomagnesemia in patients with essential arterial hypertension, Magnesium Bulletin, 9, 177–180.

Vincetti, M., Wei, E.T., Malogolic, C., Bergoni, M., Vivoli, G., 2001.Adverse health effects of selenium in humans. Rev. Environ. Health, 16(4), 233-251.

Waalkes, M.P., 2000. Cadmium carcinogenesis. J. of Inorg. Biochem .19(1), 241-244.

Wallschlager, D., Roehi, R., 2001. Determination of inorganic selenium speciation in waters by ion chromatography-inductively coupled plasma mass spectrometry using eluant elimination with a membrane suppressor. Journal of Analytical Atomic Spectrometry.16(1), 922-925.

Wals, G.D., Das, H.A., Van der Sloot, H.A., 1980. The determination of inorganic arsenic in water by thermal neutron activation analysis. Journal of Radioanalytical Chemistry. 57(1), 215-222.

Warmate, A.G., Ideriah, T.J.K., Tamunobereton, A.R.I., Udonam Inyang, U.E., Ibaraye, T. 2011. Concentrations of heavy metals in soil and water receiving used engine oil in Port Harcourt, Nigeria. Journal of Ecology and the National Enviroment. 3(2), 54-57.

WHO, 2003. Guidelines for drinking water quality, third ed. Geneva.

Wiler, R.L. 1965. Heavy metals in the environment, second ed. 12, 58-60.

Wool son, E.A., Axley, J.H., Kearney P.C., 1971. The chemistry and phytotoxicity of arsenic in soils; contaminated field soils. Soil Sci. Soc. Am. Proc. 35(6), 938–943.

Xiuxia, L., Xinchen, Q., Zhongsheng, S., 1987.The distribution and background values of trace elements in Jingpo lake water. Nuclear Techniques. 7-9.

Xu, J., Yang, F., Chen, L., Hu, Y., Hu, Q., 2003. Effect of selenium on increasing the antioxidant activity of tea leaves harvested during the early spring tea producing season. Agric. Food Chem. 15(4), 1081-1084.

Yeboua, K., Ballo, K., 2000. Soil chemistry characteristics in an oil palm plantation. Cashiers Agric. 9, 73-76.

Yilmaz, S., Yagmur, S., Saglikoglu, G., Saglikoglu, M., 2009. Direct determination of Zn heavy metal in tap water of Canakkale (Turkey) by anodic stripping voltammetry technique. Int. J. Electrochem Sci. 4(1), 288-294.

Zaini, H., Siti A. A.R., Ahmad S., Siti S.A., Zaharuddin A., 2010. Measurement of $^{226}$Ra in river water using liquid scintillation counting technique. J. of Nuc. and Related Techno. 7, 12-23.

Zaini, H., Siti, A.A.R., Ahmad, S., 2011. Measurement of $^{226}$Ra, $^{228}$Ra and $^{40}$K in soil in district of Kuala Krai using gamma spectrometry. The Malaysian J. of Ana. Sci. 15(2), 159-166.

Zhang, P.G., 1999. Determination of copper in wastewater by beta-convection new spectrophotometry. PubMed. 19(3), 471-473.

# CHAPTER FOUR

## Determination of trace and major elements in water on oil palm plantations by Inductively Coupled Plasma - Optical Emission Spectrometry

**Olafisoye O. Bola[1,4], Fatoki O. Olalekan[1], Oguntibeju O. Oluwafemi[2], Osibote O. Adelaja[3]**

*[1]Faculty of Applied Sciences, Department of Chemistry, Cape Peninsula University of Technology, Cape Town, South Africa*

*[2]Faculty of Health and Wellness Sciences, Department of Biomedical Sciences, Cape Peninsula University of Technology, Bellville, South Africa*

*[3]Faculty of Applied Sciences, Department of Mathematics and Physics, Cape Peninsula University of Technology, Cape Town, South Africa*

*[4]Faculty of Science, Department of Chemistry, Bowen University Iwo, Osun State, Nigeria.*

To whom correspondence is to be made: Osibote O. Adelaja; Faculty of Applied Sciences; Department of Mathematics and Physics; Cape Peninsula University of Technology; Cape Town; South Africa; Email: OsiboteA@cput.ac.za.; Phone number; +27842997415.

***Olafisoye O. Bola, Fatoki O. Olalekan, Oguntibeju O. Oluwafemi, Osibote O. Adelaja, 2014. Determination of Trace and Major Elements in Water on Oil Palm Plantations by Inductively Coupled Plasma Optical Emission Spectrometry, Instrumentation Science and Technology, 42(6), pp. 652.***

## Abstract

The oil palm tree is an economic crop that has gained worldwide recognition due to its importance. Produce from the tree such as the stem, fruits and leaves contain phytonutrients and antioxidants that are mediators of cellular functions and a cure for various ailments. The oil palm plantations receive inputs of elements from natural and anthropogenic sources. However, while some of the elements are beneficial, they can be toxic at high concentrations. The uptake of elements may be from water on the oil palm plantation. Trace and major element contamination has become an issue of concern due the deleterious effect of their nature. Therefore, the quality of ground water on oil palm plantations is important due to the uptake of

trace and major elements from water to parts of the oil palm tree. In the study, an attempt was made to quantify the concentration of 15 elements in ground water samples sampled on 15 oil palm plantations in the southern parts of Nigeria where the oil palm tree is extensively cultivated. Sampling was performed in March 2013. The Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) is an analytical instrument of choice because of the relatively cheapness and ability to measure elements in a wide range of spectrum. Apart from the major element concentration, the highest concentrations of trace elements were recorded for Lead (Pb) (0.090-10.29 mg/L) and the lowest for Cadmium (Cd) (0.119-0.391 mg/L) on all the plantations. The concentration of the metals found in the study was compared with the water quality standard set the World Health Organization (WHO), 2011.

*Key words: ICP-OES, Oil palm plantations, trace and major elements, water*

## 4.1 Introduction

Oil palm plantation is recognized in most countries for the extent of socio-economic influence. It has experienced rapid growth in recent decades and has become a significant contributor to the world market for vegetable oils. The main composition of palm oil and palm kernel oil, which are palmitin and olein, are major components of domestic and industrial products. Analysis on phytochemical screening of the palm oil leave extract, lipids and sterol composition of the pollen have been studied to contain diuretic, antioxidant, antimicrobial and anticancer properties. The sap from the tree is used as wine, sugar, and parts of the plants such as the palm oil, palm kernel oil, bark and leaves are used as traditional/folklore medicinal uses in some parts of Africa. Red palm oil contains phytonutrients, tocotrienols, carotenoids, phytosterols, squalene, tocopherols etc. Numerous researchers have proved these as powerful protections against diseases of the cardiovascular and neurological systems [1-4]. Although palm oil is high in saturated fat, it protects against heart diseases. Tocotrienol is an antioxidant that prevents oxidative stress by free radicals in the body. It slows the occurrences of some forms of cancer. Oxidative stress has been the cause of several diseases and ageing. Apart from antioxidants such as tocotrienols, tocopherols and flavonoids, other phytomolecules such as Copper (Cu), Iron (Fe), Manganese (Mn), Zinc (Zn), and Selenium (Se) possess antioxidant properties. These elements occur mostly in proteins in the form of metalloenzymes and are excellent antioxidant defense against reactive oxygen species that causes oxidative stress [5]. Much research is channeled in the area of the benefits of the oil palm tree in the prevention of health problems. These problems include such as osteoporosis, asthma, cataract, muscular degeneration, arthritis, liver disease, tuberculosis and even HIV/AIDS [6][3]. The management of the oil palm plantations has brought about land and water contamination due to diverse agronomy practices. The eco-toxicological contamination of heavy metals in the

environment is a great challenge to scientists all over the globe. Heavy metals are persistent in the environment, non-biodegradable and accumulate in the eco-system. Anthropogenic activities such as pesticide applications, industrialization, urbanization, crude oil exploration are immense contributors to heavy metal contamination in the environment [7-11]. Some metals are essential for the proper functioning of biological systems yet are toxic at high concentrations. Plants and animals for the proper functioning of the organs and systems also need trace elements; Cobalt (Co), Nickel (Ni) and Manganese (Mn) and major elements; Calcium (Ca), Potassium (K), Sodium (Na) and Magnesium (Mg). Other elements; Lead (Pb), Cadmium (Cd) and Arsenic (As) have no beneficial function to plants and are toxic to all forms of life above critical levels. There is actually no clear-cut boundary between the benefits and toxicity for trace elements. Toxic element contaminated ground and surface water can transmit heavy metals through crops to humans. This is hazardous since heavy metals are not metabolized by the body system causing bioaccumulation in organs such as the liver and kidneys. It is therefore pertinent to evaluate the quality of ground water on palm oil plantations by analyzing the metal concentration level. There is an increasing demand for metal analysis of environmental samples. The cost of analysis is high when different instrumental methods are suited for different analytes in a sample. The greatest challenge in creating one method for all analytes is achieving the dynamic range. This dynamic range coverage is for low parts-per-billion for toxic elements to high parts-per-million for the Group I and II elements. A general method for different analytes and sample is recommended. The (ICP-OES) with simultaneous measurement of the entire elemental spectrum facilitates such universal methods and was used for the study [12]. The ICP-OES has an advantage of being a multi-element technique that allows the determination of minor, major and trace elements in liquid samples. It offers the ideal solution in proficiency and flexibility and a cost effective solution to analysis. It is a desired technique because of its high sensitivity, wide dynamic linear range and sensitivity. The instrumentation of ICP-OES consists of a sample introduction system, plasma source and the spectrometer. The dual view ICP-OES consists of an interface for either axial or radial plasma observation. This allows the plasma to be directed to suit the linear range of the analysis [12]. The analyst is permitted to switch plasma views without instrument reassembly. The more recent Charge Couple Device (CCD) optics system has replaced the photomultiplier detector and the diffraction grating. The CCD is capable of observing all analyte wavelengths simultaneously [12]. Samples are introduced in liquid form by the use of a nebulizer in most analytical methods using the ICP-OES. The close vessel microwave assisted digestion was used for this study, which is preferred over the open vessel. This is because the closed vessel microwave assisted digestion incorporates the advantage of low reagent volume, short digestion time, low loss of volatile species and the reduced risk of cross contamination. It also

provides high precision and safety. Plants absorb dissolved minerals, elements present in surface, and ground water through the root cell hairs and this is transported through osmosis. The transportation of dissolved minerals and elements continues via the xylem and phloem vessels to other parts of the plants such as the stem, leaves and fruits. Consequently, trace and major elements are absorbed from water to plants via roots to the stem, leaves and fruits. Based on the significance of the oil palm tree, as an economic crop for food and chemical industry; a source of phytonutrients and antioxidants, the effect of the uptake of trace and major elements from surface and ground water was determined. The present research presents findings obtained by the development of the method for major and trace elements in water on oil palm plantation by ICP-OES. The microwave assisted close vessel digestion was employed using a mixture of acids.

## 4.2 Materials and methods

### 4.2.1 Instrumentation

The Spectro Arcos FHS 12 ICP-OES (Spectro Germany) equipped with radial viewed plasma was used for the research. The Radial Slide Plasma Interface (SPI) was used with the Spectro UV plus system for measurements in the UV range, which records the entire relevant spectrum (165-770 nm). The Spectro Arcos FHS 12 ICP-OES is equipped with a CCD solid-state array detector and smart analyser vision graphical user interface 4.02.0834 software. The CCD detector shows a significant advantage over the conventional technology with respect to speed, sensitivity, and lower instrument cost. Argon is continuously circulated through a small membrane pump that has the advantage over systems that use vacuum or purge gas. The radial view was used to accommodate high matrix content for major elements. An ultrasonic nebulizer with a cyclonic spray chamber was used in the sample introduction system. The instrumental parameters for the determinations of elements using the radially viewed ICP-OES are presented in Table 4.1. Sample digestion was carried using the Milestone microwave digester MLS 1200 equipped with six Teflon vessels and a ceramic jacket.

### 4.2.2 Sampling sites and sample collection

In Nigeria, oil palm cultivation is part of way of life – in fact part of culture. Areas in the Southern part of Nigeria where oil palm is greatly cultivated include the states of Edo, Enugu, Delta, Akwa Ibom, Ondo, Ekiti, Kogi, Oyo, Osun, Ogun and Lagos [13]. Table 4.2 shows the sampling sites codes, locations and the respective latitude and longitude. Water sampling was performed on fifteen major sites from areas in Nigeria. Sampling was performed in the dry season of October 2012 to April of 2013.

**Table 4.1: Parameters for ICP-OES**

| | |
|---|---|
| Power (W) | 1400W |
| Nebulizer | Cross flow (Spectro) |
| Spray Chamber | Double pass, Scott-type |
| Outer gas flow (l/min) | 12 |
| Intermediate gas flow (l/min) | 1.0 |
| Nebulizer gas flow (l/min) | 1.0 |
| Sample uptake rate (l/min) | 1.5 |
| Analytical wavelength (nm) | |
| Al (II) = 167.078 | Mg (I) = 285.213 |
| Ca (II) = 393.366 | Na (I) = 588.995 |
| Cd (I) = 228.802 | P (I) = 177.495 |
| Co (II) =230.786 | Pb (II) = 283.306 |
| Cr (II) = 205.618 | Se (I) = 196.026 |
| Cu (I) = 324.754. | Sn (II) = 189.980 |
| Fe (II) = 259.941 | Zn (II) = 213.856 |
| K (I) = 766.491 | |

*I = atomic line; II = ionic line*

Wavelengths were chosen in order of emission intensity and the most sensitive wavelength, after consideration of the upper and lower concentration limit of linearity of response was chosen. The sampling points were partitioned into four points in each state and samples were collected from boreholes at each point. The sampling locations were based on factors such as population density, farm settlements, and areas receiving significant pollution characteristics. Storage containers for sampling were sterilized 1-liter plastic containers. The samples were acidified with 10 % nitric acid per liter of sample and further preserved in an ice chest. The samples were transferred to the laboratory and stored in the refrigerator at 4˚C prior to analysis. Glassware were washed with detergent and rinsed with distilled water. They were further soaked overnight in 10 % analytical grade nitric acid, and then rinsed in high purity deionized water.

### 4.2.3 Reagents and samples

The solutions used for the analysis were prepared from analytical grade reagents using high purity deionized water (Milli-Q water purification system, Millipore, Belford, MA, USA). Analytical grade nitric acid (65% v/v) from Merck, Darmstadt, Germany and hydrochloric acid (37 v/v %) also from Merck, Darmstadt, Germany were used for the acid digestion.

### 4.2.4 Reference materials for standard calibration curves

Reference materials for standard calibration curves used for the analysis were prepared from single element standards (1000 mg/L).

**Table 4.2: Sampling sites & locations**

| Code | Location | Latitude | Longitude |
|---|---|---|---|
| **PP1** | Abak | 4.9833 | 7.7833 |
| **PP2** | Acharu | 7.5320 | 7.2792 |
| **PP3** | Agbarho | 5.5833 | 5.8667 |
| **PP4** | Ago-Emokpae | 7.3400 | 6.4500 |
| **PP5** | Apoje | 6.9644 | 4.1064 |
| **PP6** | Badagry | 6.4166 | 2.8833 |
| **PP7** | Benin city | 6.3176 | 5.6145 |
| **PP8** | Igede-Ekiti | 7.6667 | 5.1321 |
| **PP9** | Ikire | 7.3533 | 4.1833 |
| **PP10** | Iresa-apa | 8.1504 | 4.2567 |
| **PP11** | Nsukka | 6.8667 | 7.3833 |
| **PP12** | Okitipupa | 6.5025 | 4.7795 |
| **PP13** | Onishere | 6.7150 | 5.1001 |
| **PP14** | Ubiaja | 6.6597 | 6.3822 |
| **PP15** | Umuabi | 6.17 36 | 7.2233 |

The starting materials for the trace elements were measured against a certified reference material are and are traceable to NIST. Lower concentrations were prepared in the same matrix using the non-serial dilution method.

### 4.2.5 Microwave assisted digestion

The water samples may contain analytes that are organically bound in the matrix since it was sampled from an oil palm plantation. It was necessary to digest the samples using the microwave assisted digestion method in order to convert the organically bound analytes to the elemental form. The sample (10 mL) was placed in the Teflon tube of the microwave digester. Nitric acid (1 mL) and hydrochloric acid (3 mL) were added according to the aqua regia method. The contents in the Teflon tubes after microwave-assisted digestion were filtered using a 0.45 µm filter paper then transferred into a 100 mL volumetric flask. This was made up to 100 mL with ultra-pure water (Millipore distilled water 18.2 µm). 10 mL of the extract volume was put in 15 mL polypropylene tubes and stored at 4 ˚C for ICP-OES instrumental analysis. Digestion was performed using the Milestone Microwave 1200 Mega Microwave Oven according to the microwave assisted digestion program in Table 4.3. The time of increment of the microwave assisted digestion was geometrical.

### 4.2.6 Temperature, electrical conductivity, total dissolved solids and pH

Temperature, electrical conductivity, total dissolved solids and pH of the samples were determined on the site of sampling using a Multi meter meant for that purpose. The results are shown in Table 4.4

**Table 4.3: Microwave assisted digestion programme**

| Steps | Power (Watts) | Pressure (Bar) | Temperature ( ˚C) | Time (Mins) |
|---|---|---|---|---|
| **1** | 200 | 100 | 90 | 2 |
| **2** | 400 | 100 | 90 | 4 |
| **3** | 600 | 100 | 180 | 16 |
| **4** | 600 | 100 | 180 | 32 |

### 4.2.7 Validation of the analytical method:

Calibration curves were plotted for the determination of trace and major elements in the water samples using varying concentrations of standards of the metals. Table 4.5 represent the regression calibration plots of the major and trace elements under study. The linear calibration curves obtained for all the metals under study ranged from 0.995 to 1.000 mg/L. The repeatability or precision of the method was established with an evaluation of the percentage residual standard deviation of the sample microwave assisted digestion procedure. Digested samples were analyzed in triplicates and the analyzed mean, standard deviation and percentage residual standard deviation calculated from this data. The acceptable criterion for

repeatability and percentage residual standard deviation results is to be below 10 for elements determined by ICP-OES.

### 4.3 Results and discussion

Table 4.6 presents the concentration (mg/L) of trace and major elements in ground water sampled from fifteen sampling locations. The analysis of the sample was compared with regulatory standards such as the WHO guidelines for drinking water quality, 2011 and the significant deviations were equally noted. The results in Table 4.6 shows that the pH, electrical conductivity and total dissolved solid values were an indication of trace/major element contamination. Major elements recorded higher concentration. From the values of the trace element investigated on the plantations, Pb (0.09-10.3 mg/L) was the most predominant trace element and Cd (0.12-0.39 mg/L) the least on all the plantations under study.

#### 4.3.1 Lead (Pb)

Pb is a soft metal that has several applications in industry. The study revealed that the concentration of Pb metal ranged from 0.09 mg/L to 10.3 mg/L in ground water samples as recorded in Table 4.6. All the ground water samples under investigation contained Pb above the World Health Organization (WHO) permissible limit (0.01 mg/L) for Pb [14]. Highest and lowest concentration values of Pb recorded in this study were from PP10 (Iresa –apa) and PP12 (Okitipupa) plantations respectively. Okitipupa is a local government area in Ondo state which contains bitumen deposits. Bitumen contains Pb in varying proportions. River Oluwa is one of the rivers that flow through the plantation and this is located around a glass making factory and bitumen mining. These factors may contribute to high Pb concentration on these plantations. PP4 and PP9 plantations also recorded high concentration of this metal. These plantations where located near mechanic workshops where Pb acid batteries were recycled. In general, all the plantations recorded concentrations above the WHO permissible limit of Pb probably because the automobiles and machineries on the plantations were run on leaded petrol/diesel.

**Table 4.4: Physicochemical parameters of water**

| | | | Ground water | | |
|---|---|---|---|---|---|
| **Code** | **Location** | **Ph** | **Electrical conductivity (µS/cm)** | **TDS (ppm)** | **Temp (˚C)** |
| PP1 | Abak | 5.29 | 105 | 51 | 18.4 |
| PP2 | Acharu | 5.59 | 134 | 63 | 17.9 |
| PP3 | Agbarho | 5.01 | 23 | 11 | 18.4 |
| PP4 | Ago-Emokpae | 5.53 | 190 | 97 | 19.3 |
| PP5 | Apoje | 6.30 | 104 | 52 | 18.0 |
| PP6 | Badagry | 5.54 | 229 | 113 | 19.7 |
| PP7 | Benin city | 7.28 | 30 | 15 | 16.9 |
| PP8 | Igede-Ekiti | 5.59 | 137 | 68 | 18.2 |

| | | | | | |
|---|---|---|---|---|---|
| PP9 | Apomu-Ikire | 5.58 | 122 | 63 | 17.1 |
| PP10 | Iresa-apa | 4.89 | 225 | 113 | 19.3 |
| PP11 | Nsukka | 7.21 | 171 | 88 | 17.3 |
| PP12 | Okitipupa | 5.86 | 111 | 55 | 15.8 |
| PP13 | Onishere | 5.02 | 22 | 11 | 19.3 |
| PP14 | Ubiaja | 5.40 | 216 | 112 | 16.9 |
| PP15 | Umuabi | 6.28 | 19 | 09 | 19.0 |
| PPI6 | Control | 5.51 | 227 | 107 | 18.77 |

Due to awareness on the detrimental effect of Pb in recent years, its concentration in the environment has reduced. Increased exposure to Pb and its compounds have been studied to cause disorders of the blood and nervous system, infertility and miscarriages. A major pathway of environmental Pb contamination is from water and food [15-18].

### 4.3.2 Cadmium (Cd) and Zinc (Zn)

Naturally, Cd can be found in the earth crust and is released to rivers by the weathering of rocks, volcanoes and bush fires [19]. Cd is usually found in deposits where Zn is a major pollutant. All the ground water samples under investigation contained Cd and Zn above the WHO permissible limit (0.005 mg/L and 5.0 mg/L for Cd and Zn respectively) [14]. Table 4.6 recorded highest and lowest concentration values of 0.391 and 0.255 mg/L of Cd in this study were from PP6 (Badagry) and PP9 (Ikire) plantations respectively. Zn is an essential element required in minute concentrations by plants and animals for cell metabolism, cell development and enzyme activity. High concentrations can be lethal causing nervous disorders, kidney damage, [20] diarrhea and lethargy [21-22]. The highest and lowest concentrations of Zn recorded in the study were from PP6 (6.79 mg/L) and PP14 (0.06 mg/L/) respectively. Cd is a major byproduct of the paint and glass industry. It has a very low permissible limit and traces of Cd in the environment can lead to overexposure. Cd is a byproduct of industry, especially as a pigment in the paint industry and components of electronic waste. The concentration of Cd exceeded the Maximum Permissible Limit in all the plantations investigated. This can probably be because of unwholesome farm practices such as the use of Cd containing fertilizers and insecticides. Other unwholesome practices included the burning of bushes and forest fires. PP6 (Badagry) recorded the highest concentration of Cd. This sampling area received pollution characteristics from Alaba International Market, Lagos, Nigeria. The market is notorious for the sale of used electronics [23].

**Table 4.5: Regression data for calibration curve**

| Element | Wavelength (nm) | Linear range (mg/L) | $R^2$ | RSD (%) | LOD | LOQ |
|---|---|---|---|---|---|---|
| **Al (II)** | 167.078 | 0.1 | 0.999 | 0.844 | 0.096 | 0.96 |
| **Ca (II)** | 393.366 | 0.01 | 0.995 | 0.634 | 0.024 | 0.24 |
| **Cd (I)** | 228.802 | 0.03 | 0.999 | 0.989 | 0.057 | 0.57 |
| **Co (II)** | 230.786 | 0.02 | 0.999 | 0.594 | 0.006 | 0.06 |
| **Cr (II)** | 205.618 | 0.01 | 0.998 | 1.075 | 0.003 | 0.03 |
| **Cu (I)** | 324.754 | 0.01 | 0.999 | 0.845 | 0.033 | 0.33 |
| **Fe (II)** | 259.941 | 0.03 | 0.999 | 0.980 | 0.333 | 3.33 |
| **K (I)** | 766.491 | 0.002 | 1 | 0.429 | 0.021 | 0.21 |
| **Mg (I)** | 285.213 | 0.001 | 0.999 | 0.899 | 0.084 | 0.84 |
| **Na (I)** | 588.995 | 0.001 | 0.999 | 0.843 | 0.006 | 0.06 |
| **P (I)** | 177.495 | 0.001 | 0.999 | 0.982 | 0.333 | 3.33 |
| **Pb (II)** | 283.306 | 0.05 | 0.999 | 0.360 | 0.045 | 0.45 |
| **Se (I)** | 196.026 | 0.5 | 0.999 | 0.374 | 0.065 | 0.65 |
| **Sn (II)** | 189.980 | 1 | 1 | 0.635 | 0.041 | 0.41 |
| **Zn (II)** | 213.856 | 0.002 | 0.999 | 0.337 | 0.087 | 0.87 |

***RSD (%) n = 3***
***LOD = 3∂***
***LOQ = 10 X LOD***

The Ologe lagoon flows through the plantation has pollution characteristics from electronic waste from the Alaba International market, Ojoo, Lagos state. Electronic waste contains significant concentrations of Cd primarily from Cd batteries, chip resistors and used monitors [24.] Cd is one of the most deleterious toxic trace metals both to plants and to animals. It is designated as a human and a potent multi-tissue animal carcinogen [23]. Cd has the tendency to accumulate in organs such as the liver and kidney causing defects such as osteomalacia, pulmonary emphysema, infer tility and renal tubular damage [25-27].

### 4.3.3 Aluminium (Al)

Environmental contamination of Al in the environment can originate from water and the preparation of food. However, Al is the third most abundant metal in the earth crust, studies on its toxicity has revealed it a cause of many diseases in plants and animals. Al toxicity has been traced to the use of Al utensils and cosmetics containing aluminum [28]. The signs of Al toxicity in plants include the yellowing of leaves. Al has never been considered as an essential element although some plants have shown cases of Al tolerance and resistance [29-31] Plant species with hyperactive accumulation characteristics usually concentrate high levels of Al to levels very toxic to animals [32]. Studies present evidence of lung diseases linked to occupational hazards in employees in Al smelting companies [33-36]. It is a major cause of Alzheimer's disease, neurotoxicity and encephalopathy in humans [17].

**Table 4.6: Concentration of metals (water mg/L)**

| Mg | Na | P | Pb | Se | Sn | Zn |
|---|---|---|---|---|---|---|
| 121±0.01 | 234±0.02 | 32.9±0.01 | 1.13±0.04 | 0.05±0.01 | 0.73±0.05 | 5.06±0.01 |
| 78.5±0.06 | 218±0.01 | 21.9±0.04 | 1.36±0.15 | 0.01±0.01 | 0.36±0.01 | 4.07±0.02 |
| 98.2±0.03 | 130. ±0.02 | 12.2±0.07 | 1.43±0.38 | 0.06±0.03 | 0.82±0.07 | 4.93±0.01 |
| 113±0.07 | 57.0±0.02 | 47.8±0.04 | 1.39±0.24 | 0.03±0.01 | 0.04±0.05 | 4.86±0.02 |
| 89.1±0.09 | 87.0±0.06 | 11.1±0.38 | 0.85±0.04 | 0.01±0.04 | 0.08±0.25 | 6.54±0.01 |
| 34.9±0.05 | 87.6±0.44 | 24.0±0.99 | 1.39±0.24 | 0.07±0.02 | 0.03±0.06 | 6.79±0.04 |
| 77.0±0.01 | 132 ±0-07 | 18.1±0.07 | 1.15±0.23 | 0.02±0.001 | 0.02±0.51 | 4.94±0.02 |
| 115. ±0.08 | 81.3±0.08 | 25.6±0.99 | 0.78±0.23 | <0.01 | 0.25±0.69 | 5.35±0.25 |
| 89.1±0.02 | 275±0.48 | 65.4±0.11 | 5.29±0.01 | 0.03±0.002 | <02.4 | 3.10±0.29 |
| 91.0±0.06 | 139±0.82 | 22.9±0.44 | 10.3±0.21 | 0.02±0.001 | 0.43±0.01 | 3.49±0.24 |
| 85.3±0.43 | 123±0.02 | 33.5±0.04 | 0.17±0.05 | 0.05±0.002 | 0.16±0.08 | 6.09±0.09 |
| 158±0.09 | 32.0±0.32 | 59.0±0.11 | <0.09 | <0.04 | 0.23±0.04 | 6.22±0.68 |
| 119±0.02 | 88.0±0.54 | 18.1±0.88 | 0.27±0.21 | 0.03±0.001 | 1.43±0.40 | 2.36±0.03 |
| 57.0±0.36 | 72.2±0.33 | 45.0±0.63 | 0. 30±0.11 | 0.01±0.012 | 0.63±0.01 | <0.06 |
| 63.1±0.01 | 56.1±0.09 | 29.9±0.55 | 10.1±0.12 | <0.21 | 0.05±0.09 | 4.84±0.36 |
| 18.7±0.62 | 37.8±0.01 | 16.8±0.76 | 0.13±0.14 | <0.03 | 0.02±0.01 | 1.33±0.64 |

| | Al | Ca | Cd | Co | Cr | Cu | Fe | K |
|---|---|---|---|---|---|---|---|---|
| PP1 | 0.12±0.02 | 5.91±0. 03 | 0.26±0. 01 | 0.61±0. 03 | 0.97±0.01 | 1.01±0. 01 | 0.63±0. 02 | 12.9±0.01 |
| PP2 | 0.09±0. 01 | 6.67±0. 02 | <0.26 | 0.32±0.09 | 0.96±0.03 | 0.99±0.02 | 0.81±0. 01 | 8.75±0.02 |
| PP3 | 0.09±0. 03 | 10.1±0. 04 | 0.26±0. 01 | 0.31±0. 04 | 0.98±0.02 | 1.31±0.09 | 0.09±0. 01 | 9.13±0.04 |
| PP4 | 0.12±0. 01 | 8.94±0. 04 | 0.26±0. 02 | 0.30±0.02 | 0.95±0.05 | 0.10±0.01 | 0.02±0. 02 | 4.39±0.35 |
| PP5 | <0.070 | 4.69±0. 02 | 0.33±0.03 | 0.31±0. 01 | 0.90±0.01 | 0.12±0.01 | 0.05±0. 11 | 2.86±0.03 |
| PP6 | 0.08±0. 01 | 6.90±0. 03 | 0.39±0. 02 | 0.31±0. 06 | <0.94 | 0.12±0.01 | 0.17±0. 14 | 4.45±0. 04 |
| PP7 | 0. 05±0. 01 | 8.01±0. 01 | 0.26±0. 02 | 0.31±0. 05 | 0.94±0.01 | 0.01±0.01 | 0.10±0.04 | 6.46±0. 02 |
| PP8 | 0.49±0. 04 | 3.33±0. 01 | 0.26±0. 01 | 0.31±0. 02 | 0.91±0.06 | <0.13 | 0.01±0. 01 | 3.78±0. 31 |
| PP9 | <0.07 | 12.0±0. 09 | 0.26±0. 03 | 0.435±0.06 | <0.31 | 0.10±0. 01 | 0.03±0. 01 | 6.901±0.66 |
| PP10 | 0.072±0.005 | 8.10±0.01 | 0.27±0. 01 | 0.435±0.06 | 0.02±0.02 | 1.24±0. 01 | <0.01 | 2.00±0.12 |
| PP11 | 0.084±0.001 | 3.45±0. 02 | 0.27±0.01 | 0.31±0. 05 | 0.83±0.05 | 1.37±0. 03 | 0.01±0. 01 | 5.03±0.42 |
| PP12 | <0.074 | 5.90±0.02 | 0.27±0.01 | 0.34±0. 03 | 0.86±0.05 | 1.24±0.02 | 0.02±0.02 | 4.89±0.01 |
| PP13 | 0.066±0.005 | 7.51±0.05 | 0.32±0. 03 | 0.13±0. 08 | <0.21 | 0.88±0. 02 | 0.06±0.01 | 3.00±0.02 |
| PP14 | <0.053 | <5.96 | <0.32 | 0.54±0. 01 | <0.02 | 1.01±0.01 | 0.07±0. 02 | 9.12±0.03 |
| PP15 | 0.015±0.001 | <6.90 | 0.32±0. 01 | 0.55 ±0. 01 | 0.26±0.02 | 0.56±0.01 | 0.10±0. 01 | 6.50±0.06 |
| PP16 | 0.003±0.001 | <2.79 | <0.12 | 0.23±0. 02 | 0.05±0.02 | 1.04±0.02 | 1.01±0. 01 | 1.41±0.001 |

Toxicity of Al presents negative effects on the metabolism pathways and enzyme activity of some major elements such as Ca and phosphorus (P). WHO/ MCL of Al in ground water is 0.05 mg/L [14]. Highest and lowest concentration of Al in the study was recorded from PP8 in Igede Ekiti with a concentration of 0.50 mg/L and in PP7 in Benin City with a concentration of 0.01 mg/L as shown in Table 4.6. Only Igede Ekiti recorded highest concentration of Al. This may be attributed to natural deposits of Al in Ekiti state and the establishment of Al smelting company around the vicinity to the plantation. River Osun takes its source from Osogbo and flows through Ilesha to Igede Ekiti plantation with pollution characteristics from the river. The

pollution characteristics include natural deposits of Al and anthropogenic sources from the metal smelting companies from Osogbo and Illesha.

### 4.3.4 Chromium (Cr)

Cr is one of the essential elements needed in trace amounts that prominently takes part in metabolism. It is required in enzyme activity and acts as a cofactor in the regulation of sugar levels in the body. High levels of Cr is toxic especially Cr VI which is known to be more toxic and carcinogenic when compared to Cr III [37]. Symptoms of acute Cr toxicity are related to convulsion, respiratory and stomach disorder symptoms [25]. WHO/ MCL level of Cr in drinking water is 0.1 mg/L [14]. All the plantations under study contained concentrations of Cr above the WHO/ MCL for water that is 0.1 mg/L [14]. as recorded in Table 4.6. Highest and lowest levels were recorded on PP6 (0.95 mg/L) and PP10 (0.02 mg/L) respectively. Cr is a major component of electronic waste. Improper disposal of electronic waste and the illicit disposal of used oils and automobile waste have contributed to the increase in the concentration of Cr metal in most of the plantations. PP6 (Badagry) is situated close to a notorious e- waste disposal and recycling site which may be a contributory factor to the high level of Cr on the plantation.

### 4.3.5 Copper (Cu)

Cu is an essential element possessing antioxidant properties protecting organs in animals and plants against free radicals. It is a component of hemoglobin and alongside vitamin C assist in the proper functioning of the lungs, blood vessels and epidermal tissues. Cu is a component of the enzyme ferroxidase, which regulated the transfer of iron and facilitates the release of carbohydrate from storage. It is a structural element in the enzyme tyrosine, cytochrome oxidase and ascorbic acid oxidase. Deficiency of Cu in humans causes liver malfunction and genetic disorder especially Wilson’s disease. In plants, it is needed for seed and chlorophyll formation. It is an essential part of proteins and various biochemical syntheses of plants [38]. Though Cu is an essential element necessary for proper functioning of organs and systems in the body in minute quantities, high concentrations can be toxic and lethal. Symptoms of Cu toxicity are related to liver and kidney damage. A high and toxic concentration of the essential element causes adverse health effects, which includes nausea and diarrhea. Cu occurs naturally in the environment and is used practically in industries in the manufacture of coins, electrical wiring, and pipes. The random use of Cu pesticides may cause injury to human health and environmental contamination leading to harmful levels of Cu in ground water. Cu can also be found in household and electrical waste and battery cells. Table 4.6 showed that the highest and lowest concentration of Cu in the study was recorded from PP11 (Nsukka, 1.37 mg/L) and PP7 (Benin City, 0.01 mg/L) respectively. All the ground water samples under investigation

contained Cu above the WHO permissible limit (0.01 mg/L) for Cu [14]. These plantations recorded mechanic workshops close to the plantation where waste and electrical/mechanical parts were deposited.

### 4.3.6 Cobalt (Co)

Co is an essential element required in minute quantities for proper functioning of the systems. It occurs naturally in the environment in seawater, volcanic eruptions and forest fires. Anthropogenic sources are from coal fires, burning of oil and industrial processes. Workers in industry may be exposed to Co when grinding, smelting and refining tools. Some forms of Co are also radioactive. It is an ingredient of porcelain enamel and a pigment in most paints. It is a component of vitamin B12 used in the treatment of anemia and various blood disorders. Exposure of the essential element in high concentrations is toxic and may cause infections related to lung disorders such as anemia, pneumonia and asthma. The World Health Organization (WHO) permissible limit (0.60 mg/L) for Co [14] and PP1 (Abak, 0.61 mg/L) recorded the highest concentration of the element Co. This may be due to input from seawater, crude oil drilling and mining. Input may also be from industrial and domestic sewage containing Co from magnets, utensils and keys. Lowest concentration of Co was recorded on Onishere plantation, which was 0.13 mg/L.

### 4.3.7 Iron (Fe)

Fe often occur naturally in groundwater and the weathering of rocks especially mica and clay. An anthropogenic source is usually from industries involved in the casing of wells, pipes and pumps. Other processes that contribute to levels of Fe may include effluents, acid mines, drainage and landfills. WHO permissible limit for iron is 0.2 mg/L [14]. Table 4.6 recorded highest and lowest concentration of Fe in the study in PP2 (Acharu, 0.02 mg/L) and PP11 (Nsukka, 0.01 mg/L) respectively. PP1 (Abak, 0.63 mg/L) also recorded high concentrations of Fe. This could be attributed to effluents from crude oil processing and drilling taking place not far from the vicinity of the plantation. Fe is one of the additives added to crude oil processing [22]. There were also incidences of crude oil spills in the Kwa Ibo river which passes through the plantation bringing along with it pollution characteristics of crude oil effluents. The oil palm plantation located in Acharu is a NIFOR experimental station. Fe is mined in Itakpe, a few kilometers from the plantation. Pollution characteristics may be from the Kantu River, which flows through the plantation. The Kantu River is an overflow of the Benue and Niger River. Other areas that recorded significant levels of the element Fe are Iresa apa plantation in Ogbomosho and Agbarho plantation in Delta state. These areas recorded natural Fe ore deposits and anthropogenic contributions from Fe ore smelting companies located around the vicinity of the plantation.

### 4.3.8 Selenium (Se)

Selenium is an essential element required by plants and animals in trace quantities. An excess of this essential element in plants and animals may lead to toxicity. Symptoms of acute toxicity may be systematic and manifested in respiratory and cardiovascular ailments. Other ailments are numbness of the joints; hair and nail loss and heart related ailments [39]. MCL for Selenium in ground water is 0.05 mg/L [14]. Major source of Se in groundwater is because of effluent from petroleum and metal refineries and discharge of mines. Selenium can naturally be found in ores. Selenium compounds are commonly employed in the manufacture of electronic and photocopying components. They are also used in the manufacturing industry where glass, rubber, metal, alloys, medical and therapeutic agents are being produced. The trace element Se is of fundamental importance and is a major constituent of enzymes and Seleno-proteins. It is an active enzyme in the production of thyroid hormone and the development of virulence, which inhibits the development of the HIV hormone to AIDS. Vitamin C and E alongside Selenium inhibits free radical damage to cells and DNA. Selenium in the diet increases fertility and reduces the incidence of miscarriage. Selenium is abundant naturally in the atmosphere from the weathering of rocks and soils, burning of fossil fuels and electronic waste [40]. Highest and lowest concentrations were recorded in PP6 (0.07 mg/L) and PP14 (0.01 mg/L) respectively. This is presented in Table 4.6. PP6 (Badagry) recorded pollution characteristics from an electronic waste disposal/recycling site located close to the plantation.

### 4.3.9 Tin (Sn)

Sn is not known as an essential element to plants nor animals neither has its deficiency been known. It has no known biological activity and it is not easily absorbed. Its low toxicity is related to its use in kitchenware and canning though the organic compounds of Sn is very toxic. Chronic toxicity of Sn from canned food leads to the development of nausea, diarrhea, migraines, urinary tract infections, heart, brain and liver diseases, stomach disorders and skin and eye irritation in humans. Symptoms of morphological changes are exhibited such as reduction in size and loss of plant shape and colour [40]. Organic compounds of Sn are known to be very toxic. Tributyltin has been extensively used in the maritime industry as an antifouling agent in paints and has caused long-term pollution in waters due to its non-biodegradable nature and persistence in the environment. However, depending on the organic group type, some organotin compounds are powerful bactericides and fungicides. Recently, some researchers have found that selected compounds of Sn have exhibited anti-tumor and anticancer properties and can be useful in chemotherapy treatment [40-42]. WHO /MCL of tin in ground water is 0.01 mg/L [14]. Highest and lowest concentration of Sn metal was recorded in Table 4.6 on PP1 (Abak plantation, 0.73 mg/L) and PP7 (Benin City plantation, 0.02 mg/L)

respectively. Abak plantation is located some kilometers from the Atlantic Ocean. Many activities occur along the harbor some of which include the antifouling of ships with paint to prevent rusting of metal parts, soldering of metal and automobile parts. Most of the paints used for antifouling and solder iron contain organic compounds of Sn. This can be attributed to the significant high level of Sn element in the water sampled on Abak plantation.

### 4.4 Macro elements

Macro elements are elements needed in large quantities for proper functioning of systems in plants and animals. In most occasions access to these elements are readily available to plants and animals although some occur in trace quantities. These include elements like Ca, K, Mg and Na [40-42]. They are essential dietary elements necessary by living things for proper functioning for organs and systems. Ca is a co-factor of many enzymes necessary for the production of cell wall in plants and strong bones and teeth in animals. Deficiencies of Ca causes shoot root necrosis in plants, and osteoporosis in humans. Mg functions as a fundamental constituent of chlorophyll in plants and bone structure in humans. Deficiency of Mg causes tetany and Ca deficiency. Na and K both function as a significant component for the maintenance of pH and cellular fluid. K is required for the synthesis of protein, enzyme activation and the transportation of membrane. Deficiency of these macro elements is exhibited by necrosis and decrease in growth. Table 4.6 showed that the concentrations of the macro elements are within the MCL for the elements in ground water found on the plantations. Sources of the macro elements in ground water can be linked to natural and anthropogenic sources. Natural sources of K in water can attributed to feldspar. Anthropogenic sources may be from water softeners, ion exchangers and fertilizers. Ca and Mg are naturally abundant in soil and rocks such as limestone, dolomite, calcite and magnetite. No numerical guideline exists for Ca and Mg although high concentrations of these elements in the systems may prevent the absorption of other essential elements. Na is also naturally present in rock salt. High levels are indicative of salt-water intrusion from sewage, industries and leachates from landfills and dumpsites. Although Na is an essential element that functions actively in body fluids, high concentrations of the element in diet of patients on low Na intake may lead to heart and kidney problems [40-42].

## 4.5 Conclusion

The results of the study conducted on the trace and major elements in ground water on the oil palm plantations extensively show that elemental inputs in the water may be from natural and anthropogenic sources. Most often, anthropogenic sources generally outweigh the natural sources of contamination. The results of the analysis affirm that one of the pathways of elemental contamination in plants is from water. Plants are also more prone to absorb ground

water from roots than flowing water. The ICP-OES was an excellent instrument of choice because it simultaneously measured the major and trace elements. Due to its multielement capability, it was able to save time and cost.

## 4.6 References


[1] Goldhaber, S.B. Trace Element Risk Assessment: Essentiality vs. Toxicity. Regulatory Toxicology and Pharmacology, 2003, 38 (1), 232-242.

[2] Tiahou, G.; Maire, B.; Dupuy, A.; Delage, M.; Vernet, M.H.; Mathieu-Daude, J.C.; Michel, F.; Sess, E.D.; Cristol, J.P. Lack of Oxidative Stress in a Selenium Deficient Area in Ivory Coast: Potential Nutritional Antioxidant Role of Crude Palm Oil. European Journal of Nutrition. 2004, 43, 367–374.

[3] Oguntibeju, O. O.; Esterhuyse, A. J.; Truter, E. J. The Role of Red Palm Oil Supplementation in Reducing Oxidative Stress in HIV/AIDS and TB Patients; A Review. Journal of Medicinal Plants Research. 2010, 4(2), 188-196.

[4] Oluba, O.M., Eidongbe, G.O., Ogieh, G.C., Idonije, B.O. Palm and Egusi Melon Oils lower Serum and Liver Lipid Profile and Improve Antioxidant Activity in Rats Fed on a High Fat Diet. International Journal of Medicine. 2011, 3(2), 47-51.

[5] Valko, M.; Leibfritz, D.; Moncol, J.; Cronin, T.D.M.; Mazur, M.; Telser, J. Free Radicals and Antioxidants in Normal Physiological Functions and Human Disease. The international Journal of Biotechnology and Cell biology. 2007, 39, 44-84.

[6] Qureshi, A. A.; Bradlow, B. A.; Brace, L.; Manganello, J.; Peterson, D. M.; Pearce, B. C.; Wright, J. J.; Gapor, A.; Elson, C. E. Response of Hypercholesterolemic Subjects to Administration of Tocotrienols. Lipids. 1995, 30, 1171-1177.

[7] Osibote, O.A.; Olomo, J. B.; Tchokossa, P.; Balogun, F.A. Radioactivity in Milk Consumed in Nigeria ten years after the Chernobyl Reactor Accident. Nuclear instruments and Methods of Physics Research. 1999, 422, (3), 778-783.

[8] Ayodele, J.T.; Oluyomi, C.D. Gas Contamination by Trace Metals from Road Traffic. Journal Environmental Chemistry and Ecotoxicology. 2011, 3(3), 60-67.

[9] Obi A.L.; Jonah, S.A.; Umar, J. Determination of Trace elements in Some Nigerian based Oils by Neutron Activation Analysis. Journal of Radioanalytical and Nuclear Chemistry. 2001, 249, 669-671.

[10] Awodugba, A.O.; Tchokossa, P. Assessment of Radionuclide Concentration in Water Supply from boreholes in Ogbomosoland. Indoor and Built Enviromental. 2008, 71(2), 183-186.

[11] Asemave, K.; Ubwa, S.T.; Anhwange, B.A.; Gbaamende, A.G. Comparative Evaluation of Some Metals in Palm Oil. International Journal of Modern Chemistry. 2011, 1(1), 28-35.

[12] Bradshaw, D.K.; Thompson, L. The Analysis of Water and Waste Water by USEPA Method, 200.7 using the Optima 8300 ICP-OES and Prep Fast Auto Dilution/Calibration System. USA, Perkin Elmer. 2007.

[13] Benson, N.U.; Etesin, U. M. Metal Contamination of Surface Water, Sediment and *Tympanotonus fuscatus* of Iko River and Environmental Impact due to Utapete Gas Flare Station, Nigeria. The Environmentalist, 2008, 28(3), 195–202.

[14] UNESCO. Ground Water Pollution. International Hydrological Programme. Guidelines for Drinking Water Quality, 4 th edition, WHO, 2011.

[15] Rabinowitz, M.B.; Bellinger, D.C. Soil Lead, Blood Lead Relationship among Boston Children. Bulletin of Environmental Contamination and Toxicology. Springer-Verlag, New York. 1993.

[16] Staudinger, K.C.; Roth V.S. Occupational Lead Poisoning. American Family Physician. 1998, 57 (4), 719–726.

[17] Ogunseitan, O.A.; Schoenung J.M.; Saphores J.D.; Shapiro A.A. The Electronics Revolution: from e-Wonderland to e-Wasteland. Science. 2009, 326 (5953), 670-671.

[18] Chen, Y.; Yu, M.; Xu, J.; Chen, X.; Shi, J. Differentiation of Eight Teas (Camellia sinensis) Cultivars in China by Elemental Fingerprint of their Leaves. Journal of the Science of Food and Agriculture. 2011, 89, 2350-2355.

[19] Waalkes, M.P. Cadmium Carcinogenesis. Journal of Inorganic Biochemistry. 2000. 19(1), 241-244.

[20] Hartley, C.N. The Oil Palm, 1st. ed. Longman Scientific Technical, UK. 1988.

[21] Fosmire, G. J. Zinc Toxicity. American Journal of Clinical Nutrition. 1996, 51(2): 225-227.

[22] Hajo, H.; Lothar, R. The Immune System and the Impact of Zinc during Aging. Immunity and Aging. 2009, 6(9), 1-17.

[23] Olafisoye, O.B.; Adefioye, T.; Osibote, O.A. Heavy Metals Contamination of Water, Soil and Plants around an Electronic Waste Dumpsite. Polish Journal of Environmental Studies. 2013, 22(5), 1431-1439.

[24] Johri, R.; Singh, R.; Johri, P.K. Effect of Different Formulated Plant and Animal Diets on Hematology of *Clariasbatrachus Linn*. Under Laboratory Conditions. Biochemical and Cellular Archives. 2010, 10(2), 283-291.

[25] Adriano, D. C. Trace Elements in the Terrestrial Environment. 1986, 105-123.

[26] Alloway B.J. Heavy Metals in Soils. John Wiley and Sons Inc. NewYork. 1990.

[27] Cunningham, S.D.; Ow, D.W. Promises and Prospects of Phytoremediation. Plant Physiology. 1990, 110(3), 715-719.

[28] Barabaaz, W.; Albinska, D.; Jaskowska, M.; Lipiec, J. Ecotoxicology of Aluminium. Polish Journal of Environmental Studies. 2002, 1193, 199-203.

[29] Ma, J.F. Role of Organic Acids in Detoxification of Aluminium in Higher Plants. Plant Cell Physiology. 2000, 41(4), 383-390.

[30] Vardar, F.; Unal, M. Aluminium Toxicity and Resistance in Higher Plants. Advances in Molecular Biology. 2007, 1, 1-12.

[31] Ma, J.F.; Ryan, P.R.; Delhaize, E.; Aluminium Tolerance in Plants and the Complexing Role of Organic acids. Trends in Plant Science. 2007.

[32] Sparling, D.W.; Lowe, T.P. Environmental Hazards of Aluminium to Plants, Invertebrates, Fish and Wildlife. Reviews of Environmental Contamination and Toxicology. 1996, 145(1), 127-128.

[33] Priest, N.D. Proceedings of the International Conference on Managing Issues in the Aluminium industry. Montel, Canada, 26-29, October. 1997

[34] Donoghue, A.M. Occupational Hazards in Mining: An Overview. Occupational Medicine. 2004, 54, 288-289.

[35] Foulke Jnr E.G. Guidance for the Identification and Control of Safety and Health Hazards in Metal Scrap Recycling. Occupational Safety and Health Administration. 2008, 1-44.

[36] William, R.N.; David, R.LS. Diseases Caused by Respiratory Infants and Toxic Chemicals. Encyclopaedia of Occupational Health and Safety. International Labour Organization, Geneva, 2011.

[37] Arogunjo, M.A. Heavy Metal Composition of Some Solid Minerals in Nigeria and their Health Implications to the Environment. Pakistan Journal of Biological sciences. 2007, 10(1), 4438-4443.

[38] Acosta, A.; Munevar, F. Bud Rot on Oil Palm Plantations: Link to Soil Physical Properties and Nutrient Status. Better Crops International. 2003, 17(2), 22-25.

[39] ATSDR, Agency for Toxic Substances and Disease Registry. Toxicology Profile for Selenium. US Department of Health and Human Services. Atlanta, Georgia. 2003.

[40] ATSDR, Agency for Toxic Substances and Disease Registry. Toxicology Profile for Selenium. US Department of Health and Human Services. Atlanta, Georgia. 2005.

[41] Arogunjo, M.A. Heavy Metal Composition of Some Solid Minerals in Nigeria and their Health Implications to the Environment. Pakistan Journal of Biological sciences. 2007, 10(1), 4438-4443.

[42] Itumoh, E.J.; Uraku, A.J; Omaka O.N.; Nwabue, F.J. Trace Metal Toxicity in our Environment: Case Studies of Influx of Metals in Soils, Crops, Waters and Air in Ebonyi State. Global Journal of Bio-science and Bio-technology. 2013, 2(1), 33-36.

## 4.7 Acknowledgement

The work was carried out through the URF funding provided by the Cape Peninsula University of Technology, Cape Town, South Africa.

# CHAPTER FIVE

## An assessment of the bioavailability of heavy metals in soils on oil palm plantations

*Olafisoye O. B.[1], Oguntibeju O. O.[2], Osibote O. A.[3]*

*[1]Faculty of Applied Sciences, Department of Chemistry, Cape Peninsula University of Technology, P.O. Box 652, Cape Town, South Africa 8000. abogunrinob@gmail.com.*

*[2]Faculty of Health and Wellness Sciences, Department of Biomedical Sciences, Cape Peninsula University of Technology, P.O. Box 1906, Bellville, South Africa oguntibejuo@cput.ac.za.*

*[3]Faculty of Applied Sciences, Department of Mathematics and Physics, Cape Peninsula University of Technology, P.O Box 652, Cape Town, South Africa 8000*

***Correspondence: osiboteA@cput.ac.za***

***Tel: +27733545569***

***Olafisoye O. B.[1], Oguntibeju O. O.[2], Osibote O. A.[3]*. 2016. *An assessment of the bioavailability of heavy metals in soils on oil palm plantations in Nigeria. Polish Journal of Environmental Studies, 25(3), 1125-1140.***

## Abstract

We investigated the speciation, bioavailability, and mobility of metals in soils from selected states on oil palm plantations in southwest south east and south south states of Nigeria. Soils were analysed for total metal content and speciation on all sampling locations. Metal concentrations were compared against pH, electrical conductivity (EC) and soil organic matter (SOM), which were high at all the sampling locations. The speciation results deduced that the concentrations of the different fractions vary widely at each sampling location. Cd is mostly abundant in the exchangeable phase in all the samples analysed in the various locations. Ni

in the Iresa-apa plantation (29.9 %) and Co in the Acharu plantation (29.9 %) also showed appreciable concentrations in the Fe/Mn oxide fractions. The concentrations of Pb and Cu were highest in the organic fraction. Metals in the organic phase are more released into soil solution when compared to the residual phase fractions. Chromium and Zinc were mostly associated with the residual phase when the values of the residual phase were compared with other geochemical fractions. The plantations under study, which recorded the highest concentrations of Cr and Zn in the residual fractions, were 87.9 % (Okitipupa), 86.3 % (Ikire), 82.7 % (Apoje), 90.3 % (Onishere), 89.7 % (Benin City), and 85.6 % (Nsukka). The results of the sequential extraction show that mostly Cr and Zn were strongly bound to the residual/inert phase in all the soils under investigation. The potential mobility of the metals with high fractions in the residual phase is as follows: Cr (74.8 %), Zn (74.0 %), Pb (73 %), Fe (69.5 %), Ni (67.0 %), Cu (63.8 %), Mn (30.5 %), Co (30.7 %), and Cd (25.9 %). These values were high when compared to the values of other metals in the other mobile and potentially mobile fractions.

***Key words***

***Oil palm planations, bioavaliability and bioaccessibility, heavy and trace metals, sequential extraction.***

## 5.1 Introduction

The socio-economic impacts of oil palm plantations are numerous in a good number of countries. The ostensive environmental effects of the cultivation and management of the oil palm tree cuts across land and water contamination [1]. Many physical, biological, industrial, and agricultural processes bring about the pollution of soils since soils represent a vibrant and vigorous structure. The contamination of soils may arise from the build-up of trace and heavy metals owing to the application of natural and synthetic fertilizers, effluent and slush [2]. This poses a risk to humans, animals, and plants. Plants and animals are exposed to pollutants from the ingestion of plants grown on polluted soils or water on such soils. Municipal areas where oil palm trees are greatly cultured in Nigeria are the states in southern areas of Nigeria [3]. The oil palm (Elaeis guineensis) is a prolific oil producing plant, which grows on low pH soils in the tropical regions of Nigeria between 15° N and 15° S. This is aboriginal to the southern parts of Nigeria where it is a stable crop grown by numerous diminutive landowners. This segment provides raw materials for the food and chemical industry; providing employment for the populace [4]. The contamination of soil by heavy and trace elements limits the usability of the land for agronomical purposes. This has an adverse effect on crop growth and food quality [5]. Accumulation of heavy and trace elements is an ecotoxicological issue presenting adverse effects to the environment. The contamination of heavy metals in the environment is

irreversible; it persists and is usually non-biodegradable. Heavy and trace elements have long residence time in the environment, ending up in the food chain. A natural factor such as geology of heavy and trace element contamination of the environment is minimal [6]. Majorly, contamination arises from anthropogenic sources such as unwholesome farming practices, which include bush burning and the use of fertilizers and pesticides containing heavy and or trace elements. Other sources of anthropogenic contamination are from crude oil exploration and spillage, urbanization and industrialization. At acute concentrations, the potential toxic heavy and trace elements present in the environment makes it an issue of concern. The effects of trace and heavy elements are frequently present in industrial, municipal and crude oil spills leading to soil contamination [7]. Not all elements present in soil are toxic. Elements such as Zinc (Zn), Iron (Fe), Copper (Cu), and Chromium (Cr) are essential nutrients yet toxic at elevated concentrations. Others like Lead (Pb), Mercury (Hg), Arsenic (As) and Cadmium (Cd) are toxic with no beneficial properties. A serious environmental problem is the accumulation of these elements in plants due to the phytoxicity of most of these elements affecting vegetation and wildlife. Metals with a density greater than 6.0 $gcm^{-1}$ are known as heavy metals. These are deleterious to life at the lowest concentrations in the atmosphere. Heavy metals are bound in soils in various oxidation states. The toxicity of such metals differs with oxidation states. Major concerns of regulatory agencies in countries worldwide are the susceptibility of heavy metals in the environment [8] [9]. The contamination of soils and its susceptibility determine the bioavailability of the elements to plants and animals. Bioavailability of heavy metals in soils differs extensively from the bio-accessibility. The speciation of the heavy metals, its biotransformation, the weathering of the parent material and its adsorption, organic matter content, electrical conductivity and pH are factors responsible for its bio-accessibility and bioavailability. Biological, geological, and anthropogenic factors affect the bioavailability and bio-accessibility of the concentration of heavy metals in soils. Total metal concentration is not sufficient to qualify and quantify the metal speciation or the behaviour of heavy metals in soils because such metals are present in soils in various oxidation states, which influence their availability and uptake by plants [10-15]. Speciation is used to determine the forms or fractions of heavy metals in soils. Heavy metals are usually present in different forms such as exchangeable fractions, carbonate bound, bound to iron, manganese oxides and carbonates, organic bound and residual fractions. Therefore, knowledge on the total concentrations of metals alone is not adequate to evaluate the environmental effect of heavy metals in soils. In order to qualify and quantify the fractions or forms in which a metal exists in soils, it is crucial to obtain a detailed knowledge and perception of the probable and genuine effects of the concentration of the heavy metals in the soils. Other factors to consider include high concentrations of the heavy metals under study, translocation and transportation and altering

climatic situations [10-16]. An extraction scheme was developed [11] to establish an extraction procedure, which permits the classification of the total metal concentration into five segments: exchangeable, carbonate bound, iron/manganese oxide bound, organic bound and residual fraction. Initially, this scheme was applied for sediments but it has now been used extensively in soil speciation. A number of researches have been conducted on the speciation of heavy metals in soils [16-22]. The study aimed to investigate the relationship between heavy metals and the most important soil factors, which influence heavy metal concentrations in soils. The mobility and availability of heavy metals in the soils depend on how the metals are associated with the components of the soil. The study was to initiate and evaluate a measure of the mobility and availability of the heavy metal concentration and their speciation on oil palm plantations in South western, South southern and South eastern States of Nigeria. The plantations were selected from areas, which receive significant pollution from domestic and industrial activities, which serves to predict the behaviour of the metals in the soil. The following elements Al, Cd, Co, Cr, Cu, Fe, Mn, Pb, Sn, and Zn were determined.

## 5.2 Experimental procedures

### 5.2.1 Description of sampling areas

The states in southern Nigeria nearly exclusively depend on the oil palm tree for their source of revenue. The main station of the organization comprises of a campus of 1735 hectare of property situated near Benin City approximately 29 km from the metropolis. Areas in the southern part of Nigeria where oil palm is greatly cultivated include the states of Edo, Enugu, Delta, Akwa-Ibom, Ondo, Ekiti, Kogi, Oyo, Osun, Ogun, and Lagos. The states in southern Nigeria have a tropical weather. Soil samples were collected in fifteen sampling areas to characterize different fraction of metals and their bioavailability in surface soils.

### 5.2.2 Sampling sites and sample collection

Soil sampling was accomplished on fifteen main sites in land areas in Nigeria. These sites are the nine sub-stations of NIFOR (Nigeria Institute for Oil Palm Research) located at Abak in Akwa-Ibom state, Acharu in Kogi state, Agbarho in Delta state, Onishere in Ondo state, Ubiaja in Edo state, Umuabi in Enugu state, Nsukka in Enugu state, Ago-Emokpae in Edo state and from their headquarters at Benin. Five samples were also collected from other locations in the south west of Nigeria from oil palm plantations receiving substantial pollution of heavy metals. These locations were Iresa-apa in Oyo state, Igede-Ekiti in Ekiti state, Ikire in Osun state, Okitipupa oil palm plantation in Ondo state and Apoje oil palm farm settlement in Ogun state. Execution of sampling was done in October 2012 to April of 2013. A composite sample was used for analysis, which was achieved by partitioning the sampling locations into four parts in

each state, and samples were collected from each part in each state. The sampling locations were centered on reasons such as population density, farming communities and regions receiving major contamination. An auger was used for soil sample collection and the samples were stored in black sterilized plastic bags. This was preserved instantly in an ice chest at 4 ˚C. Soils were air-dried, sieved and preserved in plastic bags and further dried at 105±50˚C for 3 hours. The apparatus used for sampling were properly washed in nitric acid and rinsed with high purity deionized water (Milli-Q water purification system, Millipore, Belford, MA, USA).

### 5.2.3 Reagents and samples

The solutions used for the analysis were prepared from analytical grade reagents using high purity deionized water (Milli-Q water purification system, Millipore, Belford, MA, USA). Analytical grade chemicals from Merck, Darmstadt, Germany, and Sigma-Aldrich were used for all the analysis.

### 5.2.4 Reference materials for standard calibration curves

Reference materials for standard calibration curves used for the analysis were prepared from single element standards (1000 mg/L). The starting materials for the trace element were measured against a certified reference material and are traceable to National Institute for Standards and Technology (NIST). Lower concentrations were prepared in the same matrix using the non-serial dilution method.

### 5.2.5 Electrical conductivity and pH determination:

Saturated extracts of samples were obtained by dissolving 20 g of soil sample in 100 $cm^3$ of ultra-pure water (Millipore distilled water 18.2 µm) in a beaker for 30 minutes at 40 °C for the determination of electrical conductivity and pH. A multipurpose hand held pH and conductivity meter was used for this purpose. The soil mixture was stirred for 30 minutes at 40 °C and allowed to cool for an hour. The saturated soil mixture was used for the determination of pH and electrical conductivity as described [23].

### 5.2.6 Organic matter determination: Loss on Ignition Method (LOI)

Application: The routine estimation of soil organic matter by the loss of weight was achieved using the Loss on Ignition Method (LOI) procedure. This involves heating of the sample to a temperature as high as 600 ˚C to decompose most or all organic matter and carbonates in the soil sample. The previously dried and sieved samples were oven dried at 105 ˚C, cooled in a desiccator, and weighed. The weighed samples were further combusted in a muffle furnace (Memmert oven, Model 380) at 600 ˚C for 4 hours, cooled in a desiccator and reweighed. The

modified equation of Schulte and Hopkins (1996) was used in the estimation of the Soil Organic Matter [23].

### 5.2.7 Total metal extraction using microwave assisted digestion

Digestion was performed using the Milestone Ethos Microwave Lab station. Total Metal Extraction using Microwave Assisted Digestion was performed as follows. 1g of finely ground and homogenized soil was digested using the aqua regia digestion method ($HNO_3$/HCl in 1:3 ratio). Millipore distilled water (18.2 µm) was added to the digested soil volume and the volume made to 100 mL. The contents in the Teflon tubes after microwave-assisted digestion was transferred to centrifuge tubes, centrifuged at 3000 rpm for 30 mins and filtered through a filter paper (0.45 µm). The extract volume (10 mL) was put in polypropylene tubes (15 mL) and stored at 4˚C for ICP-OES instrumental analysis.

### 5.2.8 Sequential extraction procedure

The principle of sequential extraction procedure is based on the selective extraction of different fractions of metals with the use of specific reagents. Various procedures have been used for the determination of the bioavailability and bio-accessibility of heavy metals but the most conventional methods are the five and the six-step methods. Numerous researches has been done using the two methods and adaptations performed for best results. The BCR three-step method was recommended by the European Community Bureau of Reference in 1992 to harmonize the various procedures on sequential extraction by researchers [11] [12] [13] [14] [15] [16].

### 5.2.9 BCR Sequential Extraction Procedure

The modified BCR procedure recently referred to as the Standard Methods and Testing consists of three different steps; acid soluble fractions, reducible fraction, oxidizable fraction and residual fraction.

#### 5.2.9.1 First step

The first step of the analysis consists of the acid soluble fraction which is bound to carbonates. Samples of soil (0.5 g) which were previously air dried and sieved were placed in polypropylene centrifuge tubes (50 mL). Immediately, 0.11mol/L of acetic acid (20 mL) was added to each of the sample in the polypropylene tubes. The polypropylene tubes were shaken for 16 hours at room temperature prior to centrifuging. Centrifugation was performed at 3000 rpm for 30 minutes. The top liquid layer was poured into a 15 mL polypropylene tube and stored at 4˚C prior to elemental analysis in the fraction. The residue from the first step was washed with 10

mL ultra-pure distilled water (Millipore water 18.2 µm). The residue was washed to remove all traces of the acetic acid. It was consequently shaken for 10 minutes and centrifuged at 3000 rpm [11] [12] [13] [14] [15] [16] [17].

#### 5.2.9.2 Second step

The second step of the analysis consists of the reducible fraction which is bound to Fe and Mn oxides. The metals bound to Fe and Mn oxides were separated from the residue from the first step by using 0.5 mol/L hydroxylamine hydrochloride (20mL) and adjusted to the pH of 2 with nitric acid. The contents in the polypropylene tubes were shaken for 16 hours, and further centrifuged for about 10 minutes. The supernatant from the second step was poured into a 15 mL polypropylene tube and stored at 4˚C prior to elemental analysis. The soil residue from this step was washed with 20 mL ultra-pure distilled water (Millipore water 18.2 µm) centrifuged and the supernatant discarded [11] [12] [13] [14] [15] [16] [17].

#### 5.2.9.3 Third step

The oxidizable fraction is the fraction that is bound to organic matter and sulphides in the soil sample. Approximately 10 mL of 8.8 mol/L hydrogen peroxide was added drop wise to the residue from Step 3 and digested in a water bath at 30 ºC for 1 hour. The 50 mL centrifuge tube was lightly capped and digestion was continued at 85 ºC for 30 minutes till the volume of liquid in the centrifuge reduced to 2 mL. The procedure was continued with 5 mL of 8.8 mol/L $H_2O_2$ till when the volume reduced to near dryness. The contents were cooled and 25 mL of 1.0 mol/L ammonium acetate added. This was shaken and centrifuged at 3000 rpm for 16 hours. This was further centrifuged and decanted and the extract stored at 4˚C for elemental analysis [11-17].

#### 5.2.9.4 Fourth step

The analysis of the residue was done using the aqua regia method. The extract from the third step was digested using the microwave assisted digestion method. This was done for metals that were not soluble in the preceding step [11-17].

### 5.2.10 Instrumentation

The Spectro Arcos FHS 12 ICP-OES (Spectro Germany) equipped with radial viewed plasma was used for the research. The Radial Slide Plasma Interface (SPI) was used with the Spectro UV plus system for measurements in the UV range, which records the entire relevant spectrum (165-770 nm). The Spectro Arcos FHS 12 ICP-OES is equipped with a CCD solid-state array detector and smart analyser vision graphical user interface 4.02.0834 software. The CCD

detector shows a significant advantage over the conventional technology with respect to speed, sensitivity, and lower instrument cost. The essential operating principle in Inductively Coupled Plasma- a cyclonic spray chamber was used in the sample introduction system. Sample digestion was carried using the Milestone microwave digester MLS 1200 equipped with six Teflon vessels and a ceramic jacket [24] [25].

### 5.2.11 Validation of the analytical method

The repeatability or precision of the method was established with an evaluation of the percentage residual standard deviation of the sample microwave assisted digestion procedure. Digested samples were analyzed in triplicates. The mean, standard deviation, and percentage residual standard deviation calculated from this data. The acceptable criterion for repeatability, percentage residual standard deviation results is to be below 10 for elements determined by ICP-OES.

## 5.3 Discussion of results

Soil properties are found to control the bioavailability and uptake of heavy metals in soils. The chemical extraction procedures are based on the assumption that a relationship exists between the bioavailable fractions in the soil and the soil properties. As shown in Table 5.1, soil pH obtained in the study ranged from 4.96 to 7.01. Bioavailability and transport of heavy metals decreases with increase in pH due to precipitation of hydroxides, carbonates, or formation of insoluble organic complexes. Heavy metals are more mobile at acidic pH. This is consistent with the results obtained from studies conducted [25] [26]. Soil pH is a useful indication of toxic elements in soil and plants have difficulty in absorbing some elements such as Cu, Zn, Mg and Fe in basic soils. The values of the pH from the study areas indicated the tendency of the availability of the heavy metals and high metal uptake by plants. The soil pH serves as a useful index of availability of nutrients and the potency of toxic substances present on soils from the plantations. The values of pH in Table 5.1 varied slightly and this could be related to indigenous deposits of pollutants from the different sampling sites. Electrical conductivity is a measure of the salinity of the soil. The results for the electrical conductivity in the study ranges from 22 to 229 $Scm^{-1}$. It is important and influences major key processes. The soil electrical conductivity was more variable than the pH as seen in Table 5.1, which could be due to the content of available soluble salts. Electrical conductivity has been correlated to the concentration of elements in soils. High values of soil organic content can be attributed to arable and cultivated soils, the presence of vegetation cover and decomposition of organic matter. Low organic matter content in soils indicates low electrical conductivity. Interactions among these factors appear to be in control in the distribution of the heavy metals among the

different plantation sites. This correlated with the bioavailability of the metals in the soil. Soil properties can additionally be considered when predicting the bioavailability and bio accessibility of heavy metals in soils and is consistent with studies conducted by some researchers [24] [25].

The heavy metal distribution in the sample under study was used to assess their mobility and bioavailability. The mean and standard deviation results got from each extraction and residual step using the BCR sequential extraction procedure are discussed in Tables 5.2 for soils from 15 sampling locations on oil palm plantations in southern Nigeria. The mobility order is as follows for the first, second, third and fourth fractions respectively.

Cd>Mn>Co>Pb>Zn>Cu>Ni>Fe>Cr
Mn>Co>Cd>Ni>Pb>Zn>Fe>Cu>Cr
Cd>Pb>Mn>Co>Zn>Cr>Cu>Ni>Fe
Fe>Cu>Ni>Zn>Cr>Pb>Mn>Co>Cd

### 5.3.1 Mobile element

#### 5.3.1.1 Cd

The bioavailable fractions are the exchangeable fractions and have potential hazardous effect on man and the environment. Incoming pollutants from sources may first exist in an unstable form, which later degrade to pollutants forming precipitates. Cd is the most available and assessable heavy metal in the four fractions. Cd was observed to be the most mobilisable element and 86 mg/kg of the mobilisable form is found in the first to third fractions in the extraction stages. About 40 mg/kg, 20 mg/kg and 26 mg/kg were found in the first to third extraction stages respectively. This shows that Cd is found in the soluble fraction or the non-residual fractions and not the insoluble or residual fractions, which is consistent with findings obtained by some researchers [10] [11] [12]. It is the most available heavy metal in soils and it is mainly bound to the acid soluble and carbonates fractions. This demonstrates that Cd is easily available in the soil and transferable to humans through the food chain [25]. Intensive review has been conducted on the toxic effect of Cd in the environment because it is an experimental animal carcinogen [8] [27] [28]. Natural and anthropogenic sources of Cd in the environment are from the weathering of rocks, volcanoes, and bush fires. Other sources include electronic waste especially from cadmium batteries. Soils can be polluted by the application of fertilizers, sewage, and/or sludge from automobile, metallurgical, and mining industries. Effects of Cd in humans include osteomalacia, pulmonary emphysema, infertility, and renal tubular damage [8] [27] [28].

**Fairly mobile elements**

**5.3.1.2 Co, Pb and Mn**

About 40 mg/kg of the total Co present in soil is distributed in the residual fraction, which is the insoluble part of the soil. The remaining is distributed in the reducible fraction, which is bound to Fe and Mn oxides (26 mg/kg). The other fraction is the oxidisable fraction, which is bound to organic matter and sulphides (16.5 mg/kg). A form in which Co exists in the oxidisable fraction is CoS (Cobalt Sulphide). Co is similar to Fe and Ni in physical properties 2003 [29] [30]. It exists in the diet as Vitamin B12, which is necessary for good health and in the treatment of anaemia and various blood disorders. Pregnant women require Co because it stimulates the production of red blood cells needed for foetal development. It occurs naturally in the environment in seawater, volcanic eruptions, and forest fires. Anthropogenic sources are from coal fires, burning of oil and industrial processes. Workers in industry may be exposed to cobalt when grinding, smelting, and refining tools. Some forms of cobalt are also radioactive. It is an ingredient of porcelain enamel and a pigment in most paints. High concentration of Co may cause asthma and pneumonia in workers in occupational settings where cobalt is used as a major element. Plants cultivated on soils where cobalt is mined or smelted may accumulate significant amounts of the element. Effects of Cobalt in humans are vomiting/nausea, eye, heart and thyroid gland damage, sterility, hair loss, diarrhoea and death. Other effect of high concentrations of cobalt is manifested by weight loss, skin lesions and breathing disorders. It is a known experimental animal carcinogen [29] [30]. Soluble lead, which is dissolved in soil, is bound to organic matter and carbonates. This greatly reduces the solubility and mobility of lead in soils making it strongly held by soil constituents to a greater degree. The results obtained agree with the findings of some researchers [10-14]. Lead in the environment can be from sources such as the exhaust pipes of petrol engines and lead acid battery recycling. Soils may be contaminated with lead when located close to Pb mines, glass making factories, pesticides, fertilizers, smelting operations and the combustion of fossil fuels [30] [31]. Zinc is an essential element required in minute concentrations by plants and animals for cell metabolism, cell development, and enzyme activity. High concentrations can be lethal causing blood and nervous system disorders, kidney damage, diarrhoea, infertility, miscarriages and lethargy [32] [33]. Mn is partitioned between the reducible and residual phase as 34.8 mg/kg and 38.4 mg/kg in the fractions. It is mobile, therefore the potential of transfer either through the soil profile down to the ground water is possible [10-14]. The bioavailability of heavy metals is important when it concerns the food chain. Mn is an essential element, which has excellent antioxidant properties vital in oxidative stress. For instance, Manganese superoxide dismutase is the primary antioxidant enzyme in mitochondria, which consumes nearly all the oxygen used by cells. Research has shown that various manganese-activated enzymes play important roles

in metabolism of starch, amino acids, and lipids. It is the ideal co-factor of enzymes (glycosyltransferases) required for secretion of proteoglycans for the development of strong bones and cartilage. Mn is also responsible for the secretion of the enzyme prolidase. Prolidase is responsible for amino acid, a key component in collagen production and wound healing. Although an essential element, it can be toxic at elevated concentrations. It plays an important role in enzyme synthesis [34] [35]. The elements are associated with the organic matter fraction and in oxidizing conditions may be remobilized into the environment. This has a deleterious impact on plants and animals because the heavy metals become toxic and persistent in the environment.

### 5.3.2 Immobile elements

#### 5.3.2.1 Cr, Cu, Fe, Ni, and Zn

In the metabolism of carbohydrates, hexavalent Cr is the toxic form of Cr. It has high antioxidant properties, which is crucial for carbohydrate metabolism, prevention of some form of diabetes and cardiovascular diseases. Cr may occur in the environment from tanning and electroplating sewage and sludge [36] [37] Sources of Cr in foods include cereals, nuts among others. High consumption of Cr containing foods may lead to gastrointestinal and blood disorders and convulsion. Research has proved that cancer of the respiratory tract is common in occupational settings where high concentration of Cr is prevalent. The analysis shows that in all four fractions, Cr can be considered as an almost immobile and insoluble heavy metal because the value of the percentage of the residual concentration is very high. The Cr ions are held tightly to the compounds in solution and are not easily solubilized. Cr does not present high risk of environmental contamination because its compounds are not available for plant uptake. It is neither bio accessible nor bioavailable for plants and hence presents no risk to the food chain [38] [39]. The category of these elements are associated with the residual phase and represents metals largely embedded in the crystal lattice of the soil fraction and are not available for remobilization except under extremely severe conditions.

Copper is predominantly found in the insoluble fractions making it neither poorly oxidized nor reduced. Its percentages are 7.6, 5.6, 6.7, and 86.5 mg/kg in the exchangeable, reducible, oxidizable and immobile fractions respectively. Its predominantly high percentage in the residual fraction signifies its immobility at high percentages. Cu is strongly held to minerals and components that are neither oxidizable nor reducible. Copper is usually held in soils through adsorption and exchange processes by soil [10-14]. Copper is an essential element possessing antioxidant properties which protects organs in humans against the action of free radicals. It is a component of haemoglobin and alongside vitamin C assist in the proper functioning of the lungs, blood vessels, and epidermal tissues. For plants, this is needed for

seed and chlorophyll formation [40] [41]. It is an essential part of proteins and various biochemical syntheses of plants. Though copper is an essential element necessary for proper functioning of organs and systems in the body in minute quantities, high concentrations can be toxic and lethal. A high and toxic concentration of the essential element causes adverse health effects, which includes nausea, diarrhoea, liver and kidney damage. Anthropogenic sources of copper in industries include the manufacture of coins, electrical wiring, and the use of copper pesticides in agriculture. Due to immobile and persistent nature of copper in the soil fractions, it does not pose high risk to the environment [42] [43].

Iron is a very essential element especially in cells for the production of haemoglobin. It presence in the blood ensures a strong immune and digestive system and mental alertness. Iron is crucial to human health but it not excreted or used by the body. High concentrations of the essential metal in blood leads to acute toxicity manifested by oxidative stress and inability of the body to metabolise or absorb nutrients [44] [45]. Other defects are anaemia, stunted growth, and death. It often occurs naturally in groundwater and the weathering of rocks especially mica and clay. An anthropogenic source is usually from industries involved in the casing of wells, pipes, and pumps. Other processes that contribute to levels of Fe may include effluents, acid mines, drainage, and landfills [46-48]

Metals associated with Fe-Mn oxides may change in medium during redox conditions. The oxides exist in the form of cements between the particles of the metals and are excellent scavengers. Zinc is readily absorbed by clay minerals, carbonates, and hydroxides. The total Zn in contaminated soils was associated with the residual fractions. Zinc is an essential element with high antioxidant properties protecting humans from the actions of free radicals [49-51]. It is required for metabolism of cells, enzyme activation, foetus development, and protein and DNA synthesis. A deficiency of the essential element in the diet may cause growth and reproductive disorders, nausea and lethargy [52-54].

## 5.4 Conclusion

The maximum permissible concentrations of heavy metals in surface soils are usually based on the concentrations of their total concentration but it is the concentration of the bioavailable metal fraction that possess the most environmental concern. These factors are also insufficient since they are related to the soils physicochemical characteristics and the forms in which the metals exist. The presence of heavy metals in soils was identified through speciation studies on all sampling locations. Furthermore, this may cause uptake of heavy metals by the trees on the plantations that can cause serious environmental problems due to bioaccumulation and bioaccumulation in the food chain and consequently affect human and animal health. The research work shows the application of sequential extraction procedures for the process of

controlling and influencing the speciation of heavy metals in soils. It provides information on the dangerous effects of these heavy metals since the mobility, Eco toxicity depends on their chemical forms, and they tend to be easily mobilized and dispersed. The bioavailability of heavy metals in soils responds to the fraction that is phyto-available to them. The heavily soluble fractions that are generally the exchangeable and the fractions bound to organic matter are generally considered phytoavailable. The accurate evaluation of the concentration of the phytoavailability of heavy metals in soils is becoming a useful tool for risk assessment and remediation studies. The study acknowledges the fact that total metal concentration may not be a very important tool for predicting metal phyto-availability on the plantations.

## 5.5 References


1. OBIDZINSKI K., ANDRIANI R., KOMARUDIN H., ANDRIANTO A. Environmental and social impacts of oil palm plantations and their implications for biofuel production in Indonesia, Ecology and Society 17 (1), 131-168, 2012.
2. STRUEBIG J., PAOLI G., KOH L.P. Mitigating the biodiversity impacts of oil palm Development-Reviews. In: Perspectives in Agriculture, Veterinary Science, Nutrition and Natural Resources 5 (19), 1-11, 2010.
3. GILBERT D. Oil palm and the palm oil industry in Ghana, A brief history, International Research Journal of Plant Science 4 (6) 158-167, 2013.
4. OLAGUNJU F. I. Economics of oil palm processing in south-western Nigeria, International Journal of Agricultural Economics and Rural Development 1 (2) 69-77, 2008.
5. YAO Z., LI J., XIE H., YU C. Review of remediation technologies of soil contaminated by heavy metals, Proceduris Environmental Sciences 16 (1) 722 -729, 2012.
6. KHAN S., CAO Q., ZHENG Y.M., HUANG Y.Z., ZHU Y.G. Health risks of heavy metals on contaminated soils and food crops irrigated with waste water in Beijing, China, Environmental Pollution 152 (3) 686-692, 2008.
7. RAYMOND A.W., FELIX E.O. Heavy metals in contaminated soils: A review of sources, chemistry, risks, and best available strategies for remediation, ISRN – Ecology 1 1-20, 2011.
8. SINGH R., GUATAM N., MISHRA A., GUPTA R. Heavy metals and living systems: An overview, Indian Journal of Pharmacology 43 (3) 246-253, 2011.
9. BARAKAT M.A. Review article: New trends in removing heavy metals from industrial waste water, Arabian Journal of Chemistry, 4 (4) 361-377, 2011.

10. TOKALIOGU S., KAFTAL S., BIROL G. Application of a three stage sequential extraction procedure for the determination of extractable metal contents in highway soils, Turkish Journal of Chemistry 27 (2003) 333-346, 2001.
11. TESSIER A., CAMPBELL P.G.C., BISSON M. Sequential extraction procedure for the speciation of particulate trace metals, Analytical Chemistry, 51 (7) 844-851, 1979.
12. ZIMMERMAN A.J., WEINDORF D.C. Heavy metal and trace metal analysis in soil by sequential extraction: A review of procedures, International Journal of Analytical Chemistry, 2010 (2) 1-7, 2010.
13. LELEYTER L., PROBST J.L. A sequential extraction procedure for the speciation of particulate trace elements in river sediments, International Journal of Environmental Analytical Chemistry, 73 (2) 109-128, 1999.
14. HE Q., REN Y., MOHAMMED I., ALI M., HASSAN W., ZENG F. Assessment of trace and heavy metal distribution by four sequential extraction procedures in a contaminated soil, Soil and Water Reserve 8 (2) 71-76, 2013.
15. OKORO H.K., FATOKI O.S., ADEKOLA F.A., XIMBA B.J., SNYMAN R.G. A review of sequential extraction procedures for heavy metals speciation in soils and sediments, Open Access Scientific Reports 1 (1) 181-190, 2011.
16. CAPPUYNS V. A critical evaluation of single extractions from the SMT program to determine trace element mobility in sediments, Applied and Environmental Science. 2010 (2010) 1-15, 2012.
17. YU B., WAG Y., ZHOU Q. Human health risk assessment based on toxicity characteristics leaching procedure and simple bioaccessibility extraction test of toxic metals in urban street dust of Tianjin, China, PLoS ONE 9 (3), 2014.
18. FU X., CUI Z., ZANG G. Migration, speciation and distribution of heavy metals in an oil polluted soil affected by crude oil extraction processes, Environmental Science: Processes and Impacts 16 (1) 1737-1744, 2014.
19. URE A.M., QUEVAUVILLER P.H., MUNTAU H., GRIEPINK B. Speciation of heavy metals in soils and sediments; An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the commission of the European communities, International Journal of Environmental Analytical Chemistry 51 (4) 135-151, 1993.
20. ASHRAF M.A., MAAH M.J., YUSOFF I. Chemical speciation and potential mobility of heavy metals in the soil of a former tin mining catchment, The Scientific World Journal 2012 (2012) 1-11, 2012.

21. RODRIGUEZ L., RUIZ E., ALONSO-AZCARATE J., RINCON J. Heavy metal distribution and chemical speciation in tailings and soils around a Pb-Zn mine in Spain, Journal of Environmental Management 90 (2) 1106-1116, 2009.
22. LAKE D.L., KIRK P.W.W., LESLER J.N. Fractionation, characterization and speciation of heavy metals in sewage, sludge and sludge-amended soils: A review, Journal of Environmental Quality 13 (2) 175-183, 1984.
23. HE O.B., SINGH R. Effect of organic matter on the distribution, extractability and uptake of cadmium in soils, Journal of Soil Science 44, 641-650, 1993.
24. BRANDSHAW D.K., THOMPSON L. The analysis of water and waste water by U. S. EPA method 200.7 using the optima 8300 ICP-OES and prepFAST Auto dilutin/calibration system 2003.
25. SHRIVASTAVA S. K, BANERJEE D.K. Speciation of metals in sewage sludge amended soils, Water, Air and Soil Pollution 152, 219-232, 2004.
26. SOBCZYNSKI T., SIEPAK J. Speciation of heavy metals in bottom sediments of lakes in the area of Wielkopolski National Park, Polish Journal of Environmental Studies 10 (6) 463-474, 2001.
27. ANJU M., BANARJEE D.K. Associations of cadmium, zinc and lead in soils from a lead and zinc mining area as studied by single and sequential extractions, Environmental Monitoring and Assessment, 176 (1) 67-85, 2011.
28. KASHEM M.A., SINGH B.R., KONDO T., IMAMUL HUQ S.M., KAWA S. Comparison of extractability of Cd, Cu, Pb and Zn with sequential extraction in contaminated and non-contaminated soils, International Journal of Environmental Science and Technology 4 (2) 169-176, 2007.
29. NORDBERG G.F. Chelating agents and cadmium toxicity: Problems and prospects", Environmental Health and Perspective 54 (1) 213-218, 1984.
30. SEARS M.E., KER K.J.R., BRAY R.I. Arsenic, cadmium, lead and mercury in sweat: A systematic review, Journal of Environmental and Public Health, 2012 (2012) 1-10, 2012.
31. NG S.K., EBNETER A., GILHOTRA J.S. Hip-implant related chorio-retinal cobalt toxicity, Indian Journal of Ophthamology, 63 (1) 35-37, 2013.
32. ZHANG M.K., LIU X.Y., WANG H. Use of single extraction methods to predict the bioavailability of heavy metals in polluted soils to rice, Communications in Soil Science and Plant Analysis 41 (7) 820-831, 2010.
33. CHEN Y., XU M., CHEN J., SHI X. Differentiation of eight teas (Camellia sinensis) cultivars in China by elemental fingerprint of their leaves, Journal of the Science of Food and Agriculture 89 (1) 2350-2355, 2011.

34. RABINOWITZ M.B., BELLINGER D.C. Soil lead blood lead relationship among Boston children, Bulletin of Environmental Contamination and Toxicology, Springer-Verlag, New York, 1993.
35. STAUDINGER K.C., ROTH V.S. Occupational lead poisoning, American Family Physician 57 (4) 719–726, 1998.
36. OGUNSEITAN O.A., SCHOENUNG J.M., SAPHORES J.D., SHAPIRO A.A. The electronics revolution: From e-wonderland to e-wasteland, Science 326 (5953) 670-671, 2007.
37. LIANG Q., ZHOU B. Copper and manganese induce yeast apoptosis via different pathways, Molecular Biology of the Cell 8 (13) 4741-4749, 2007.
38. LAWRENCE A.L., FOX J., CASTILLE JR. F.J. Decreased toxicity of copper and manganese ions to shrimp Nauplii in the presence of EDTA, Journal of the World Aquaculture Society 12 (1) 271-280, 2009.
39. MOHAMMED S.S., BATU M.A., MOHAMMED M.B. Analysis of chromium in dumpsite samples using AAS and EDXRF techniques, Research Journal of Chemical Science 2 (12) 65-68, 2012.
40. IWEGBUE C.M.A, AROMORO F.O., IWEGBUE C.E., EGUAVOEN O. Levels of Cd, Cu, Cr, Ni, Zn, Pb and Mn in some species from Orogodo river, Nigeria, Journal of the Chemical Society of Nigeria 36 (1) 37-41, 2011.
41. SCHWARZ K. Elements newly identified as essential for animals, International Atomic Energy, 5th ed. Vienna, 1972.
42. SEIDAL J.C., CORWIN C.J. Total chromium and hexavalent chromium occurrence analysis, Water Reserve Foundation, USEPA, Denver, 2007.
43. ACOSTA A., MUNEVAR F. Bud rot on oil palm plantations: Link to soil physical properties and nutrient status, Better Crops International, 17 (2) 22-25, 2003.
44. AWETO A.O., ENARUVBE G.O. Catenary properties of soil properties under oil palm plantations in southwestern Nigeria, Ethiopian Journal of Environmental Studies and Management, 3 (1) 1-7, 2007.
45. FRY R.S., ASHWELL M.S., LLOYD K.E., O'NAN A.T., FLOWERS W.L., STEWART K.R., SPEARS J.W. Amount and source of dietary copper affects small intestine morphology, duodenal lipid peroxidation, hepatic oxidative stress and MRNA expression of hepatic copper regulatory proteins in weanling pigs, Journal of Animal Science, 90 (90) 3112-3119, 2012.
46. ZHANG P.D. Determination of copper in wastewater by beta-convection new spectrophotometry, Public Medicine, 19 (3) 471-473, 1999.

47. STEVENS R.G., JONES D.Y., MICOZZI M.S., TAYLOR P.R. Body iron stores and the risk of cancer, Northern England Journal of Medicine, 319 (1) 1047-1052, 1988.
48. COMRAD M.E. Excess iron and catastrophic illness, American Journal of Hematology 43 (1) 234-236, 1993.
49. CHEN J.B., SIGNY B.U., GAILLARDET J., LOUVAT B., YANG Y.N. Iron isotopes in the Seine river (France): Natural versus anthropogenic sources, Geochimica et Cosmochimica Acta, 128 (1) 128-143, 2014.
50. WELCH A.H., WESTJOHN D.B., HELSEL D.R., WANTY D.B. Arsenic in ground water in the United States. Occurrence and geochemistry, Ground Water, 38 (1) 589-604, 2000.
51. HAJO H., LOTHAR R. The immune system and the impact of zinc during aging, Immunity and Aging, 6 (9) 1-17, 2009.
52. HARTLEY C.N. The Oil palm, 1st ed. Longman Scientific Technical, UK, 1988.
53. FOSMIRE J. Zinc toxicity, American Journal of Clinical Nutrition, 51 (2) 225-227, 1990.
54. KUCHA H., MARTINS A., OTTENBURGS R. Primary minerals of Zn-Pb mining and metallurgical dumps and their environmental behaviour at Pllombiers, Belgium, European Journal of Mineralogy, 8 (1) 93-102, 1996.

**Table 5.1: Physical characteristics of soil**

| Location | pH | Electrical Conductivity ( S/cm) | Soil Organic Matter (%) |
|---|---|---|---|
| Abak | 5.12 | 105 | 3.26 |
| Acharu | 5.58 | 134 | 7.86 |
| Agbarho | 5.15 | 23 | 3.39 |
| Ago-Emokpae | 5.41 | 190 | 9.73 |
| Apoje | 5.51 | 104 | 3.54 |
| Badagry | 5.01 | 229 | 4.06 |
| Benin City | 5.06 | 30 | 3,45 |
| Igede- Ekiti | 7.01 | 137 | 3.82 |
| Ikire | 5.47 | 122 | 4.08 |
| Iresa-apa | 5.37 | 225 | 5.03 |
| Nsukka | 5.16 | 171 | 3.45 |
| Onishere | 5.02 | 22 | 3.79 |
| Okitipupa | 5.18 | 111 | 3.24 |
| Ubiaja | 4.96 | 216 | 4.47 |
| Umuabi | 5.41 | 19 | 2.76 |

**Table 5.2: Concentration of metals in soil (mg/L)**

| Location | Fraction | Cd | Co | Cr | Cu | Fe | Mn | Pb | Ni | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| Abak | Exchangeable | 44.7±0.1 | 12.7±0.1 | 3.9±0.1 | 8.9±0.1 | 3.1±0.1 | 16.3±0.1 | 14.5±0.1 | 7.5±0.1 | 10.9±0.1 |
| | Bound to Fe and Mn oxides | 18.1±0.2 | 29.9±0.1 | 1.5±0.1 | 4.5±0.1 | 4.7±0.1 | 35.6±0.1 | 13.9±0.1 | 8.5±0.1 | 9.7±0.1 |
| | Bound to organic matter | 20.5±0.1 | 18.2±0.3 | 9.0±0.1 | 10.6±0.1 | 1.8±0.1 | 17.5±0.1 | 22.7±0.1 | 8.1±0.1 | 9.2±0.1 |
| | Residual | 25.6±0.1 | 54.6±0.4 | 90.9±0.1 | 89.4±0.1 | 99.2±0.2 | 39.4±0.1 | 57.0±0.1 | 83.0±0.2 | 84.5±0.1 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Acharu | Exchangeable | 49.0±0.1 | 19.7±0.1 | 3.0±0.1 | 8.2±0.1 | 5.3±0.1 | 20.0±0.1 | 19.6±0.1 | 6.9±0.1 | 13.4±0.2 |
| | Bound to Fe and Mn oxides | 18.4±0.1 | 29.7±0.1 | 4.8±0.2 | 8.8±0.1 | 3.6±0.1 | 40.5±0.1 | 11.4±0.1 | 6.1±0.1 | 9.9±0.1 |
| | Bound to organic matter | 26.5±0.2 | 14.2±0.1 | 8.1±0.1 | 7.8±0.1 | 3.6±0.1 | 15.8±0.1 | 23.2±0.1 | 6.4±0.1 | 7.5±0.1 |
| | Residual | 21.8±0.1 | 53.0±0.1 | 93.4±0.4 | 89.0±0.3 | 93.3±0.1 | 37.6±0.1 | 55.1±0.1 | 85.8±0.2 | 83.6±0.2 |
| Agbarho | Exchangeable | 44.9±0.1 | 16.9±0.1 | 6.8±0.1 | 14.6±0.1 | 6.1±0.1 | 13.1±0.1 | 12.4±0.1 | 8.8±0.2 | 18.0±0.1 |
| | Bound to Fe and Mn oxides | 18.1±0.1 | 28.6±0.1 | 4.6±0.1 | 6.8±0.1 | 5.3±0.1 | 49.0±0.1 | 11.7±0.3 | 4.3±0.1 | 7.7±0.1 |
| | Bound to organic matter | 22.4±0.1 | 13.1±0.1 | 8.5±0.1 | 5.7±0.1 | 3.4±0.1 | 16.7±0.1 | 19.8±0.1 | 7.7±0.2 | 7.1±0.1 |
| | Residual | 22.3±0.1 | 41.9±0.1 | 81.3±0.1 | 94.2±0.1 | 94.8±0.1 | 36.7±0.2 | 58.2±0.2 | 85.9±0.1 | 87.9±0.1 |
| Ago-Emokpae | Exchangeable | 43.9±0.1 | 22.7±0.4 | 4.7±0.1 | 6.9±0.1 | 5.6±0.1 | 13.7±0.1 | 15.1±0.1 | 7.4±0.1 | 13.9±0.1 |
| | Bound to Fe and Mn oxides | 18.0±0.1 | 30.1±0.1 | 1.8±0.1 | 4.8±0.1 | 6.1±0.1 | 43.4±0.1 | 12.3±0.1 | 4.6±0.1 | 2.0±0.1 |
| | Bound to organic matter | 22.5±0.1 | 13.8±0.1 | 8.9±0.1 | 6.7±0.1 | 2.4±0.1 | 18.9±0.2 | 12.4±0.1 | 7.1±0.1 | 6.5±0.1 |
| | Residual | 21.8±0.1 | 42.5±0.1 | 82.1±0.2 | 92.9±0.1 | 98.4±0.2 | 37.5±0.1 | 59.7±0.1 | 85.6±0.2 | 85.7±0.1 |
| Apoje | Exchangeable | 45.1±0.1 | 17.1±0.1 | 3.4±0.1 | 7.9±0.1 | 5.7±0.1 | 14.2±0.1 | 13.5±0.1 | 9.1±0.1 | 18.9±0.1 |
| | Bound to Fe and Mn oxides | 22.5±0.1 | 25.0±0.1 | 8.1±0.1 | 1.2±0.1 | 9.9±0.1 | 37.1±0.1 | 18.0±0.1 | 2.2±0.1 | 5.7±0.1 |
| | Bound to organic matter | 24.0±0.1 | 12.7±0.1 | 3.4±0.1 | 6.5±0.1 | 2.7±0.2 | 19.8±0.1 | 19.2±0.1 | 3.5±0.3 | 4.8±0.2 |
| | Residual | 37.3±0.1 | 49.2±0.3 | 82.7±0.1 | 97.7±0.2 | 93.0±0.1 | 36.2±0.1 | 59.3±0.1 | 85.9±0.1 | 89.6±0.1 |
| Badagry | Exchangeable | 48.4±0.1 | 12.1±0.1 | 1.3±0.1 | 9.1±0.1 | 1.1±0.1 | 16.5±0.1 | 12.2±0.1 | 6.2±0.1 | 8.1±0.2 |
| | Bound to Fe and Mn oxides | 28.2±0.1 | 19.5±0.1 | 9.8±0.1 | 5.8±0.1 | 9.7±0.2 | 39.7±0.1 | 9.8±0.1 | 3.4±0.1 | 6.3±0.1 |
| | Bound to organic matter | 24.5±0.2 | 19.8±0.1 | 7.6±0.3 | 6.2±0.3 | 3.9±0.1 | 18.6±0.1 | 17.0±0.1 | 4.1±0.1 | 5.0±0.1 |
| | Residual | 26.7±0.1 | 40.6±0.1 | 82.6±0.1 | 93.9±0.1 | 94.2±0.1 | 34.9±0.1 | 56.5±0.1 | 89.7±0.2 | 89.7±0.1 |
| Benin City | Exchangeable | 44.2±0.1 | 12.1±0.1 | 3.5±0.1 | 8.3±0.1 | 3.4±0.1 | 16.4±0.1 | 14.4±0.1 | 8.6±0.1 | 8.8±0.1 |
| | Bound to Fe and Mn oxides | 19.5±0.1 | 16.4±0.2 | 6.2±0.3 | 6.2±0.1 | 5.7±0.1 | 36.9±0.2 | 8.8±0.1 | 4.2±0.1 | 7.9±0.1 |
| | Bound to organic matter | 28.7±0.1 | 22.0±0.1 | 5.4±0.1 | 6.5±0.1 | 2.1±0.1 | 19.3±0.1 | 22.9±0.1 | 6.3±0.1 | 7.3±0.2 |
| | Residual | 28.9±0.2 | 45.5±0.1 | 84.7±0.1 | 94.7±0.1 | 88.5±0.1 | 43.3±0.1 | 55.7±0.1 | 86.0±0.1 | 98.1±0.3 |
| Igede-Ekiti | Exchangeable | 47.9±0.1 | 11.1±0.1 | 3.4±0.1 | 7.3±0.1 | 6.5±0.1 | 18.1±0.1 | 13.2±0.1 | 4.1±0.1 | 9.7±0.1 |
| | Bound to Fe and Mn oxides | 22.7±0.1 | 17.3±0.1 | 6.4±0.1 | 9.6±0.1 | 3.6±0.1 | 27.9±0.1 | 2.6±0.1 | 3.2±0.1 | 8.5±0.1 |
| | Bound to organic matter | 26.2±0.2 | 17.5±0.1 | 8.3±0.1 | 6.8±0.1 | 2.6±0.1 | 18.7±0.1 | 22.9±0.1 | 2.7±0.1 | 9.2±0.1 |
| | Residual | 39.4±0.1 | 39.9±0.2 | 73.4±0.1 | 76.0±0.3 | 97.9±0.1 | 44.8±0.1 | 59.6±0.1 | 86.5±0.2 | 82.3±0.1 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Ikire | Exchangeable | 49.5±0.1 | 12.8±0.1 | 2.2±0.1 | 6.8±0.1 | 3.9±0.1 | 14.7±0.1 | 13.0±0.1 | 9.2±0.1 | 6.3±0.1 |
| | Bound to Fe and Mn oxides | 16.1±0.1 | 23.1±0.1 | 3.7±0.1 | 7.1±0.1 | 5.7±0.1 | 27.1±0.1 | 5.2±0.2 | 7.8±0.1 | 5.1±0.1 |
| | Bound to organic matter | 25.7±0.3 | 16.2±0.1 | 4.9±0.1 | 5.5±0.1 | 1.1±0.1 | 26.4±0.1 | 27.8±0.1 | 2.0±0.1 | 9.8±0.2 |
| | Residual | 31.2±0.1 | 36.9±0.2 | 88.0±0.2 | 85.6±0.1 | 82.8±0.1 | 34.9±0.2 | 50.9±0.1 | 97.6±0.3 | 86.9±0.1 |
| Iresa-apa | Exchangeable | 45.2±0.1 | 13.2±0.1 | 4.6±0.1 | 7.8±0.1 | 4.2±0.1 | 14.0±0.1 | 13.5±0.1 | 6.4±0.1 | 6.7±0.1 |
| | Bound to Fe and Mn oxides | 18.6±0.1 | 24.4±0.1 | 9.0±0.1 | 3.1±0.1 | 8.1±0.1 | 22.7±0.1 | 8.6±0.1 | 29.9±0.1 | 4.8±0.1 |
| | Bound to organic matter | 23.9±0.1 | 15.5±0.1 | 6.7±0.1 | 5.4±0.1 | 1.8±0.1 | 29.6±0.1 | 24.2±0.1 | 3.2±0.1 | 7.3±0.1 |
| | Residual | 29.7±0.1 | 27.8±0.1 | 80.8±0.2 | 76.5±0.1 | 83.5±0.1 | 49.4±0.1 | 50.8±0.3 | 67.1±0.2 | 82.4±0.3 |
| Nsukka | Exchangeable | 54.2±0.1 | 14.9±0.1 | 3.2±0.1 | 5.7±0.1 | 7.1±0.1 | 17.0±0.1 | 12.5±0.1 | 3.5±0.1 | 9.6±0.1 |
| | Bound to Fe and Mn oxides | 15.9±0.1 | 23.4±0.1 | 4.5±0.1 | 3.2±0.3 | 9.8±0.1 | 35.8±0.1 | 8.6±0.1 | 27.3±0.1 | 7.2±0.1 |
| | Bound to organic matter | 27.9±0.1 | 16.1±0.2 | 9.1±0.1 | 6.3±0.1 | 2.6±0.1 | 23.2±0.2 | 27.0±0.1 | 9.4±0.1 | 7.5±0.1 |
| | Residual | 28.1±0.1 | 27.5±0.1 | 88.5±0.1 | 79.2±0.1 | 85.5±0.1 | 44.6±0.1 | 65.2±0.1 | 61.0±0.1 | 88.1±0.1 |
| Okitipupa | Exchangeable | 44.5±0.1 | 14.6±0.1 | 8.3±0.1 | 6.0±0.1 | 4.9±0.1 | 14.9±0.1 | 12.0±0.1 | 1.5±0.1 | 9.3±0.1 |
| | Bound to Fe and Mn oxides | 27.8±0.1 | 29.0±0.1 | 5.7±0.1 | 3.4±0.1 | 8.6±0.1 | 38.2±0.1 | 7.1±0.1 | 34.7±0.1 | 5.5±0.1 |
| | Bound to organic matter | 33.4±0.1 | 18.6±0.1 | 3.0±0.1 | 6.0±0.1 | 1.1±0.1 | 23.7±0.1 | 27.6±0.1 | 68.8±0.1 | 6.7±0.1 |
| | Residual | 29.6±0.1 | 13.9±0.1 | 88.8±0.2 | 83.5±0.1 | 64.3±0.1 | 41.5±0.1 | 58.5±0.3 | 51.1±0.1 | 69.0±0.1 |
| Onisher e | Exchangeable | 41.9±0.1 | 13.7±0.1 | 8.6±0.2 | 4.7±0.1 | 7.8±0.1 | 12.1±0.2 | 16.3±0.1 | 1.9±0.1 | 7.0±0.1 |
| | Bound to Fe and Mn oxides | 15.6±0.1 | 33.8±0.2 | 5.1±0.1 | 5.9±0.1 | 3.4±0.1 | 35.8±0.1 | 5.9±0.1 | 33.1±0.1 | 8.1±0.1 |
| | Bound to organic matter | 23.2±0.1 | 12.7±0.1 | 2.7±0.1 | 6.8±0.1 | 3.2±0.3 | 22.7±0.1 | 33.8±0.1 | 6.6±0.1 | 2.4±0.1 |
| | Residual | 25.0±0.2 | 20.1±0.1 | 81.9±0.1 | 82.4±0.1 | 72.1±0.1 | 33.6±0.1 | 57.0±0.2 | 80.5±0.3 | 96.7±0.1 |
| Ubiaja | Exchangeable | 38.7±0.1 | 15.8±0.1 | 7.9±0.1 | 5.1±0.3 | 6.2±0.1 | 15.2±0.1 | 14.6±0.1 | 3.7±0.1 | 5.9±0.1 |
| | Bound to Fe and Mn oxides | 17.1±0.1 | 33.0±0.1 | 2.1±0.1 | 8.2±0.1 | 6.8±0.1 | 33.4±0.1 | 5.5±0.2 | 33.2±0.1 | 5.0±0.2 |
| | Bound to organic matter | 28.6±0.2 | 19.4±0.2 | 9.9±0.1 | 6.6±0.1 | 2.4±0.2 | 18.7±0.1 | 30.7±0.1 | 9.0±0.1 | 2.6±0.1 |
| | Residual | 39.4±0.1 | 26.5±0.1 | 72.0±0.1 | 85.4±0.2 | 76.3±0.1 | 39.0±0.1 | 52.1±0.1 | 81.8±0.1 | 99.1±0.1 |
| | | | | | | | | | | |
| Umuabi | Exchangeable | 35.4±0.1 | 21.3±0.1 | 3.1±0.1 | 6.0±0.1 | 6.5±0.1 | 17.2±0.1 | 19.7±0.1 | 4.1±0.3 | 9.6±0.1 |
| | Bound to Fe and Mn oxides | 17.5±0.2 | 38.6±0.1 | 2.8±0.1 | 4.7±0.2 | 8.0±0.3 | 18.7±0.1 | 33.0±0.2 | 37.5±0.1 | 33.1±0.1 |

# CHAPTER SIX

## Natural radionuclide activities in soil on oil palm plantations

Otolorin Adelaja Osibote[1*], Oluwafemi Oguntibeju[2], Bola Oladunni Olafisoye[3]

[1*]Faculty of Applied Sciences, Department of Mathematics and Physics, Cape Peninsula University of Technology, Cape Town, South Africa

[2]Faculty of Health and Wellness Sciences, Department of Biomedical Sciences, Cape Peninsula University of Technology, Bellville, South Africa

[3]Faculty of Applied Sciences, Department of Chemistry, Cape Peninsula University of Technology, Cape Town, South Africa

**Abstract**

Naturally occurring radionuclide activity was investigated on soils from oil palm plantations using a Hyper-Pure Germanium detector with appropriate shielding coupled to a Canberra Multichannel Analyser. Activity concentrations of the radionuclides $^{238}$U, $^{232}$Th and $^{40}$K were obtained from the activity concentrations of their respective daughter radionuclides. The activity concentrations at a soil depth 0 – 15 cm ranged from 187.4 to 514.4, 2.328 to 6.571, and 1.509 to 6.121 Bq/kg for $^{40}$K, $^{238}$U, and $^{232}$Th, respectively. For the risk assessments, the Absorbed Dose Rate (D) ranged from 11.5 to 24.54 nGy/h, while the Annual Effective Dose Equivalent (E) ranged from $1.4 \times 10^{-2}$ to $2.98 \times 10^{-2}$ mSv/y and the Radium Equivalent ranged between 21.72 to 49.14 Bq/kg in soils of depth 0-15 cm. The values were lesser than the worldwide values. None of the samples exceeded the permissible levels of 370 Bqkg$^{-1}$ recommended for radium equivalent by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). Other radiological hazards in terms of Internal and External hazard indices and Representative hazard index were determined and found to be within safe limits.

***Keywords: Oil palm plantation Radionuclide, Activity Concentration, Dose Rate, gamma-ray, HPGe detector***

### 6.1 Introduction

Naturally Occurring Radioactive Materials (NORM) are radioactive substances which occur naturally in the environment. Humans are exposed to radiations from NORM mainly from decay

series headed by $^{238}U$ and $^{232}Th$, and a third non-series natural radionuclide, $^{40}K$ in the soil and rocks in our environment and other human activities such as as the fallout from nuclear weapon testing and nuclear accidents [1-2]. As reported, no matter the origin; natural or human made, these radioactive materials pass through the food chain in the same way as non-radioactive materials [3].

The degree of harm to human health depends on the type of radionuclides and the length of time people are exposed to it. The amount of radiation people are exposed to vary from place to place and among individuals [3-5]. In addition, background levels of radionuclides vary and depend on factors such as the geographical region, farming practises on agricultural lands, abandoned mines and industrial sites and thermonuclear testing of nuclear power plants, all these can lead to increase in the risk of radionuclide contamination via ground water and soil to food. The determination of the level of radionuclides is essential since their radiotoxicity could subsequently contribute to a high contribution of cumulated dose to man.

The common radionuclides in food and environmental samples are Potassium-40 ($^{40}K$), Thorium-232 ($^{232}Th$) and Uranium 238 ($^{238}U$) and their associated progeny [4]. In general, $^{40}K$ is the most commonly occurring natural radioisotope. Other natural radioisotopes exist in much lower concentrations, and originate from the decay of Uranium and Thorium [5]. As reported by the World Health Organisation (WHO), the main health concern for consumers in the long term due to high radiation exposure is development of cancer. Cancer types and target organs depend on the radionuclides [5]. Data on the analysis of gamma radiation on soil samples from oil palm plantations is sparse or none existent. Therefore, it is necessary to study the radioactivity in soil from oil palm plantation as radionuclides are transferred through soil into crops and animals, or into rivers, lakes and the sea where fish and other seafood could take up the radionuclides as reported by World Health Organization [3-5]. This work presents the evaluation of the activities of naturally occurring radioactive materials studied in soil samples from oil palm plantations.

## 6.2 Materials and methods

### 6.2.1 Sampling area and sampling preparations

The study area comprises of the Nigeria Institute for Oil Palm Research (NIFOR) Headquarters and its substations in states located at the southern area of Nigeria. The topography and physiology of the area falls within a humid tropical region and vegetation is mostly forest type. The choices of sampling locations were centred on reasons such as population density, farming communities and regions receiving major contamination from industrial activities. A composite sample was collected and used for analysis, which was achieved by partitioning the sampling locations into four parts. Soils collected were sampled at a depth of 0-30 cm. An

auger was used for soil sample collection and the samples were stored in black sterilized plastic bags. The apparatus used for sampling were properly washed in nitric acid and rinsed with high purity deionized water (Milli-Q water purification system, Millipore, Belford, MA, USA). The collected samples were then placed in labelled polythene bags and transferred to Center for Energy and Research Development (CERD) laboratory, Obafemi Awolowo University, Ile Ife for preparation and analysis. Soil samples were air-dried, sieved using a 2 mm sieve, and further dried at 105±50˚C for 3 hours. The soils were then tightly sealed in Marinelli beakers using the same geometry as the reference samples. They were kept for 28 days to achieve secular equilibrium prior to gamma spectroscopy [6-8].

### 6.2.2 Gamma spectrometry

The gamma-counting equipment was a Canberra vertical high-purity coaxial germanium (HPGe) crystal detector, model GC2018-7500, series number b 87063 enclosed in a 100 mm thick lead shield and coupled to a Canberra Multichannel Analyser (MCA) computer system. Calibration of the energy and efficiency of radionuclides was performed with the aid of a well-calibrated standard soil reference standard source supplied by the International Atomic Energy Agency (IAEA), Vienna. The MCA was calibrated to display gamma photopeaks in the energy range of 200—1500 keV, this being the energy range covering all the gamma energies of radionuclides of interest identified with reliable regularity (many other peaks outside this energy range are useful too). The detector chamber was shielded with three layers of copper, cadmium, and lead of 30 mm, 3 mm and 100 mm thick, respectively.

The analytical method was effective because it provided a non-destructive method of analysis for quantification and qualitative identification of radionuclides in environmental samples. The photo-peaks observed with regularity in the samples were identified to belong to the natural radioactive decay series headed by $^{238}$U and $^{232}$Th, and a third non-series natural radionuclide, $^{40}$K, for a counting time of 36000 seconds. The activity of the natural radionuclides was calculated using equation 6.1.

$$A_s = \frac{C_a}{E\ P_r\ M_s} \ldots\ldots\ldots Equation\ 6.1$$

where $Ca$ is the net counting rate of gamma ray (counts per second), $E$ is the detector efficiency of the specific gamma ray, $Pr$ is the absolute transition probability of gamma decay and $Ms$ the mass of the sample (kg) [8-9].

### 6.3 Calculation of the radiological effect

To compare the combined radiological effect of the soil containing these radionuclides by a single quantity, a collective index called the Radium Equivalent was used to describe the gamma radiation from the varying mixtures of the radionuclides in the soil [4, 7-10].

Radium equivalent ($Ra_{eq}$), Absorbed Dose (D), Annual Effective Dose Equivalent (E), External Radiation Hazard Index (Hex) and Internal Radiation Hazard ($H_{in}$) have been used for the assessment of naturally occurring radioactive materials $^{238}U$, $^{232}Th$ and $^{40}K$.

#### 6.3.1 Radium equivalent ($Ra_{eq}$)

Radium Equivalent was used to describe the gamma radiation from the varying mixtures of the radionuclides in the soil and is calculated using the relation

$$Raeq = CRa + 1.43CTh + 0.077CK \ldots\ldots\ldots Equation\ 6.2$$

Where: $CRa$, $CTh$ and $CK$ are the activity concentrations of $^{226}Ra$, $^{232}Th$ and $^{40}K$ respectively. The index represents a weighted total of the above-mentioned radionuclides' activity concentrations because of an assumption that states that 1 Bq/Kg of $^{226}Ra$, 0.7 Bq/Kg of $^{232}Th$ and 13 Bq/Kg of $^{40}K$ produce an equal amount of gamma radiation dose [11, 12, 14-18].

#### 6.3.2 Absorbed dose rate (D)

United Nations Scientific Committee on the Effects of Atomic Radiation [UNSCEAR] defines the Absorbed dose rate as a quantity which is a measure of the energy deposited in matter by ionizing radiation per unit mass [13]. D was calculated using equation 6.3.

$$D\left(\frac{nGy}{h}\right) = 0.462CRa + 0.604CTh + 0.0417CK \ldots\ldots\ldots Equation\ 6.3$$

This is the absorbed dose rate in air outdoor at 1 m above the ground surface due to specific activity concentrations of $^{238}U$, $^{232}Th$ and $^{40}K$ [4, 8, 13].

#### 6.3.3 Annual effective dose equivalent (E)

Annual effective dose equivalent E is the parameter to determine the overall effects of the radiation on health due to the absorbed dose rate and calculated by the equation

$$E\left(\frac{mSv}{y}\right) = D\left(\frac{nGy}{h}\right) X\ 8760\left(\frac{h}{y}\right) X\ 0.2\ X\ 0.7\left(\frac{Sv}{Gy}\right) X\ 10^{-6} \ldots\ldots\ldots Equation\ 6.4$$

Where the values 0.7 $SvGy^{-1}$ is the conversion coefficient from absorbed dose in the air 1m above ground to effective dose received by adults, 8760 is the time taken in hours in a particular year, 0.2 represents the outdoor occupancy factor [13] and D and is the observed dose rate.

### 6.3.4 External and Internal hazard index and representative level index

**External Hazard Index** is used to estimate the external exposure and it is calculated using the equation

$$Hex = CRa/(370\ Bq/kg) + CTh/(259\ Bq/kg) + CK/(4810\ Bq/kg) \ldots\ldots\ldots Equation\ 6.5$$

Where $CRa$, $CTh$ and $CK$ are the activity concentrations in Bq/kg for $^{226}Ra$, $^{232}Th$ and $^{40}K$ respectively and this value must be less than unity which means that the radiation dose must be in the accepted dose limit of 1 mSv/y and this corresponds to the upper limit of $Ra_{eq}$ of 370 Bq/kg [14].

**Internal Hazard Index** is used to estimate the internal exposure to radon and its daughter products, which must be less than unity is calculated using the equation

$$Hin = CRa/(158\ Bq/kg) + CTh/(259\ Bq/kg) + CK/(4810\ Bq/kg) \ldots\ldots\ldots Equation\ 6.6$$

**Representative level index** is the approximation of gamma radiation associated with natural radionuclide activity that is calculated from the equation

$$H\gamma r = CRa/(150\ Bq/kg) + CTh/(100\ Bq/kg) + CK/(1500\ Bq/kg) \ldots\ldots\ldots Equation\ 6.7$$

This value must be less than unity [14].

## 6.4 Results and discussions

The activities of various radionuclides were determined in Bq $kg^{-1}$ using the count spectra obtained from each of the samples. The gamma ray photopeaks corresponding to the energy of 295.1 keV and 352 keV ($^{214}Pb$), 609.3 keV and 1120.3 keV ($^{214}Bi$) were considered to determine the activity concentration of $^{238}U$. The $^{232}Th$ activity concentration was determined from the gamma peaks of 238.6 keV ($^{212}Pb$) and 338.4, 911.2, and 969 keV ($^{228}Ac$) and 583.0 keV ($^{208}Tl$). The $^{40}K$ activity concentration was calculated from the 1460 keV gamma ray line. The mean and standard deviations activity concentrations of $^{40}K$, $^{238}U$, and $^{232}Th$ in soils on the oil palm plantations are presented in Table 6.1. The Radium equivalent, Dose rate and Annual

effective dose equivalent at 0 -15 cm depths are presented in Table 6. 2. Table 6.3 represents the internal and external hazard index and representative level index in soils at depth 0-15 cm and 15-30 cm.

**Table 6.1: Concentration values for NORM in soils**

| (0-15) cm | Activity of $^{40}K$ ($Bqkg^{-1}$) | Activity of $^{238}U$ ($Bqkg^{-1}$) | Activity of $^{232}Th$ ($Bqkg^{-1}$) | (15-30) cm | Activity of $^{40}K$ ($Bqkg^{-1}$) | Activity of $^{238}U$ ($Bqkg^{-1}$) | Activity of $^{232}Th$ ($Bqkg^{-1}$) |
|---|---|---|---|---|---|---|---|
| Abak | 430.9±0.07 | 4.905±0.02 | 4.929±0.06 | Abak | 343.2±0.03 | 2.467±0.01 | 4.935±0.09 |
| Acharu | 444.66±0.01 | 3.228±0.07 | 1.820±0.01 | Acharu | 421.6±0.01 | 2.392±0.02 | 4.365±0.01 |
| Agbarho | 345.0±0.17 | 5.176±0.19 | 3.148±0.05 | Agbarho | 463.2±0.02 | 4.877±0.03 | 5.041±0.02 |
| Ago-Emokpae | 389.7±0.08 | 5.778±0.02 | 3.426±0.02 | Ago-Emokpae | 653.4±0.03 | 6.575±0.04 | 4.770±0.02 |
| Apoje | 434.6±0.01 | 4.153±0.04 | 1.777±0.09 | Apoje | 219.2±0.01 | 4.680±0.05 | 1.476±0.13 |
| Badagry | 193.9±0.67 | 3.812±0.45 | 2.732±0.04 | Badagry | 211.4±0.02 | 1.802±0.02 | 4.007±0.22 |
| Benin City | 187.4±0.34 | 6.173±0.23 | 4.816±0.01 | Benin City | 281.1±0.02 | 9.410±0.09 | 6.275±0.34 |
| Igede Ekiti | 411.5±0.05 | 5.030±0.01 | 6.121±0.02 | Igede Ekiti | 467.5±0.05 | 6.579±0.02 | 4.237±0.98 |
| Ikire | 514.4±0.04 | 3.471±0.13 | 4.237±0.03 | Ikire | 169.0±0.01 | 1.726±0.01 | 1.829±0.22 |
| Iresa Apa | 455.8±0.03 | 6.571±0.23 | 4.121±0.09 | Iresa Apa | 163.4±0.03 | 1.345±0.03 | 3.613±0.12 |
| Nsukka | 309.2±0.01 | 2.328±0.11 | 4.760±0.01 | Nsukka | 318.8±0.02 | 1.789±0.03 | 3.500±0.32 |
| Okitipupa | 302.7±0.04 | 3.189±0.02 | 5.988±0.03 | Okitipupa | 602.7±0.04 | 3.788±0.12 | 4.239±0.11 |
| Onishere | 405.5±0.08 | 5.462±0.11 | 3.855±0.21 | Onishere | 507.4±0.05 | 5.775±0.99 | 5.472±0.01 |
| Ubiaja | 458.5±0.01 | 3.106±0.03 | 5.476±0.02 | Ubiaja | 451.7±0.02 | 5.064±0.34 | 2.343±0.01 |
| Umuabi | 475.6±0.03 | 2.884±0.01 | 1.509±0.02 | Umuabi | 281.3±0.01 | 2.327±0.15 | 4.264±0.02 |

**Table 6.2: Values for Ra, D and E in soils**

| | Soil depth 0-15 cm | | |
|---|---|---|---|
| | $Ra_{(eq)}$ (Bq/kg) | D (nGy/h) | E(mSv/y) ($\times 10^{-2}$) |
| Abak | 45.13 | 23.21 | 2.82 |
| Acharu | 38.07 | 21.13 | 2.59 |
| Agbarho | 36.25 | 21.12 | 2.56 |
| Ago-Emokpae | 40.69 | 20.99 | 2.55 |
| Apoje | 40.15 | 21.11 | 2.56 |
| Badagry | 22.65 | 11.50 | 1.40 |
| Benin City | 27.49 | 13.58 | 1.65 |
| Igede Ekiti | 45.47 | 23.18 | 2.81 |
| Ikire | 49.14 | 23.17 | 2.81 |
| Iresa Apa | 47.56 | 24.54 | 2.98 |
| Nsukka | 37.19 | 16.85 | 2.04 |

| | | | |
|---|---|---|---|
| Okitipupa | 21.72 | 17.71 | 1.41 |
| Onishere | 42.20 | 21.76 | 2.64 |
| Ubiaja | 46.25 | 23.87 | 2.90 |
| Umuabi | 41.66 | 22.07 | 2.68 |

**Table 6.3: Hx, Hin and Hyr**

| Sampling sites | Hex Soil depth 0-15 cm | Hex Soil depth 15-30 cm | Hin Soil depth 0-15 cm | Hin Soil depth 15-30 cm | Hyr Soil depth 0-15 cm | Hyr Soil depth 15-30 cm |
|---|---|---|---|---|---|---|
| Abak | 0.121 | 0.097 | 0.139 | 0.106 | 0.813 | 0.370 |
| Acharu | 0.108 | 0.111 | 0.119 | 0.119 | 0.336 | 0.341 |
| Agbarho | 0.098 | 0.129 | 0.117 | 0.147 | 0.297 | 0.392 |
| Ago-Emokpae | 0.110 | 0.172 | 0.131 | 0.196 | 0.333 | 0.528 |
| Apoje | 0.108 | 0.064 | 0.123 | 0.081 | 0.336 | 0.192 |
| Badagry | 0.061 | 0.064 | 0.079 | 0.467 | 1.345 | 0.193 |
| Benin City | 0.074 | 0.108 | 0.097 | 0.143 | 0.214 | 0.317 |
| Igede Ekiti | 0.123 | 0.034 | 0.141 | 0.058 | 0.369 | 0.086 |
| Ikire | 0.133 | 0.046 | 0.145 | 0.053 | 0.408 | 0.143 |
| Iresa Apa | 0.129 | 0.052 | 0.153 | 0.057 | 0.389 | 0.154 |
| Nsukka | 0.071 | 0.681 | 0.080 | 0.067 | 0.270 | 0.217 |
| Okitipupa | 0.032 | 0.152 | 0.043 | 0.164 | 0.081 | 0.470 |
| Onishere | 0.100 | 0.143 | 0.120 | 0.164 | 0.345 | 0.433 |
| Ubiaja | 0.125 | 0.117 | 0.136 | 0.135 | 0.382` | 0.538 |
| Umuabi | 0.113 | 0.081 | 0.123 | 0.090 | 0.351 | 0.246 |

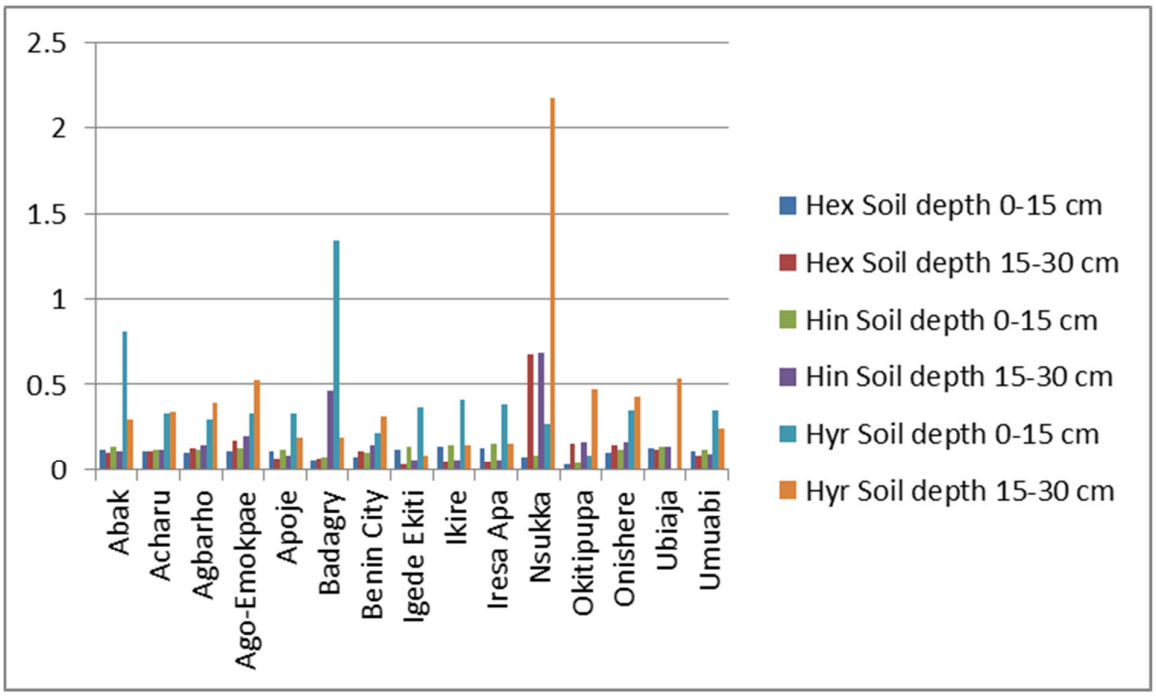



**Fig 6.1: Hazard and gamma index in soil**

The activity concentrations of $^{40}K$ from soil depth of (0 – 15 cm) ranged from 187.4 – 514.4 Bq/kg. The activity concentrations of $^{238}U$ from soil depth of (0 – 15) cm ranged from 2.328 -

6.571 Bq/kg. The activity concentrations of $^{232}$Th from soil depth of (0 - 15 cm) ranged from 1.509 - 6.121 Bq/kg. This was based on the analysis of the soil within the range of 0 -15 cm. For the risk assessments, the Absorbed Dose Rate (D) ranged from 11.5 to 24.54 nGy/h, while the Annual Effective Dose Equivalent (E) ranged from $1.4 \times 10^{-2}$ to $2.98 \times 10^{-2}$ mSv/y and the Radium Equivalent ($Ra_{eq}$) ranged between 1.4 to 2.98 Bq/kg in soils of depth 0-15 cm. This was based on the analysis of the soil within the range of 0 -15 cm. Values were lesser than worldwide average values of 370 Bqkg$^{-1}$ recommended for radium equivalent by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). The calculated values for external hazard index illustrated in Figure 6.1 range from 0.032 – 0.133 on soils (0-15 cm) in Okitipupa and Umuabi plantations. The Values for Internal Hazard index and representative index were 0.043-0.153 (0-15 cm; Okitipupa/Iresa-apa) and 0.081-1.345 (0-15 cm; Okitipupa/Badagry) respectively. Most of the values of hazard and gamma index in the soil samples obtained in the study were below the critical value of unity and this is below the recommended safe limit of 1 mSv/y [14-16]. None of the samples exceeded the permissible levels of 370 Bqkg$^{-1}$ recommended by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) for the Radium Equivalent. In addition, the calculated values of hazards in terms of Internal and External hazard indices and Representative hazard index were determined and found to be within safe limits. [17].

## 6.5 Conclusion

The activity concentrations of $^{238}$U, $^{232}$Th and $^{40}$K in soils of oil plantations from Nigeria have been determined by gamma ray spectroscopy. The absorbed dose rates at 1m in air associated with these activities have been calculated. Other radiological indices derived from the activities have been calculated. It can be concluded from the result that the soil of the oil plantations sampled, pose no radiological health hazard to the workers of the plantation and the public.

## 6.6 References

[1] International Atomic Energy Agency (IAEA), Naturally Occurring Radioactive Materials (NORM). Proceedings of an International Synposium, Marrakesh, Morocco, 22-26 March, 2010.

[2] Jabbar, A., Arshed, W., Bhatti A.S., Ahmed, S.S., Akhter, P., Rehman, S.V., Anjum, M.I., Measurement of soil radioactivity levels and radiation hazard assessment in mid Rechna interfluvial region, Pakistan. Journal of Radioanalytical and Nuclear Chemistry, 2010. 283: p. 371-378.

[3] Ahmad, N., Jaafar, M.S., Bakhash, M., Rahim, M., An overview on measurements of natural radioactivity in Malaysia. Journal of Radiation Research and Applied Sciences, 2015. 8(1): p. 136-141.

[4] Mehra, R., Measurement of Radioactivity of $^{238}U$, $^{226}Ra$, $^{232}Th$ and $^{40}K$ in Soil of Different Geological Origins in Northern India. Journal of Environmental Protection, 2011. 02(07): p. 960-966.

[5] World Health Organization and Food Agriculture Organization of the United Nations reports on Nuclear accidents and radioactive contamination of foods, 2011. p. 1-5.

[6] Navas, A., J. Soto, and J. Machn, $^{238}U$, $^{226}Ra$, $^{210}Pb$, $^{232}Th$ and $^{40}K$ activities in soil profiles of the Flysch sector (Central Spanish Pyrenees). Applied radiation and isotopes: including data, instrumentation and methods for use in agriculture, industry and medicine, 2002. 57(4): p. 579-89.

[7] Osibote O. A., Olomo J. B., Tchokossa P., Balogun F. A., 1999. Radioactivity in Milk Consumed in Nigeria Ten Years after Chernobyl Accident, Nucl. Instr. And Meth. A422, Nos 1-3, 778-783. DOI**:** 10.1016/S0168-9002(98)00996-6.

[8] Oladapo, O.O., et al., Assessment of Natural Radionuclides Level in Wasteland Soils. 2012. 2(3): p. 38-43.

[9] El, N.A., Studying of Naturally Occurring Radionuclides for Some Environmental Samples and Its Hazardous Effects. 2014, Fayoum University.

[10] Jabbar, A., PhD Thesis (Measurement of Environmental Radioactivity and Assessmrnt of Dose to the General Public in Rechna Doab, Pakistan) COMSATS Institute of Information Technology Islamabad, Pakistan. 2010.

[11] Yang, Y.X., et al., Radioactivity concentrations in soils of the Xiazhuang granite area, China. Applied Radiation and Isotopes, 2005. 63(2): p. 255-259.

[12] Tzortzis, M., et al., Gamma-ray measurements of naturally occurring radioactive samples from Cyprus characteristic geological rocks. Radiation Measurements, 2003. 37: p. 221-229.

[13] United Nations Scientific Committee on the Effects of Atomic Radiation, Exposures of the public and workers from various sources of radiation, Assembly, Editor. 2010, United Nations Publishers: New York. p. 223-463.

[14] Ajayi, O.S., Measurement of activity concentrations of $^{40}K$, $^{226}Ra$ and $^{232}Th$ for assessment of radiation hazards from soils of the southwestern region of Nigeria. Radiation and Environmental Biophysics, 2009. 48(3): p. 323-332.

[15] El-Taher, A. and J.H. Al-Zahrani, Radioactivity measurements and radiation dose assessments in soil of AlQassim region, Saudi Arabia. Indian Journal of Pure and Applied Physics, 2014. 52(3): p. 147-154.

[16] Darwish, D.A.E., K.T.M. Abul-Nasr, and A.M. El-Khayatt, The assessment of natural radioactivity and its associated radiological hazards and dose parameters in granite samples from South Sinai, Egypt. Journal of Radiation Research and Applied Sciences, 2015. 8(1): p. 17-25.

[17] Alzahrani, J.H., et al., Radiological Impacts of Natural Radioactivity and Heat Generation by Radioactive Decay of Phosphorite Deposits from Northwestern Saudi Arabia. 2011. 5(6): p. 683-690.

[18] Papp, Z., Z. Dezső, and S. Darczy, Measurement of the radioactivity of $^{238}$U, $^{232}$Th, $^{226}$Ra, $^{137}$Cs and $^{40}$K in soil using direct Ge(Li) gamma-ray spectrometry. Journal of Radioanalytical and Nuclear Chemistry, 1997. 222: p. 171-176

[19] Agbalagba, E.O. and Onoja, R.A., 2011. Evaluation of natural radioactivity in soil, sediment and water samples of Niger Delta (Biseni) flood plain lakes, Nigeria. Journal of environmental radioactivity, 102(7), pp.667-671.

## CHAPTER SEVEN

# An evaluation of the level of synthetic phenolic antioxidants in virgin palm oil

*Oladunni B. Olafisoye*
*Department of Chemistry, Cape Peninsula University of Technology, Cape Town, South Africa*
*Email: abogunrinob@gmail.com*

*Olalekan S. Fatoki, Oluwafemi O. Oguntibeju and Adelaja O. Osibote**
*Department of Chemistry, Biomedical Sciences and Physics and Mathematics; Cape Peninsula University of Technology, Cape Town, South Africa*
*Email: {fatokio, oguntibejuo, osiboteA@cput.ac.za*

***Oladunni B. Olafisoye, Olalekan S. Fatoki, Oguntibeju O, Omoniyi, Osibote O. Adelaja. An evaluation of the level of synthetic phenolic antioxidants in virgin palm oil. International Journal of Food Engineering. 1(2), 2015.***

**Abstract**

Palm oil contains important dietary nutrients and it is important to humans since it contains antioxidants, which are mediators of various diseases especially of the cardiovascular system. Virgin palm oil pressed from the oil palm fruit is stored in vessels prior to usage. During storage, virgin palm oil undergoes various oxidation processes making it rancid. This reduces its shelf life and causes it to change in colour and composition giving off an offensive odour. It is possible for small and large-scale oil palm plantation owners to preserve the virgin palm oil by some natural means or artificially with the use of synthetic phenolic antioxidants. Synthetic phenolic antioxidants are added to food for preservation and to prolong its shelf life. In this study, virgin palm oil was analysed for synthetic phenolic antioxidants by Reverse Phase-High Performance Liquid Chromatography (RP-HPLC) coupled with an Ultraviolet /Visible (UV-Vis) detector. A mixture of solvents, hexane, and acetonitrile was used for the extraction method. Virgin palm oil was analysed qualitatively and quantitatively to determine the concentration of Butylatedhydroxytoluene (BHT), butylatedhydroxyanisole (BHA), propyl gallate (PG) and 2-ethylhexyl 4-methoxycinnamate (EEMC). PG was detected below the detection of the method. A new extraction method was proposed to validate the experimental procedure.

Manuscript received August 23, 2015; revised October 23, 2015.
Adelaja O. Osibote is the Corresponding author: Tel. +27733545569.

Index Terms—***Virgin palm oil, RP-HPLC, UV-Vis detector, synthetic phenolic antioxidants***

## 7.1 Introduction

Edible oils are needed for cooking and for most industrial processes. They are also an active ingredient in most processed foods. Edible oils could be extracted from plants, seeds, nuts, or fruits. Irrespective of the method of extraction, they are extensively used in food and non-food productions and a feedstock for the production of biodiesel. There is a growing desire for edible oils due to an increasing world population and improved diets. *Elaeis guineensis* is commonly known as African oil palm. It consists of pinnate-leaved palms with dense clusters flowers and bright red fruit that produce rich quality red palm oil [1]. It is aborigine to West Africa (Madagascar and Nigeria) [2], [3], and some parts of Asia [4] and widely propagated in the tropical regions of these countries. Virgin palm oil (*Elaeis guineensis*) is edible oil used in several culinary dishes in improving the diets of the populace. In addition, it contains tocotrienols, tocopherols and carotenes among other antioxidants that are useful mediators in the prevention of several diseases especially heart maladies. It is important to monitor the processes for the production of the red palm especially the finished products prior to storage. Rancidification of oil and fat containing foods due to oxidation is a common problem. It affects food quality. To prevent this, synthetic or phenolic antioxidants are added [5]. Butylatedhydroxytoluene (BHT), butylatedhydroxyanisole (BHA), propyl gallate (PG) and 2-ethylhexyl 4-methoxycinnamate (EEMC) are lipophilic (fat-soluble) organic compounds which are derivatives of the compound phenol. They are useful for their antioxidant properties and are used as standard for antioxidant assay [6]. BHT, BHA, PG, and EEMC are commonly used antioxidants found in several foods which include cheese, butter, chewing gums, baked foods, processed foods and pharmaceuticals. They are used to preserve odour, colour, and flavour of foods. Synthetic phenolic antioxidants find their use as food additives used to prevent rancidification, due to their suitability cheapness and availability. However, numerous studies by various researchers have shown that the use of phenolic antioxidants above the requirement limit can result to serious health risks [6]. A number of synthetic antioxidants, about thirty of them have been permitted to be used in foods as additives directly or indirectly [6]. Their use in food may be singly or in combination with other synthetic antioxidants. As a result, it is of paramount importance to determine qualitatively and the widespread use of permitted synthetic antioxidant. A number of analytical instruments and methods have been documented for the qualitative and quantitative determination of synthetic antioxidants in foods and edible oils. These methods include UV–visible photometry [6], [7], paper and thin-layer chromatography [8], gas chromatography [9] [11], and liquid chromatography [12] - [14]. The

sample extraction steps of most of the methods mentioned are time consuming and cumbersome. Phenolic antioxidants are oxidized preferentially in fats or oils and protect the foods from spoilage. There are some reports about the possible carcinogenic effect of antioxidants like BHA, BHT, PG, and EEMC in high doses and long-term use may have potential health risks [7]. Conversely, phenolic antioxidants are advocated as dietary supplements, which have antiviral properties and are useful against herpes and some family viruses [7]. In lower doses, BHT is not carcinogenic. The reason for BHT non-toxic property to be used in foodstuffs is that the tert-butyl groups surround the hydroxyl group. The alkyl groups being so bulky, the hydroxyl group is screened off from possibilities of chemical activity and above all from the possibility of hydrogen bonding [9]. Due to this controversial reports the detection and estimation of BHT in food products is considered important.

Phenolic compounds such as BHA and BHT, PG and EEMC are added singly or in combination to prevent oxidative rancidity in personal care products [3]. This makes it possible for the unstable peroxide radicals [4], [5] to inhibit reactions promoted by oxygen, thus avoiding the oxidation and are intended to prevent the appearance of ketones and aldehydes that can give a product a disagreeable smell and rancidity [5]. To prevent edible oils from peroxide radicals we must use antioxidant compounds, which have the ability to neutralize those radicals through the transfer of hydrogen to this radical, stabilizing the radicals. Analysis is performed to determine the amount of BHT, BHA, PG, and EEMC in virgin palm oil. A method was proposed to achieve high throughput, low flow rate using minimal mobile phase solvent. Reversed Phase High Performance Liquid Chromatography method with UV/Vis detector (RP-HPLC- UV/Vis) is an important analytical technique with strong chromophores that absorb light in the wavelength region from 200nm to 800nm [12]. The UV/Vis detector is a suitable detector for the determination of BHA, BHT, PG, and EEMC as a phenolic antioxidant added singly or in combination in red palm oil. To our knowledge, no method has been proposed or developed for the determination of the phenolic/synthetic antioxidants in virgin palm oil. There is need to develop a RP-HPLC method, which could be employed for the routine analysis of virgin palm oil either singly or in combination using simple mobile phase composition. The present study was undertaken to develop, optimize, and validate a RP-HPLC method for analysis of BHA, BHT, PG, and EEMC.

Therefore, the aim is to determine the optimum analysis condition and validate the method for a simultaneous detection, identification, and quantification of synthetic/phenolic antioxidants with the objectives of developing an analytical method for the evaluation and quality control of phenolic/synthetic compounds in virgin palm oil using Reverse Phase High Performance Liquid Chromatography method (RP-HPLC).

## 7.2 Methodology

### 7.2.1 Sampling sites, sample collection and preparation

Red palm oil was sampled from the Headquarters of Nigeria Institute for Oil Palm Research (NIFOR) in Benin and from its substation. One of the oils from a substation in Apoje oil palm plantation was used to validate the analytical method. The oil palm plantation sampling point was partitioned into four points and samples were collected from each point. The sampling locations were based on factors such as population density, farm settlements, and areas receiving significant pollution characteristics. Storage containers for sampling were sterilized 1-liter plastic containers. The samples were preserved in an ice chest at 4˚C. The samples were transferred to the laboratory, and stored in the refrigerator at 4˚C prior to analysis. Glassware were washed with detergent and rinsed with distilled water. They were further soaked overnight in 10 % analytical grade nitric acid, and then rinsed in high purity deionized water.

### 7.2.2 Chemicals

Butylhydroxytoluene (BHT) (≥99 % pure), Propyl gallate (PG) 99.8% pure, (HPLC grade) butylatedhydroxyanisole (BHA), 2-ethylhexyl 4-methoxycinnamate (EEMC), n-hexane, methanol (HPLC) grade, acetonitrile, ethanol, acetic acid, Petroleum ether. All chemicals were purchased from Sigma Aldrich USA and were of analytical/chromatography grade.

### 7.2.3 Preparation of standard solution

Individual stock solution of BHA, BHT, PG, and EHMC (20 mg/L in methanol) were prepared accurately. The mixture was shaken until a homogenous and clear solution was formed and a serial dilution of each was prepared to obtain a linear calibration curve. The solution was covered with aluminium foil and stored in a freezer (4℃); (this was away from heat and sunlight for a maximum of one month). Before analysis was performed, standard working solutions were prepared by diluting appropriate amounts of the stock solutions in methanol.

### 7.2.4 Extraction procedure and Instrumentation

About 0.5 g of the virgin palm oil was weighed into a centrifuge tube using an electronic weighing balance. Acetonitrile (3 mL) which was saturated with hexane was added to the mixture in the centrifuge tube. The mixture was homogenized for 5 minutes at 1800 rpm using a shaker followed by centrifugation using a centrifuge for 5 minutes at 4000 rpm.

The non-polar phase, which is the acetonitrile phase, was collected and the oily layer was re-extracted thrice using similar extraction procedures. All the acetonitrile phases were recombined into a 10 mL capacity volumetric flask and diluted to the mark with acetonitrile.

The solution was set aside to be analysed by RP- HPLC. This is a modified procedure of Dr Ancos *et al*. An ODS $C_{18}$ Chromatographic column was used (4.6 cm × 250 cm). The ODS $C_{18}$ Chromatographic column used for the analysis had a particle size of 5 µL. An Isocratic system with mobile phases of 75:25 v/v methanol: water mobile phase was employed. The Agilent Technologies (1200 series) RP-HPLC Instrument used for the analysis was equipped with UV/Vis detector and quaternary pumps. The maximum wavelength chosen was 280 nm and 1 mL/min flow rate.

## 7.3 Results and discussions

### 7.3.1 Analysis of real samples

Real samples of red palm oil were analysed. In this study, optimization of the extraction procedures for red palm oil sampled on Apoje plantation was evaluated to obtain the best analysis time was evaluated. The result of the chromatogram of the analysis is presented in fig. 7.5. A peak was observed at the retention time of 2 minutes, which could be PG. The concentration of the peak was poorly resolved. From the calibration curves represented in the graph in Figure 7.1 - 7.6, the peak area was measured and RF determined. The concentration of the calibration curve was greater than the concentration of the PG. PG was resolved within 2 minutes. The calibration curve in Figure 7.6 depicts that the analyte gave a linear curve and this determined the linear dynamic range. PG was detected in the sample but it was below the linear dynamic range

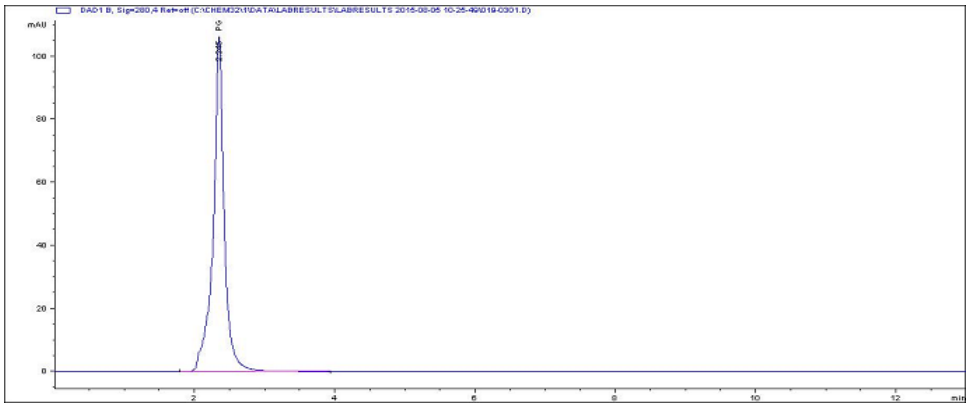



**Fig 7.1: Chromatogram for PG**

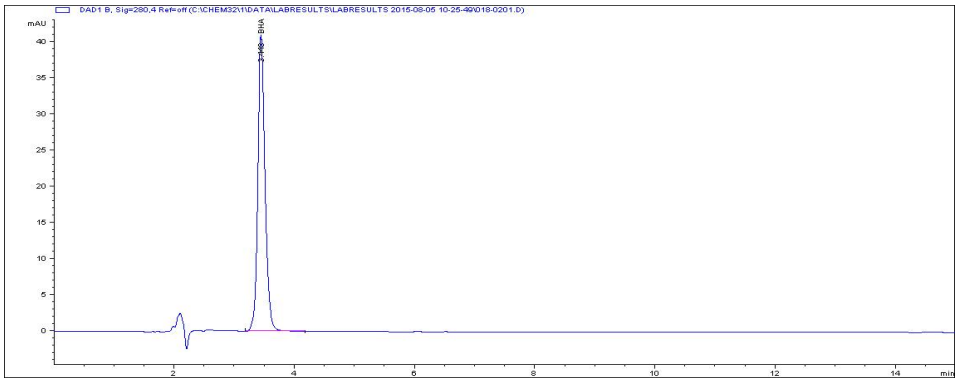



**Fig 7.2: Chromatogram for BHA**

Based on the result obtained from the initial extraction procedure which involved the use of acetonitrile and hexane, it can be deduced that the synthetic phenolic antioxidants are absent in the sample of virgin palm oil or it can be deduced that the extraction procedure is inaccurate. A new extraction technique was proposed to validate the extraction procedure. The analysis is in progress.

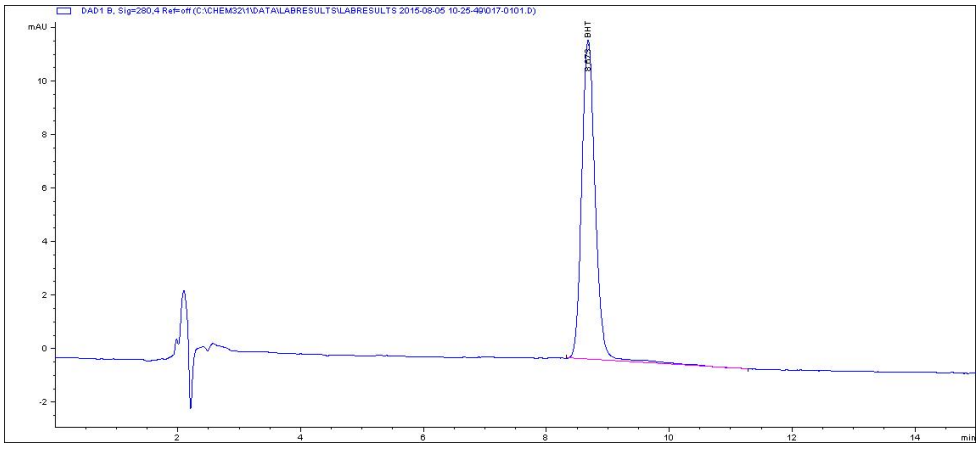



**Fig 7.3: Chromatogram for BHT**

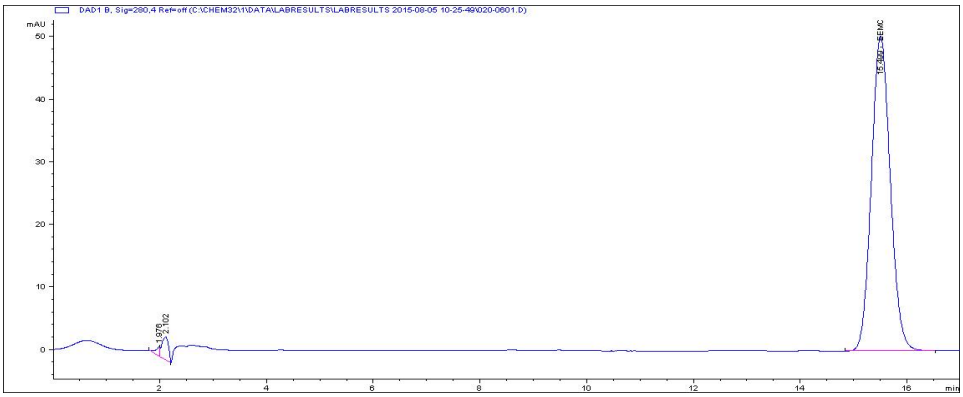


**Fig 7.4: Chromatogram for EEMC**

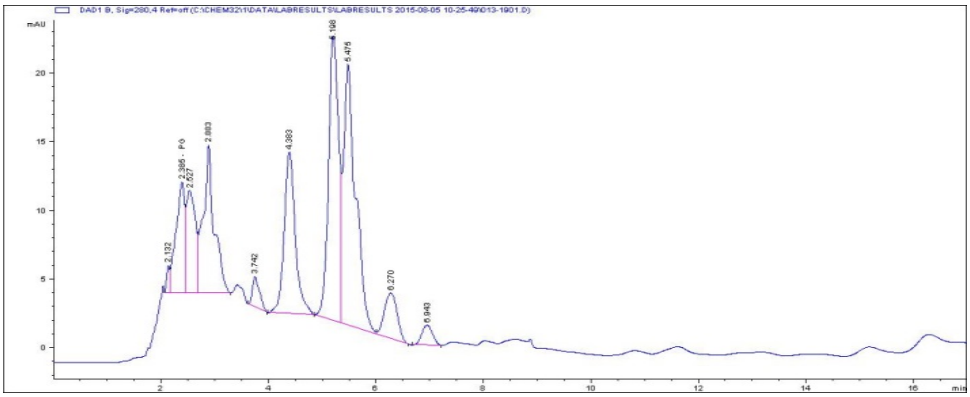


**Fig 7.5 Chromatogram for real samples**

### 7.3.2 Validation of the analytical procedure

The linearity of the method was determined by linear calibration curves for each of the antioxidants.

**Table 7.1: Calibration curve regression data**

| Antioxidant | Equations | $R^2$ | LOD | LOQ |
|---|---|---|---|---|
| PG | *y=1941x+4903* | 0.998 | 0.001 | 0.01 |

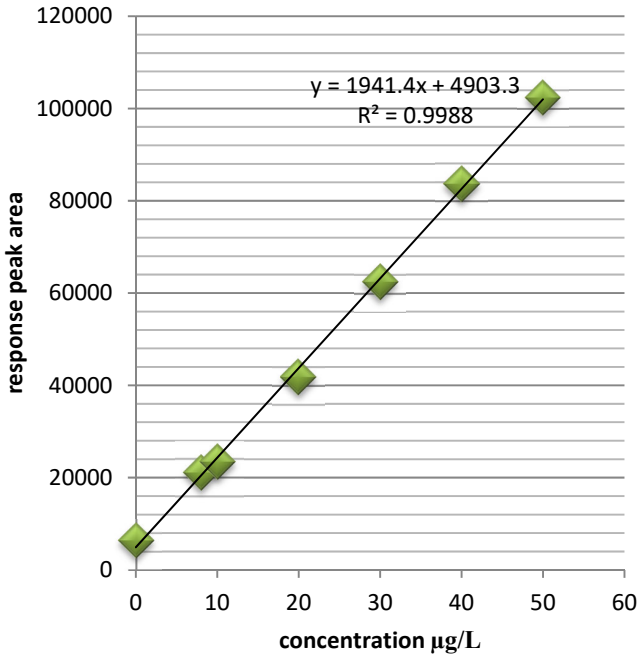



**Fig 7.6: Regression curve for samples**

Fig. 7.1 shows the chromatograph of the standard calibration curve for PG. The retention time of PG waswithin 2 minutes at a flow rate of 1mL/min and 50µL injection volume. Fig. 7.2 shows the chromatograph of the standard calibration curve for BHA. The retention time of BHA waswithin 3-4 minutes at a flow rate of 1mL/min and 50 µL injection volume. Fig.7. 3 presents the retention time for BHT which was within 8 minutes at a flow rate of 1mL/min and 50µL injection volume. Fig. 4 shows the retention time for EEMC which waswithin 15-16 minutes at a flow rate of 1mL/min and 50µL injection volume**.**

### 7.3.3 Recovery efficiency and method performance

The accuracy of the analytical method was determined using external standardization addition methods for four spiked samples at 1, 5, 10 and 25 mg/L and comparing with a standard chromatogram of similar concentration.

## 7.4 Conclusion

Virgin Palm oil was investigated to determine the levels of synthetic phenolic antioxidants. Virgin palm oil contains important dietary nutrients such as antioxidants that are mediators of cellular functions and cures for several ailments including cancer and cardio vascular diseases. The rancidity of virgin palm oil during storage causes the oil to have an offensive odor, color and taste. Synthetic phenolic antioxidants may be added to offset these changes in the oil

during storage. The study aimed to know quantitatively and qualitatively the type and amount of these synthetic phenolic antioxidants. This is of paramount importance because the levels of the synthetic phenolic antioxidants above the Recommended Dietary Allowance have been investigated to be a major contributor of some forms of cancer. Other health effects include hyperactivity, irritability, and migraines. The modified RP-HPLC procedure by Dr Ancos *et al*. with an ODS $C_{18}$ Chromatographic column was employed using 75:25 v/v methanol: water mobile phase. PG was detected below the detection limit of the machine using the procedure. A new extraction procedure was proposed and the analysis is in progress.


### 7.5 Acknowledgment

The authors wish to thank Cape Peninsula University of Technology, South Africa for funding the research.

## 7.6 References


[1] T. W. Barker and J. T. Worgen, “The utilization of palm oil processing effluents as substrates for material protein production by fungus Aspergllusoryzae,” *Eur. J. Appl. Microbio and Biotechn*. vol. 11, no. 4, pp. 234-240, 1981.

[2] W. H. Hodge, “Oil processing palms of the world: A Review,” *Principles*, vol. 19, no. 4, pp. 119-136, 1975.

[3] J. R. Adrian, A. J. Esterhuyse, A. M. Engelbrecht, and F. D. Eugene, “Health benefits of natural carotenoid rich oil: a proposed mechanism of protection against ischaemia reperfusion injuring: A review,” *Asia Pac Clin. Nutr.*, vol. 17, no. 1, pp. 316-319, 2008.

[4] H. Parcher and S. H. Golkho, “Using HPLC to determine the composition and antioxidant activity of Berberis Vulgaris,” *European Journal of Scientific Research*, vol. 29, no. 1, pp. 47-54, 2009.

[5] G. B. Nilgun, B. Zehra, and H. T. Filiz, “Phenolic composition and antioxidant activities of wines and extracts of some grape varieties grown in Turkey,” *Journal of Agricultural Sciences*, vol. 17, pp. 67-76, 2011.

[6] A. Blaszczyk, A. Augustyniak, and J. Sklimowski, “An antioxidant used in animal feed,” *International Journal of food science* 2013, pp.1-12, 2013.

[7] T. K. Choy, J. Q. Joseph Jnr, and N. J. Alicino, “Agas chromatographic method for the determination of antioxidants BHA, BHT and ethoxyquin in aqueous and in hydrocarbon soluble samples,” *Journal of chromatography A*, pp. 171-177, 1963.

[8] A. E. Witter, “The quantitative determination of ButylatedHydroxytoluene in chewing gum using GC-MS,” *J. hem.Educ.*vol. 82, no. 10, pp. 1538, 2005.

[9] L. Xu-Quin, C. S. Yan Yan, Y. Min-LI, and C. Xino- Gang, “Analysis of synthetic antioxidants and preservatives in edible vegetable oil by HPLC/TOF-MS,” *Food Chemistry*, vol. 113, pp. 692-700, 2009.

[10] M. Careri, C. Couradini, L. Elviri, L. Nicoletti, and I. Zagnoni, “Direct HPLC analysis of quercetin and transresveratol in red wine, grape and wine making by products,” *Journal of Agricultural Food Chemistry*, vol. 51, pp. 5226-5231, 2003.

[11] S. Gomez-Alonso, E. G. Romero, and G. I. Hermosin, “HPLC analysis of diverse grape and wine phenolics using direct injection and multidetection by DAD and fluorescence,” *Journal of Food Composition and Analysis,* vol. 20, pp. 618-626, 2007.

[12] B. Angos, E. M. Gonzalez, and M. P. Cano, “Ellagic acid, vitamin C and total phenolic contents and radical scavenging capacity affected by freezing and frozen storage in raspberry fruit,” *J. Agric Food Chem*. vol. 48, pp. 4565-4570, 2000.

# CHAPTER EIGHT

## Accumulation and risk assessment of metals in palm oil cultivated on contaminated oil palm plantation soils.

***OB Olafisoye[1], OS Fatoki[1], OO Oguntibeju[2], OA Osibote[3*]***

*[1]Faculty of Applied Sciences, Department of Chemistry, Cape Peninsula University of Technology, P.O. Box 652, Cape Town, South Africa 8000. oladunniolafisoye@gmail.com.*

*[1]Faculty of Applied Sciences, Department of Chemistry, Cape Peninsula University of Technology, P.O. Box 652, Cape Town, South Africa 8000. fatokio@cput.ac.za*

*[2]Faculty of Health and Wellness Sciences, Department of Biomedical Sciences, Cape Peninsula University of Technology, P.O. Box 1906, Bellville, South Africa 7535. oguntibejuo@cput.ac.za.*

*[3*]Faculty of Applied Sciences, Department of Mathematics and Physics, Cape Peninsula University of Technology, P.O. Box 652, Cape Town, South Africa 8000. osibotea@cput.ac.za.*

***Original Paper titled "Accumulation and risk assessment of metals in palm oil cultivated on contaminated oil palm plantation soils". Published in the Elsevier Journal, Toxicology Reports; Oladunni B. Olafisoye, Olalekan S. Fatoki, Oguntibeju O. Omoniyi, & Osibote O. Adelaja, 7 (2020), 324-334).***

**Abstract**

Anthropogenically polluted soils with metals are detrimental to human life. The present study assessed the concentration of metals in soil and the risks associated with the consumption of the metals when transferred from soil to palm oil. The metals of interest were Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn. Analysis was done on metals in soil and virgin palm oil from fifteen independent sampling locations in the southern states of Nigeria, which includes the Nigeria Institute for Oil Palm Research (NIFOR) and its substations. Top soils were collected at a depth of 0-15 cm and virgin palm oil in 1 litre container by grab sampling method. The method proposed was to achieve high throughput with minimal mobile phase solvent. Micro emulsion technique was involved as sample preparation method for the extraction of metals in virgin palm oil from the matrix. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used to analyse metals in virgin palm oil and soil. This reduces analysis time and does not require complex sample preparation. Zinc metal recorded the highest concentration of metal in the palm oil and Chromium metal recorded the highest concentration of metal in soil. There was a correlation between the accumulations of metals from soil to palm oil. Risk

was assessed using various indices. Cadmium metal recorded the highest concentration in the Target Hazard Quotient (THQ), Accumulation Factor (AF), and Health Risk Index (HRI). Daily Intake of Metals (DIM) was highest for Chromium metal. Cadmium was the highest accumulator of metals in the palm oil.

***Key words: Metals, oil palm plantations, palm oil, soil, micro emulsion, ICP-OES, health risk assessment.***

## 8.1. Introduction

A major pathway through which metals enter soils is by anthropogenic means [1, 2]. Plant species significantly accumulate metals in various parts especially the fruits thereby remediating soils. This leads to bioaccumulation and bio magnifications in the food chain and the disruption of chemical and biological activities in the human body [3, 4]. The routes through which metals enter the food chain are via inhalation and ingestion. Although literature reveals that, some species of plants can bio accumulate metals more than the other species [5]. Anthropogenic sources of metal pollution are mostly from industries and unwholesome farming practices. Wastewaters from factories usually drain to farmlands elevating the levels of metals in soils. The populace is incessantly exposed to metals through the consumption of food grown on such soils. Numerous literatures supported this fact [6-10].

The study of metals in soils requires systematic assessment as monitoring approach to eradicate the effects on the food chain. Risk assessment have been studied using various tools such as the Accumulation Factor (AF), Hazard Quotient (HQ), Health Risk Index (HRI), Daily Intake of Metals (DIM), Target Hazard Quotient (THQ), Morbidity Status (MS), Enrichment Factor (EF), and Degree of Contamination ($C_{deg}$) [2]. Overtime, non-essential metals bio accumulates in plant parts that become toxic to animals and humans when consumed as food. Application of fertilizers, untreated sewage water from municipal and industrial applications, leaching from dumpsites, fertilizer application, and waste from mining have contributed significantly to the build-up of metals in soils.

The oil palm tree (*Elaeis guineensis)* is a perennial crop. It is an excellent source of fatty acids, minerals, and vitamins for the food and chemical industry [11]. Palm oil from the oil palm fruit has been proven to cure various diseases especially cancer and heart maladies [12, 13, 14, 15, 16]. Nigeria is a tropical country characterized by a wet and dry climate at various times of the year. This is particularly beneficial for the production of the oil palm fruit. The oil palm fruit produces palm oil that is a stable ingredient in most local dishes consumed by Nigerians [17]. Metals are also present in palm oil due to various reasons ranging from environmental and processing operations to unwholesome agronomical methods. Ayodele and Oluyomi in 2011 [9] reported on the issue of contamination arising during cultivation of the oil palm tree and

harvesting of the oil palm fruit due to pre-planting and post-planting farming practices such as the use of fungicides and fertilizers residues. Contamination may also arise from a number of factors that includes washing of the oil palm fruit with water from lead/metal pipes or rivers. In addition, mechanical stripping of the oily flesh from the oil palm fruit, cooking and sieving of the flesh to obtain the virgin palm oil, corrosion of the processing equipment and storage in large metal vessels; are sources of metal contamination [18]. Other sources of anthropogenic contamination may also arise from the oil palm plantation situated close to domestic and industrial sources of pollution [8].

The determination of elements in virgin palm oil is of economic importance because palm oil is a very important cash crop for the food and chemical industry. It is essential to determine the presence of metals in palm oil as this is one of the criteria for oil quality. Metals in palm oil are deleterious because this affects the shelf life and aesthetic quality of the oil. Metals in the oil enhance the oxidation of fatty acids to esters, which affects the nutritional value and the properties of the oil [19, 20, and 21]. Metals are toxic at elevated concentrations. However, some metals are essential to humans, their presence in palm oil, which is a raw material for a variety of food and chemical industries may not be ideal for production processes. This is particularly an issue in the production of biodiesel due to the presence of such metals that consequently affects the quality of the oil.

Hence, an analysis was performed to determine metals (Cadmium Cd, Cobalt Co, Chromium Cr, Copper Cu, Iron Fe, Manganese Mn, Nickel Ni, and Zinc Zn) in virgin palm oil from fifteen independent sampling locations. The proposed method of micro emulsion as sample preparation method alongside with the instrumental analysis using the ICP-OES for this analysis was initiated to achieve high throughput and low flow rate with minimal mobile phase solvent. It was able to eradicate the impending problem of former analysis that was majorly the dense matrix of oil samples and the concentration of metals in oil samples at very critical concentrations [22]. Analytical chemists have also employed several instrumental techniques for the determination of elements in oil samples, the most common technique being Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) [9, 8, and 23]. The determination of elements in oil using AAS recently by some scientists was not adequate due to the nature of the matrix and the difficulty in separating the analyte from such matrix [24, 25]. This could be attributed to the instability of the analyte in the oil and the high organic content of the oil. The use of hazardous solvents has to be employed to destroy or dissolve the matrix as the case may be so that the analyte may be free in solution. Sample separation and pre-treatment steps were long and laborious. Such sample preparation steps such as solid phase extraction, microwave assisted acid digestion and wet/dry ashing, involving hazardous acids or a mixture of both was normally employed. Another disadvantage of using AAS process was the use of

very expensive organometallic standards for instrument calibrations. The proposed method eradicated the use of hazardous chemicals and the use of expensive unstable organometallic standards for calibration [25, 26]. Hence, micro emulsions were employed as sample preparation method for the determination of metallic elements in this study. The micro emulsions were stable thermodynamically when tested using a UV spectrometer after being observed for about three hours. The micro emulsions were composed of water, oil, and alcohol. In addition, the micro emulsion particles were homogenous and were actually in the order of 5-100 nm in size suspended in a phase that is continuous [27 - 29].

The proposed ICP-OES analysis using oil-water micro emulsion as sample preparation method was not only reproducible, accurate and reliable but also equally convenient because it provided a sample extraction capable of breaking down the complex matrix in virgin palm oil. This was for metal analysis by ICP-OES [30].

## 8.2. Materials and methods

### 8.2.1. Sampling and chemicals

Virgin palm oil and soils were sampled from fifteen sampling locations in the Nigeria Institute for Oil Palm Research (NIFOR); the headquarters in Benin city and substations in the south western area of Nigeria. The choice of the sampling areas was based on Oil Palm Plantations in the region receiving significant input of pollution characteristics from crude oil in crude oil producing areas of the region. Other inputs were from effluents of domestic, industrial, and electronic waste. Oil palm fruits were pressed from the bunch and the virgin oil was collected in 1 litre plastic containers in all the sub sites by random sampling for each site. The collected palm oil samples were mixed in order to achieve a grab sample and to give a true representative of all the plantations. Choice of sampling sites was also based on densely populated areas. Soil sampling was also performed by random and grabs sampling. The soils were collected from a depth of 0-15 cm. Majorly the choice of the sampling areas were based on oil palm plantations in the region receiving significant input of pollution characteristics from crude oil in crude oil producing areas of the region. Other inputs were from effluents of domestic, industrial, and electronic waste. Soil samples were collected from topsoil using a spiral auger of 2.5 cm at a depth of 0-15 cm. A total of fifteen soil and virgin palm oil samples, one from each site was transferred into cleaned polythene bags and 1-litre containers for soil and virgin palm oil samples respectively, labelled and transported to the laboratory. Figure 8.1 shows the sampling locations. They were stored in pre sterilized ice chest at lower temperatures prior to transportation to the laboratory for chemical analysis. The soil samples were air dried for over a week, ground with a porcelain mortar and pestle, passed through a 2 mm aperture sieve, further dried in the oven at 105±5˚C for about 4 hours, well labelled

accordingly, and kept in clean polythene bags for further analysis. The virgin palm oil samples were kept in a cool dry cupboard awaiting further analysis. All apparatus used for the analysis have been previously soaked in nitric acid, washed with detergent, and rinsed twice with deionized water. The sampling containers were sterilized and the samples preserved in a refrigerator prior to analysis in the laboratory. High purity analytical grade chemicals and reagents (purchased from Sigma Aldrich (USA) and Merck, (Germany.) were used alongside deionized water (Milli-Q water, Belford, America). Standard calibration curves for the analysis were prepared from single element standards that were certified and traceable to the National Institute of Standards and Technology (NIST). Non-serial dilutions of much lower concentrations of the standards were also prepared in making the calibration curve throughout the analysis.

### 8.2.2. Analysis of soil samples

The soil samples were tested for parameters such as the electrical conductivity, pH and organic matter. The pH of the soil was measured with a pH meter in a suspension of the soil and water [31]. One part of soil by weight to 5.0 parts of deionized water by volume was measured and analysed using the glass electrode pH meter. The solid to liquid ratio of 1:5 soils: deionized water suspension is sensitive to seasonal variation in the pH of soil solution. Organic matter was measured using the modified Walkey and Black method [32]. Total metal extraction was accomplished using the microwave assisted digestion method.

### 8.2.3. Analysis of palm oil samples by the micro emulsion method

About 0.5 g of each of the oil samples was accurately weighed into a 100 mL polypropylene tube with lid. HCl was added (c.a 2 mL) and propan-2-ol to a final volume of 10 mL. The mixture was shaken vigorously on a shaker for 30 minutes to obtain an evenly dispersed homogenous emulsion that remained stable without dispersing when left for about four hours [33, 34]. This was kept in the fridge at 4 ℃ for metallic element analysis using the ICP-OES. The instrument of choice for the analysis of metals in soil and the palm oil was the Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) [23, 25, and 35]. In order to validate the analytical method, the following method validation parameters such as instrumental detection limit, limit of detection, limit of quantification, precision, and accuracy studies were carried out. The Instrumental detection limit (IDL) is the smallest signal above background noise that an instrument can reliably detect. This can be calculated to be the concentration that is equal to thrice the standard deviation of the signal produced by the blank. In this study, the IDL for each metal was calculated from the analysis of seven replicates of the blank concentration. This

was represented as; IDL = 3 × Sbl; where Sbl is the standard deviation of the calibrated blank solution.

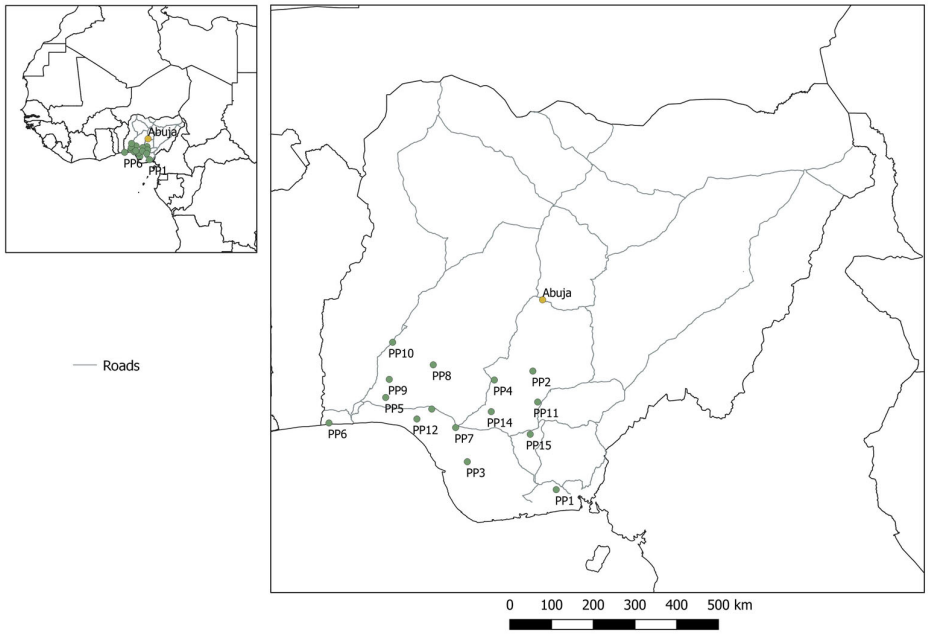



**Fig. 8.1 Map of Nigeria showing sampling points**

The limit of detection (LOD) is the minimum concentration of the analyte that can normally be detected without necessarily quantifying it. This has an acceptable level of uncertainty. Calculations for the LOD for each metal was made by determining the analysis of seven replicates of the method blank which was digested in the same way as the samples. This was represented as; LOD = 3 × Sbl; where Sbl is the standard deviation of the method blank solution.

The limit of quantification (LOQ) is the lowest concentration of an analyte in the sample which can be quantitatively determined with some levels of uncertainty. This can be achieved in triplicate of seven method blanks which are digested as the actual samples. This is represented as; LOQ = 10 × Sbl; where Sbl is the standard deviation of the method blank solution [36, 37].

### 8.2.4. Accumulation Factor Calculation (AF)

The movement of metals from the soil to various parts of the plants especially the edible parts can be described by the accumulation factor using Equation 1 [2, 38]

$$\mathrm{AF} = \frac{\text{Heavy metal concentration in virgin palm oil}}{\text{Heavy metal concentration in the soil}} \qquad Equation\ 1$$

#### 8.2.4.1. Metals Daily Intake (DIM)

Equation 2 was used in the calculation of the daily intake of metals ingested by human [39, 40].

$$DIM = \frac{A_{\ intake}\ X\ B_{metal}\ X\ C_{factor}}{D_{weight}} \qquad Equation\ 2$$

$A_{intake,}$ $B_{metal}$, $C_{factor}$, and $D_{weight}$ are the average daily intake of the oil samples by humans, metals present in the oil sample, a constant that is the conversion factor (0.085) and the average human weight (55.5 kg) respectively. A factor of 0.0527 kg person$^{-1}$ day$^{-1}$ was used as the average daily intake of palm oil per person per day [40].

#### 8.2.4.2. Health Risk Index (HRI)

This was achieved by comparison of the ratio of the daily intake of metals in the oil to the oral reference dose (RfD) [40].

$$HRI = \frac{DIM}{RfD} \qquad Equation\ 3$$

The RfD is quantitatively used in risk assessment to evaluate the ingestion of a non-carcinogenic contaminant per milligram per kilogram per day. An HRI greater than one signifies that the population suffers a health risk when such food is consumed [2, 39].

#### 8.2.4.3 The Target Hazard Quotient (THQ)

It was of paramount importance to investigate the health risk associated with the consumption of the palm oil. This was achieved by the use of the Target Hazard Quotient (Equation 4). The THQ describes the ratio of the evaluated dose to the reference dose by the following equation [2, 39, and 41].

$$THQ = \frac{Efr\ X\ ED\ XFI\ XMC\ X\ 0.001}{RfD\ XBW\ XAT} \qquad Equation\ 4$$

The exposure frequency (*Efr*) was calculated as 365 days in a year and the duration (ED) as 60 years for an adult. FI and MC signify the ingestion and metal concentration in the food. The

average body weight (BW) and exposure time (AT) are 60 kg and 365 days in 60 years for adults when considering non-carcinogenic effects. A THQ value greater than one is very risky to the population consuming such food [2, 39].

## 8.3. Results and discussion

### 8.3.1. Soil properties

Soil properties such as pH, electrical conductivity, organic matter, and particle size are significant contributors to bioaccumulation and magnifications of metals in plant parts especially the fruits and bioaccumulation of metals in different fractions of the soil. The study on the soil properties and the bioavailability of the metals in the soil to investigated toxicity and mobility has been extensively discussed in Olafisoye *et al.,* 2016 [42, 43]. The soils investigated had a pH of four which shows acidic soils and hence an increase in toxicity and mobility of metals with decrease in pH, particle size and organic matter. In the present study toxic metals (Cd, Co, Cr, Ni) were found in soil and palm oil at elevated concentrations so were the essential metals (Cu, Fe, Mn, Zn) which invariably would be toxic at high concentrations. Metals such as Cu, Zn, Fe, and Mg possess antioxidant properties and are components of antioxidant enzymes. Acidic soils generally favour the transport of metals from soil to edible plant parts. This assessed the possible human health threats linked with the intake of palm oil contaminated with toxic metals. Contaminated palm oil with essential metals above the recommended values also become toxic. A possible route of human contact to slow poisoning is from the ingestion of contaminated food [42, 43]. Several sources of contamination of the oil palm plantations were identified in this study such as anthropogenic sources of metal pollution in soil mostly from industries and unwholesome farming practices. Application of fertilizers, untreated sewage water from municipal and industrial applications, leaching from dumpsites, fertilizer applications, and waste from mining and crude oil spills have contributed significantly to the build-up of metals in soils. Ayodele and Oluyomi [9] reported on the issue of contamination arising during cultivation of the oil palm tree and harvesting of the oil palm fruit due to pre-planting and post-planting farming practices. The application and use of fungicides and fertilizers residues, palm oil production using corroded vessels and storage of the palm oil in metal vessels are great contributors to metal build-up in the oil [18, 44].

### 8.3.2. Metal concentrations in soil and palm oil

The results for the analysis of metals in virgin palm oil and soil are presented in Tables 8.1 & 8.2 respectively. The results revealed detectable levels of the metals as most of the metals in palm oil and soils exceeded the WHO permissible limits for metals in vegetable oils and soil [45]. The authors observed that the metal concentration in the soils were a bit lower than those

in the palm oil due to bioaccumulation and bio magnifications in the tissues of the plant. This is in agreement with the study by El-Hassain *et. al.* 2020 [46] that cultivated plants in polluted soils would have higher levels of heavy metals, as well as exceeding the permissible levels.

**Table 8.1: Concentration of metals in palm oil**

| Location | Cd | Co | Cr | Cu | Fe | Mn | Ni | Zn |
|---|---|---|---|---|---|---|---|---|
| Abak | 12.7 ±0.001 | 9.8±0.003 | 5.6±0.004 | 7.0±0.002 | 21.1±0.007 | 6.6±0.001 | 6.8±0.001 | 8.3±0.002 |
| Acharu | 13.9±0.001 | 10.4±0.001 | 4.7±0.001 | 11.7±0.001 | 9.1±0.004 | 7.3±0.004 | 16.4±0.003 | 34.2±0.001 |
| Agbarho | 68.3±0.001 | 23.9±0.001 | 3.4±0.002 | 7.5±0.001 | 15.9±0.005 | 2.3±0.001 | 8.9±0.005 | 12.6±0.001 |
| Ago-Emokpae | 14.0±0.001 | 10.4±0.001 | 6.8±0.001 | 7.0±0.003 | 16.8±0.013 | 6.4±0.001 | 20.2±0.004 | 18.2±0.002 |
| Apoje | 26.6±0.002 | 45.8±0.001 | 77.8±0.002 | 8.3±0.002 | 15.2±0.009 | 45.6±0.002 | 78.6±0.001 | 162.1±0.073 |
| Badagry | 12.7 ±0.001 | 9.1±0.002 | 2.8±0.003 | 18.4±0.003 | 17.4±0.043 | 7.1±0.001 | 18.4±0.003 | 9.6±0.001 |
| Benin city | 55.7±0.002 | 33.2±0.001 | 66.1±0.002 | 9.1±0.002 | 13.9±0.005 | 7.3±0.001 | 76.0±0.002 | 10.0±0.001 |
| Igede-Ekiti | 76.2±0.002 | 55.1±0.002 | 43.0±0.002 | 9.0±0.001 | 13.7±0.002 | 7.6±0.001 | 17.7±0.001 | 5.3±0.003 |
| Ikire | 13.8±0.001 | 10.3±0.001 | 3.2±0.001 | 10.9±0.001 | 18.4±0.005 | 7.0±0.001 | 18.2±0.002 | 9.2±0.001 |
| Iresaapa | 13.9±0.001 | 13.1±0.001 | 4.6±0.001 | 8.2±0.002 | 13.6±0.001 | 6.8±0.001 | 16.7±0.001 | 32.9±0.001 |
| Nsukka | 61.1±0.001 | 66.5±0.004 | 33.4±0.002 | 2.2±0.001 | 3.3±0.002 | 48.2±0.001 | 67.2±0.003 | 45.2±0.001 |
| Okitipupa | 38.9±0.002 | 31.1±0.002 | 2.8±0.001 | 33.2±0.002 | 11.2±0.001 | 67.2±0.003 | 67.2±0.003 | 11.1±0.001 |
| Onishere | 44.5±0.0050 | 88.7±0.002 | 1.1±0.001 | 44.6±0.006 | 67.3±0.003 | 11.3±0.002 | 54.3±0.003 | 66.3±0.002 |
| Ubiaja | 13.7±0.001 | 10.2±0.001 | 99.8±0.001 | 7.6±0.005 | 18.7±0.023 | 3.7±0.002 | 17.4±0.001 | 64.2±0.001 |
| Umuabi | 13.1±0.001 | 10.0±0.001 | 4.0±0.001 | 10.1±0.007 | 17.0±0.003 | 26.4±0.003 | 17.8±0.002 | 77.9±0.001 |

***FAO/WHO maximum permissible limits for Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn are 9, 0.06, 0.1, 30, 48, 20, 300 and 60 mg/L respectively. (mg/L) (n=3)***

Chromium, Copper, Nickel, and Zinc recorded rather high concentrations of metals in soils on all the fifteen sampling plantations in the study. Iron recorded a high concentration in Acharu while manganese was high in Acharu and Benin City respectively. Highest value of metals in soils was recorded in Chromium in Agbarho plantation. This is evident in Table 8.2. Rich deposits of Iron were found in Acharu. Acharu is a local government in Kogi state near Itakpe, a famous Iron smelting company in Nigeria. The soils of the area are also rich in Iron Ore. Iron is a trace element necessary for proper functioning of the body and haemoglobin. Benin City is a haven for Bronzes and Brass ornaments, smelting of metals, and artwork. High values of Copper and Zinc were recorded in soils sampled from Benin City. These metals are components of antioxidant metals in trace concentrations. The rather high concentrations of these metals in soil are toxic and detrimental to humans when transferred to consumable parts of plants. The high concentration in soil is fatal. Elevated concentrations of these metals in soils and their detrimental effect on humans have been broadly discussed in a previous study [42].

Table 8.2 shows the accumulation of metals from soil to palm oil. Chromium and Copper generally recorded high concentrations of metals in all plantations under study. A high value of Cadmium in palm oil was also noted in Igede Ekiti and Cobalt in Apoje. Igede-Ekiti, Nsukka, and Onishere plantations respectively. Chromium metal recorded high concentrations of the metals in palm oil in Apoje, Benin City, and Ubiaja. Copper and Nickel and iron recorded high values in palm oil in Onishere. High values were also noted for Nickel in Apoje, Benin City, and Okitipupa in palm oil. High values of Manganese, and Zinc metals were noted in palm oil in Apoje, Nsukka and Okitipupa respectively. The plantations, which recorded the highest value of metal, was Apoje with the highest concentration of Zinc metal The data obtained was compared with Balkhair and Ashraf [2]. Nearly all the concentrations of the metallic elements exceeded the permissible limits in palm oil and soils analysed from the plantations. The deleterious effects of the metals in elevated concentrations and their beneficial outcomes have been discussed in a previous study [42]. In addition, the bioavailability fractions in which the metals exist in soil gave an insight into their mobility and toxicity as expatiated in the previous study [47, 48, 49, 50, and 51].

**Table 8.2: Concentration of metals in soils**

| Location | Cd | Co | Cr | Cu | Fe | Mn | Ni | Zn |
|---|---|---|---|---|---|---|---|---|
| Abak | 1.09 ± 0.2 | 9.42 ± 0.3 | 109.56 ± 0.1 | 39.11 ± 0.2 | 30.99 ± 0.3 | 0.88 ± 0.1 | 40.66 ± 0.1 | 63.11 ± 0.1 |
| Acharu | 1.16 ± 0.1 | 2.17 ± 0.1 | 45.67 ± 0.1 | 12.92 ± 0.1 | 40.34 ± 0.1 | 19.22 ± 0.1 | 37.24 ± 0.2 | 89.33 ± 0.2 |
| Agbarho | 1.66 ± 0.1 | 3.98 ± 0.2 | 132.21 ± 0.1 | 45.06 ± 0.4 | 12.34 ± 0.1 | 0.23 ± 0.2 | 39.11 ± 0.1 | 23.01 ± 0.1 |
| Ago-Emokpae | 0.64 ± 0.2 | 2.07 ± 0.1 | 25.50 ± 0.3 | 35.08 ± 0.1 | 9.11 ± 0.2 | 9.42 ± 0.3 | 30.27 ± 0.1 | 92.48 ± 0.1 |
| Apoje | 1.28 ± 0.1 | 1.03 ± 0.1 | 99.92 ± 0.1 | 33.22 ± 0.1 | 6.63± 0.1 | 0.45 ± 0.1 | 35.67 ± 0.1 | 96.67 ± 0.1 |
| Badagry | 4.26 ± 0.2 | 2.61 ± 0.1 | 108.67 ± 0.1 | 69.11 ± 0.1 | 1.81 ± 0.2 | 1.33 ± 0.2 | 49.08 ± 0.1 | 53.82 ± 0.2 |
| Benin city | 1.33 ± 0.1 | 1.32 ± 0.2 | 78.11 ± 0.1 | 23.02 ± 0.2 | 2.02 ± 0.1 | 29.38 ± 0.1 | 32.35 ± 0.3 | 107.33 ± 0.2 |
| Igede-Ekiti | 0.39 ± 0.2 | 1.45 ± 0.1 | 56.45 ± 0.1 | 33.41 ± 0.1 | 0.05 ± 0.1 | 0.76 ± 0.1 | 39.46 ± 0.2 | 78.62 ± 0.2 |
| Ikire | 0.27 ± 0.1 | 1.05 ± 0.2 | 34.99 ± 0.2 | 22.63 ± 0.1 | 1.10 ± 0.1 | 1.49 ± 0.2 | 44.76 ± 0.2 | 94.42 ± 0.1 |
| Iresaapa | 1.32 ± 0.1 | 2.55 ± 0.1 | 111.08 ± 0.1 | 30.82 ± 0.2 | 1.03 ± 0.1 | 0.75 ± 0.1 | 45.34 ± 0.1 | 12.36 ± 0.1 |
| Nsukka | 1.12 ± 0.1 | 2.23 ± 0.1 | 124.42 ± 0.3 | 28.56 ± 0.1 | 1.01 ± 0.2 | 0.12 ± 01 | 49.22 ± 0.1 | 37.43 ± 0.1 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Okitipupa | 0.12 ± 0.1 | 2.61 ± 0.2 | 66.89 ± 0.1 | 33.78 ± 0.2 | 1.01 ± 0.1 | 0.99 ± 0.2 | 34.04 ± 0.1 | 60.28 ± 0.1 |
| Onishere | 0.37 ± 0.1 | 0.80 ± 0.1 | 111.11 ± 0.3 | 37.99 ± 0.1 | 2.02 ± 0.1 | 0.62 ± 0.1 | 50.62 ± 0.2 | 75.07± 0.1 |
| Ubiaja | 0.32 ± 0.1 | 2.45 ± 0.1 | 42.90 ± 0.2 | 30.22 ± 0.1 | 1.06 ± 0.2 | 1.51 ± 0.1 | 59.11 ± 0.1 | 91.64 ± 0.3 |
| Umuabi | 0.32 ± 0.1 | 1.14 ± 0.1 | 111.02 ± 0.1 | 25.52 ± 0.1 | 1.13 ± 0.1 | 0.18± 0.1 | 51.02 ± 0.1 | 90.88 ± 0.2 |

***(mg/kg) (n =2)***

Metallic elements have the ability to be translocated from soil to various parts of the plants. Invariably researchers have studied the oil palm tree extensively as an effective crop in remediation technology. It is a cheap choice to phytoremediation because it is low in maintenance and eco-friendly. Soils are cleaned up as the oil palm tree translocated metallic elements from soils to parts of the plant such as fruits and stems. This provides interesting tools to sites contaminated by toxic metals. Researchers have studied the accumulation of metallic elements in parts of the oil palm tree such as the stem and the root. Research is limited in area of the virgin palm oil, which is the oil palm fruit to decide if accumulation may be higher in such parts [51- 58].

### 8.3.3. Risk Assessment

Toxic metals on-route to humans and the food chain, via consumption of food crops grown on contaminated soils [2, 59]. This is especially hazardous and a critical health risk issue when the metallic elements exceed the permissible levels in palm oil. The food chain as a pathway of toxic metallic elements is vital in risk assessment in developing countries like Nigeria since ingestion of palm oil remains deregulated. Palm oil is a stable ingredient for the preparation of most dishes in Nigeria and consumed regularly by the population at large. Horiguchi and colleagues [60] implied that the intake of metals does not equate the concentrations absorbed by humans. He further explained that part of the absorbed dose is eliminated through various biochemical processes. The remainder portion becomes bio accumulated and biomagnified in humans. This study can be used to assess crop pollution and prospective risk assessment. There is a risk to the masses since they are not aware of the nutritional content of the palm oil consumed daily in the form of an ingredient of most of their stable food.

Tables 8.3a – 8.3c presents the values for the entire Risk Assessment factors such as the Accumulation Factor (AF), Daily Intake of metals (DIM), Health Risk Assessment (HRI) and Target Hazard Quotient (THQ) calculated for each sampling location while Table 8.4 highlights the minimum and maximum values for each factor in the respective metals.

**Table 8.3a: AF, DIM, HRI, & THQ (Cd, Co, and Cr)**

| | Cd | | | | Co | | | | Cr | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | AF | DIM | HRI | THQ | AF | DIM | HRI | THQ | AF | DIM | HRI | THQ |
| Abak | 0.12 | 0.012 | 11.77 | 0.2032 | 1.04 | 0.010 | 2.86 | 0.0480 | 0.05 | 0.004 | 0.03 | $6.38E^{-4}$ |
| Acharu | 5.85 | 0.008 | 7.84 | 0.2224 | 8.45 | 0.012 | 3.43 | 0.0450 | 0.12 | 0.004 | 0.03 | $5.36E^{-4}$ |
| Agbarho | 17.16 | 0.016 | 15.68 | 0.0368 | 14.4 | 0.052 | 14.86 | 0.1092 | 0.26 | 0.002 | 0.014 | $3.88E^{-4}$ |
| Ago-Emokpae | 5.02 | 0.016 | 15.68 | 0.1024 | 21.90 | 0.072 | 20.57 | 0.0480 | 0.67 | 0.006 | 0.04 | $7.75E^{-4}$ |
| Apoje | 20.78 | 0.08 | 78.43 | 0.0720 | 44.5 | 0.024 | 6.86 | 0.2093 | 0.78 | 0.06 | 0.43 | $8.87E^{-3}$ |
| Badagry | 2.98 | 0.012 | 11.77 | 0.1136 | 3.49 | 0.010 | 2.86 | 0.0416 | 0.03 | 0.002 | 0.014 | $3.19E^{-4}$ |
| Benin City | 41.90 | 0.08 | 78.43 | 0.1168 | 25.2 | 0.04 | 11.43 | 0.1517 | 0.85 | 0.06 | 0.43 | $7.54E^{-3}$ |
| Igede-Ekiti | 52.60 | 0.12 | 117.65 | 0.1216 | 141.3 | 0.06 | 17.14 | 0.2518 | 0.76 | 0.04 | 0.29 | $4.90E^{-4}$ |
| Ikire | 51.10 | 0.010 | 9.80 | 0.1120 | 9.81 | 0.010 | 2.86 | 0.0471 | 0.09 | 0.009 | 0.06 | $3.65E^{-4}$ |
| Iresa-apa | 10.50 | 0.24 | 235.29 | 0.1088 | 5.14 | 0.010 | 2.86 | 0.0600 | 0.04 | 0.006 | 0.04 | $5.24E^{-4}$ |
| Nsukka | 29.80 | 0.012 | 11.77 | 0.7712 | 54.6 | 0.04 | 11.43 | 0.3039 | 0.27 | 0.0026 | 0.02 | $3.81E^{-4}$ |
| Okitipupa | 324.20 | 0.075 | 78.43 | 1.0752 | 11.92 | 0.04 | 11.43 | 0.1422 | 0.04 | 0.026 | 0.19 | $3.19E^{-4}$ |
| Onishere | 120.30 | 0.078 | 78.43 | 0.1808 | 110.9 | 0.04 | 11.43 | 0.4054 | 0.009 | 0.0008 | 0.006 | $1.25E^{-4}$ |
| Ubiaja | 4.16 | 0.004 | 3.92 | 0.0592 | 42.8 | 0.0010 | 2.86 | 0.0466 | 2.23 | 0.08 | 0.57 | $1.10E^{-2}$ |
| Umuabi | 40.93 | 0.0010 | 0.98 | 0.4220 | 8.77 | 0.0010 | 2.86 | 0.0457 | 0.04 | 0.004 | 0.03 | $4.56E^{-4}$ |

***(mg/kg/person/day) values for Cd, Co and Cr***

**Table 8.3b: AF, DIM, HRI & THQ ( Fe, Mn, and Ni)**

| | Fe | | | | Mn | | | | Ni | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | AF | DIM | HRI | THQ | AF | DIM | HRI | THQ | AF | DIM | HRI | THQ |
| Abak | 0.68 | 0.016 | 3.0 | $6.75E^{-6}$ | 7.5 | 0.006 | 0.04 | $7.52E^{-4}$ | 0.17 | 0.006 | 0.3 | $5.4E^{-3}$ |
| Acharu | 0.52 | 0.008 | 0.4 | $2.91E^{-6}$ | 0.34 | 0.006 | 0.04 | $8.32E^{-4}$ | 0.18 | 0.014 | 0.7 | $1.3E^{-2}$ |
| Agbarho | 1.29 | 0.012 | 0.6 | $5.09E^{-6}$ | 10 | 0.0018 | 0.01 | $2.62E^{-4}$ | 0.8 | 0.008 | 0.4 | $7.1E^{-3}$ |
| Ago-Emokpae | 1.84 | 0.014 | 0.7 | $5.38E^{-6}$ | 0.68 | 0.006 | 0.04 | $7.30E^{-4}$ | 0.66 | 0.016 | 0.8 | $1.6E^{-3}$ |
| Apoje | 2.29 | 0.012 | 0.6 | $4.86E^{-6}$ | 101.3 | 0.04 | 0.29 | $5.20E^{-3}$ | 2.20 | 0.006 | 0.3 | $6.3E^{-2}$ |
| Badagry | 9.61 | 0.014 | 0.7 | $5.87E^{-6}$ | 5.34 | 0.006 | 0.04 | $8.09E^{-4}$ | 0.38 | 0.014 | 0.7 | $1.5E^{-2}$ |
| Benin City | 6.89 | 0.012 | 0.6 | $4.45E^{-6}$ | 0.25 | 0.006 | 0.04 | $8.32E^{-4}$ | 2.35 | 0.06 | 3.0 | $6.1E^{-2}$ |
| Igede-Ekiti | 27.4 | 0.012 | 0.6 | $4.39E^{-6}$ | 10 | 0.006 | 0.04 | $8.66E^{-4}$ | 0.45 | 0.014 | 0.7 | $1.4E^{-2}$ |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ikire | 16.73 | 0.014 | 0.7 | $5.89E^{-6}$ | 4.70 | 0.006 | 0.04 | $7.98E^{-4}$ | 0.41 | 0.014 | 0.7 | $1.5E^{-2}$ |
| Iresa-apa | 13.20 | 0.002 | 0.1 | $4.35E^{-6}$ | 9.07 | 0.006 | 0.04 | $7.75E^{-4}$ | 0.37 | 0.014 | 0.7 | $1.3E^{-2}$ |
| Nsukka | 3.27 | 0.010 | 0.5 | $1.06E^{-6}$ | 1.7 | 0.038 | 0.29 | $5.50E^{-3}$ | 1.37 | 0.06 | 3.0 | $5.4E^{-2}$ |
| Okitipupa | 11.09 | 0.006 | 0.3 | $3.58E^{-6}$ | 67.9 | 0.006 | 0.04 | $7.66E^{-3}$ | 1.94 | 0.06 | 3.0 | $5.4E^{-2}$ |
| Onishere | 33.3 | 0.006 | 0.3 | $2.15E^{-5}$ | 18.2 | 0.010 | 0.07 | $1.29E^{-3}$ | 1.07 | 0.04 | 2.0 | $4.3E^{-2}$ |
| Ubiaja | 17.6 | 0.014 | 0.7 | $5.98E^{-6}$ | 2.45 | 0.004 | 0.03 | $4.22E^{-4}$ | 0.29 | 0.014 | 0.7 | $1.4E^{-2}$ |
| Umuabi | 15.04 | 0.014 | 0.7 | $5.44E^{-6}$ | 22.40 | 0.02 | 0.14 | $3.21E^{-4}$ | 0.34 | 0.008 | 0.4 | $1.4E^{-2}$ |

***(mg/kg/person/day) values for Fe, Mn, and Ni***

**Table 8.3c: AF, DIM, HRI, & THQ (Zn and Cu)**

| | Zn | | | | Cu | | | |
|---|---|---|---|---|---|---|---|---|
| | AF | DIM | HRI | THQ | AF | DIM | HRI | THQ |
| Abak | 0.13 | 0.006 | 0.0045 | $9.96E^{-5}$ | 0.17 | 0.004 | 0.003 | $7.49E^{-5}$ |
| Acharu | 0.09 | 0.02 | 0.0150 | $4.11E^{-4}$ | 0.54 | 0.010 | 0.0007 | $1.25E^{-4}$ |
| Agbarho | 0.32 | 0.010 | 0.0075 | $1.51E^{-4}$ | 0.17 | 0.006 | 0.004 | $5.63E^{-4}$ |
| Ago-Emokpae | 0.20 | 0.014 | 0.0105 | $2.18E^{-4}$ | 0.20 | 0.004 | 0.003 | $7.49E^{-5}$ |
| Apoje | 1.68 | 0.12 | 0.0902 | $1.95E^{-3}$ | 0.25 | 0.009 | 0.006 | $8.88E^{-5}$ |
| Badagry | 0.18 | 0.008 | 0.0060 | $1.15E^{-4}$ | 0.27 | 0.014 | 0.009 | $1.97E^{-4}$ |
| Benin City | 0.09 | 0.008 | 0.0060 | $1.20E^{-4}$ | 0.40 | 0.008 | 0.005 | $9.74E^{-4}$ |
| Igede-Ekiti | 0.07 | 0.004 | 0.0030 | $6.36E^{-5}$ | 0.27 | 0.008 | 0.005 | $9.53E^{-5}$ |
| Ikire | 0.10 | 0.008 | 0.0060 | $1.11E^{-4}$ | 0.48 | 0.002 | 0.001 | $1.17E^{-4}$ |
| Iresa-apa | 2.66 | 0.02 | 0.0150 | $3.95E^{-4}$ | 0.27 | 0.006 | 0.004 | $8.77E^{-5}$ |
| Nsukka | 1.21 | 0.04 | 0.0300 | $5.43E^{-4}$ | 0.08 | 0.0016 | 0.001 | $2.35E^{-5}$ |
| Okitipupa | 0.18 | 0.006 | 0.0045 | $1.33E^{-4}$ | 0.98 | 0.02 | 0.01 | $3.55E^{-4}$ |
| Onishere | 0.88 | 0.06 | 0.045 | $7.96E^{-4}$ | 1.17 | 0.04 | 0.03 | $4.77E^{-4}$ |
| Ubiaja | 0.7 | 0.06 | 0.045 | $7.71E^{-4}$ | 0.25 | 0.006 | 0.004 | $8.13E^{-4}$ |
| Umuabi | 0.86 | 0.06 | 0.045 | $9.35E^{-4}$ | 0.40 | 0.08 | 0.05 | $1.08E^{-3}$ |

***(mg/kg/person/day) values for Zn and Cu***

The Accumulation Factor (AF) summarised in Table 8.4 and Figures 8.2 & 8.3 can best be used to describe the degree in which the palm oil accumulates in the biological system, which is the oil palm fruit. The AF for the metallic elements in the palm oil ranged between 324.20-0.78 mg/kg and was greatest for Cd (324.20 mg/kg) in Okitipupa and Ni (141.3 mg/kg) in Igede-Ekiti plantations respectively. The AF value of 0.03 mg/kg (Cr) in Badagry plantation and 0.07 mg/kg (Zn) in Igede Ekiti plantations were the least AF values investigated respectively. The sequence of accumulation was can be described using the bioaccumulation factor, as Cd was the greatest bio accumulator in the palm oil. The Accumulation factor (AF) for the metallic elements Cd, Co, Fe and Mn was greater than unity in all or most of the palm oil sampled from the plantations. This is an indication of bioaccumulation in the edible part of the oil palm tree, the fruit. AF factors lesser than one and very close to unity were recorded for metallic elements

such as Ni, Cu, Cr and Zn. Lower AF values show low transfer of metallic elements and a lower risk of contamination. Overall, the value of the Accumulation Factor was maximum for Cadmium in Okitipupa plantation and the lowest value was in Zinc (Igede Ekiti).

**Table 8.4: AF, DIM, HRI, and THQ (Summary of maximum and minimum values in metals)**

| Metal | AF Highest Value | AF Lowest Value | DIM Highest Value | DIM Lowest Value | HRI Highest Value | HRI Lowest Value | THQ Highest Value | THQ Lowest Value |
|---|---|---|---|---|---|---|---|---|
| **Ca** | 324.2 (Okitipupa) | 0.12 (Abak) | 0.24 (Iresa-Apa) | 0.001 (Umuabi) | 235.29 (Iresa-Apa) | 0.98(Umuabi) | 1.0752 (Okitipupa) | 0.0368(Agbarho) |
| **Co** | 141.3 (Igede-Ekiti) | 1.04 (Abak) | 0.072 (Ago-Emokpae) | 0.001 (Ubiaja/Umuabi) | 20.57 (Ago-Emokpae) | 2.86 (Abak, Badagry, Ikire, Iresa-Apa, Ubiaja, Umuabi) | 0.4054 (Onishere) | 0.0416 (Badagry) |
| **Fe** | 33.3 (Onishere) | 0.52 (Acharu) | 0.016 (Abak) | 0.002 (Iresa-Apa) | 3.0 (Abak) | 0.1 (Iresa-Apa) | $2.15E^{-05}$ (Onishere) | $1.06E^{-06}$ (Nsukka) |
| **Cr** | 2.23 (Ubiaja) | 0.03 (Badagry) | 2.23 (Ubiaja) | 0.03 (Badagry) | 0.57 (Ubiaja) | 0.006 (Onishere) | $1.10E^{-02}$ (Ubiaja) | $1.25E^{-04}$ (Onishere) |
| **Mn** | 101.3 (Apoje) | 0.25 (Benin City) | 0.04 (Apoje) | 0.0018 (Agbarho) | 0.29 (Apoje, Nsukka) | 0.01 (Agbarho) | $7.66E^{-03}$ (Okitipupa) | 0.01 (Agbarho) |
| **Ni** | 2.35 (Ubiaja) | 0.29 (Ubiaja) | 0.06 (Benin City, Nsukka, Okitipupa) | 0.006 (Abak/Apoje) | 3.0 (Benin City, Nsukka, Okitipupa) | 0.3 (Abak/Apoje) | $6.3E^{-02}$ (Apoje) | $1.6E^{-03}$ (Agbarho) |
| **Zn** | 2.66 (Iresa-Apa) | 0.07 (Igede-Ekiti) | 0.12 (Apoje) | 0.004 (Igede-Ekiti) | 0.0902 (Apoje) | 0.003 (Igede-Ekiti) | $1.95E^{-03}$ (Apoje) | $6.36E^{-05}$ (Igede-Ekiti) |
| **Cu** | 1.17 (Onishere) | 0.17 (Abak/Agbarho) | 0.08 (Umuabi) | 0.0016 (Nsukka) | 0.05 (Umuabi) | 0.0007 (Acharu ) | $1.80E^{-03}$ (Umuabi) | $2.35E^{-05}$ (Nsukka ) |

***Summary of maximum and minimum values in metals***

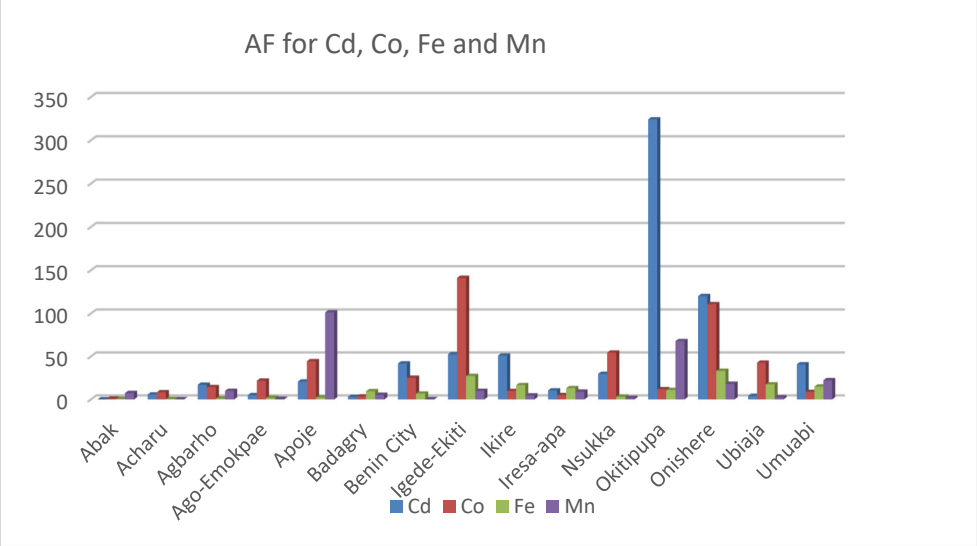



**Fig. 8.2: AF for Cd, Co, Fe & Mn**

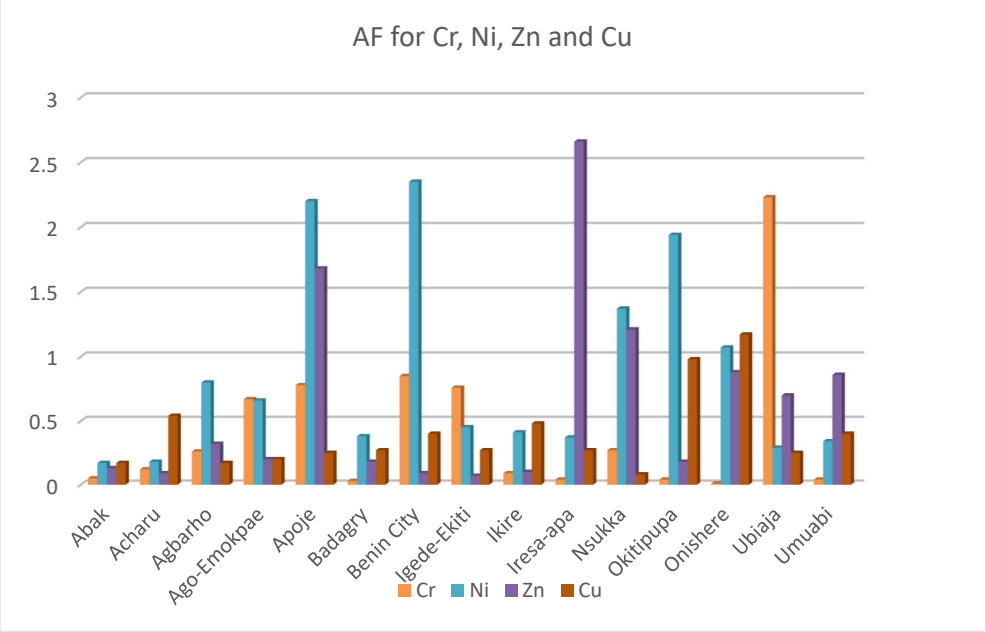



**Fig. 8.3: AF for Cr, Ni, Zn & Cu**

## 8.4 Daily Intake of Metals and Health Risk Index

Risk assessment of the palm oil in humans was best described by the Metals Daily Intake (DIM) and Health Risk Index (HRI) values. The exposure of the pollutants is the target organism. This is particularly risky and hazardous to the food chain. Risk assessment is of paramount significance in developing countries like Nigeria where the disposal of waste on agricultural lands is largely unregulated. Although several pathways of exposure such as the

air, water, and soil may contribute to contamination, food is significantly a higher route of exposure. The consumption of palm oil as the stable ingredient in most foods is the pathway to the ingestion of the metallic elements in this study. The index that describes the average consumption of the palm oil is the DIM and HRI values (Table 8.3a, b, and c). The values obtained for DIM and HRI in the plantations are summarised in Tables 8.4 and Figures 8.4 & 8.5.

The DIM values of the contaminated palm oil were highest for Chromium (2.23) in Ubiaja plantation and Cadmium (0.24) in Iresa Apa plantation respectively. Lowest values were recorded for Chromium (0.0016) and Manganese (0.00180) at Nsukka and Agbarho plantations respectively. The DIM and HRI values were close to unity/greater than unity in most of the plantations indicating a high risk to the food chain. The Oral Reference Dose, (RfD) was earlier defined as a tool quantitatively used in risk assessment to evaluate the ingestion of a non-carcinogenic contaminant per milligram per kilogram per day. An HRI greater than one signifies that the population suffers a health risk when such food is consumed. The RfD is related to the HRI by an equation earlier explained [40]. Much lower values of HRI were found in metallic elements Cu, Mn and Zn. HRI values above unity signifies an indication of future toxicity to humans via the food chain. Essential and non-essential metallic elements at high and low concentration are detrimental at the risk assessment point of view. The values of HRI obtained in this study are in agreement with those obtained by [2, 61, and 62].

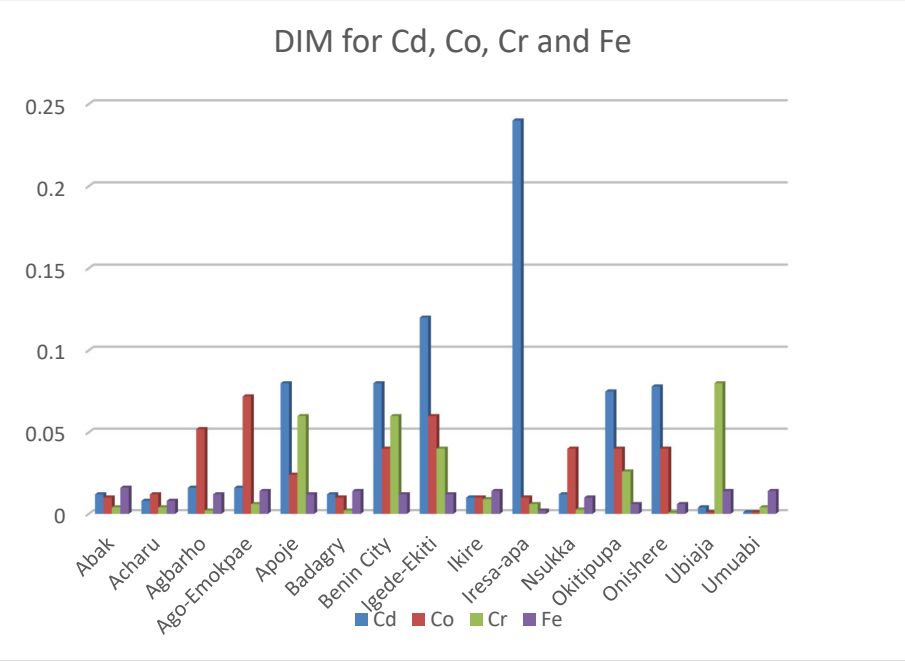


**Fig. 8.4: DIM for Cd, Co, Cr & Fe**

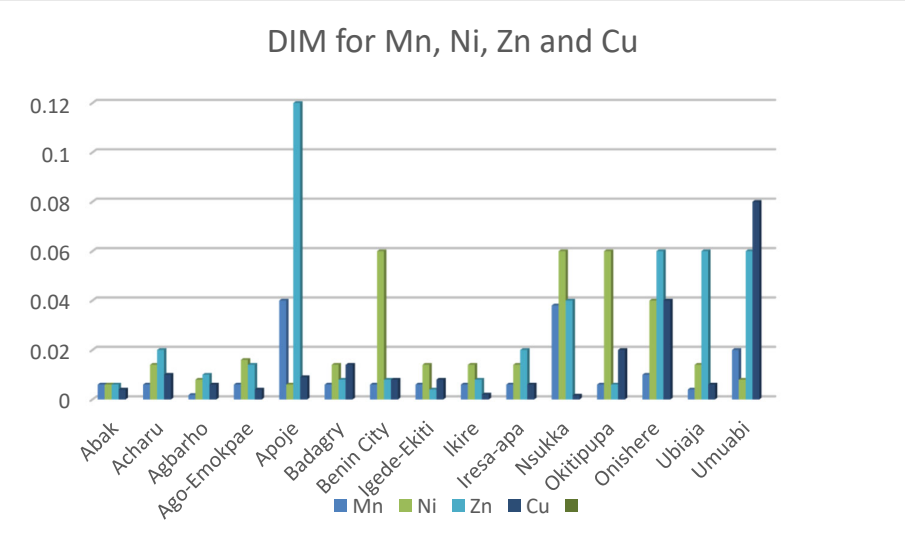



**Fig. 8.5: DIM for Mn, Ni, Zn & Cu**

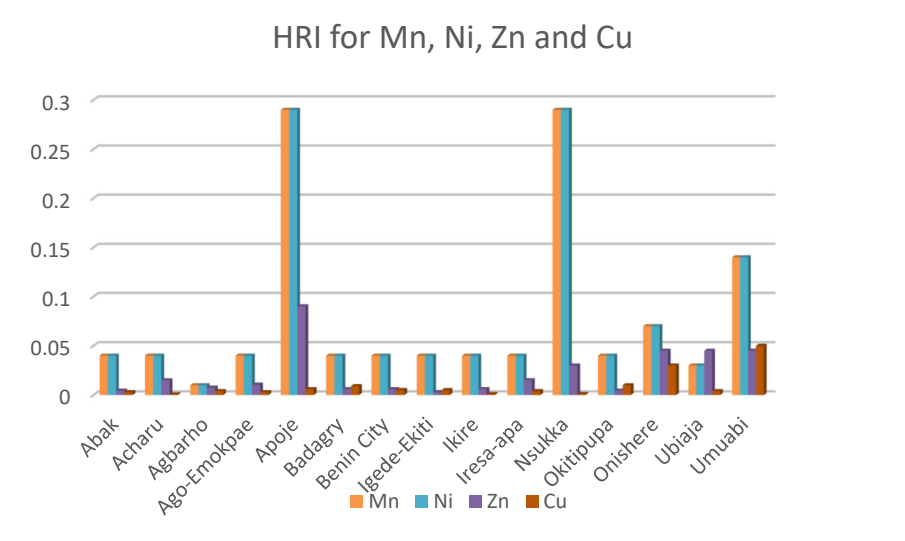



**Fig. 8.6 : HRI for Mn, Ni, Zn & Cu**

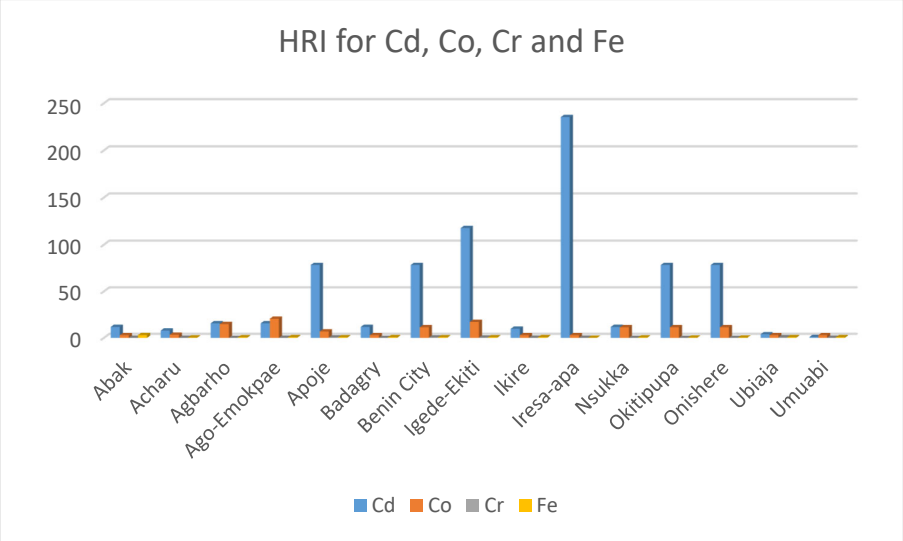



**Fig.8.7: HRI for Cd, Co, Cr, & Fe**

## 8.5 Target Hazard Quotient

Another important tool for the evaluation of risk assessment with the intake of toxic metallic elements in food is the Target Hazard Quotient (THQ) [2, 59]. Toxicity of the palm oil is a possibility since most of the THQ values obtained in the present study were above the permissible limits as shown in Table 8.4 and Figures 8.8 & 8.9. Although non-essential elements such as Cr, Ni, and Cd were present in the palm oil at elevated concentrations, biochemical processes are available for their reduction in the human system. Biochemical processes emphasize that ingested metallic elements from food is not only absorbed into tissues as some may be excreted by the skin, kidneys etc.

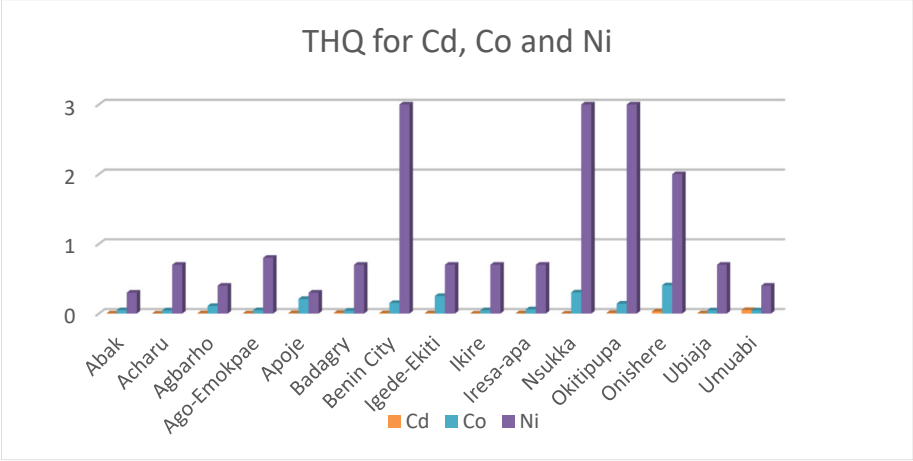



**Fig. 8.8: THQ for Cd, Co & Ni**

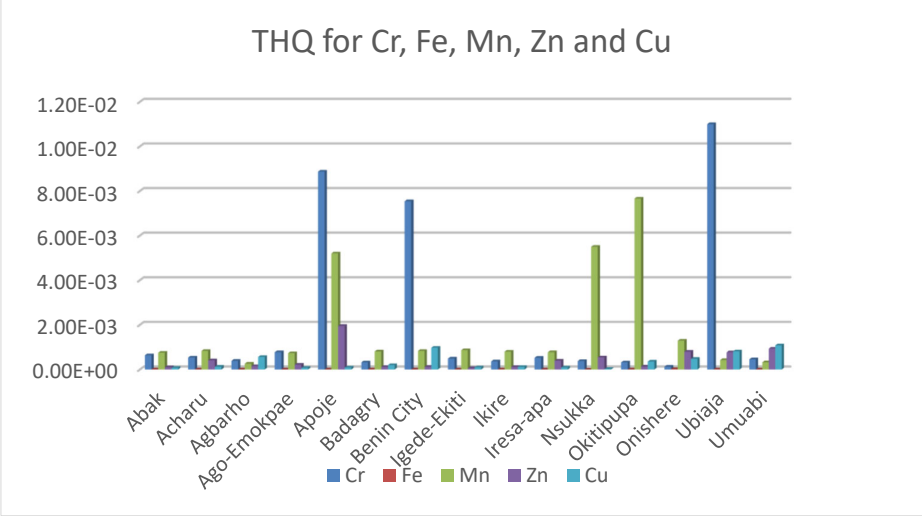



**Fig. 8.9 : THQ for Cr, Fe, Mn, Zn, & Cu**

## 8.6 Correlation studies and the distribution of metals in palm oil and soils

The mobility and transfer of metals from soil to palm oil showed a positive correlation in the metals Copper and Zinc (+0.218 and +0.266) respectively. Negative correlation was exhibited with metals Cadmium, Cobalt, Chromium, Iron, Manganese and Nickel which showed negative correlation of -0.106, -0.352, -0.196, -0.113, -0.253 and -0.266 values respectively. Figures 10-17 depicts the correlation between the concentrations of metals in soil and palm oil.

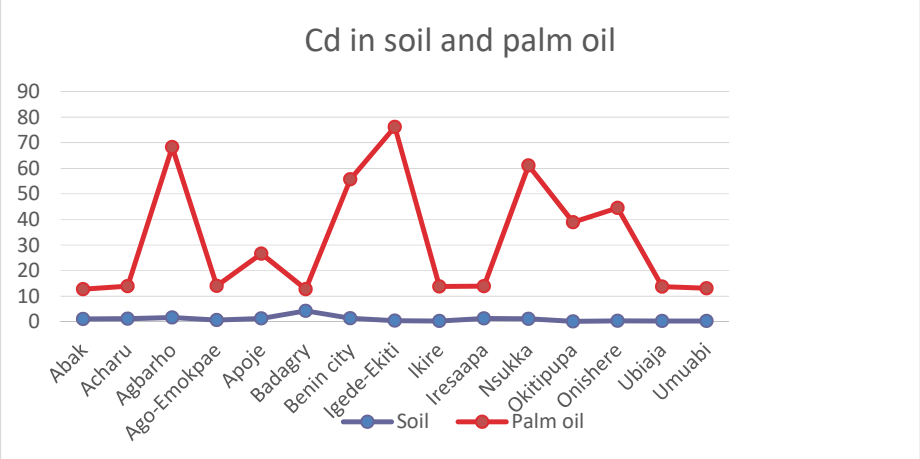



**Fig. 8.10: Correlation of Cd in soil and palm oil**

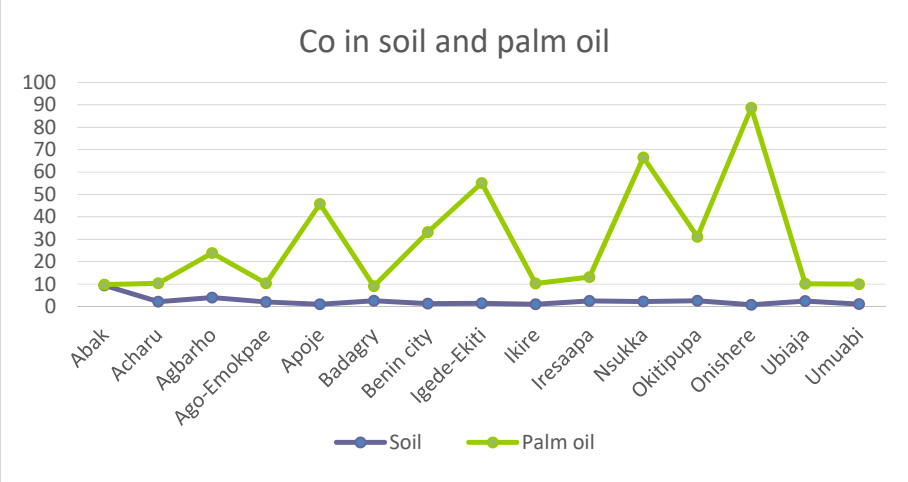



**Fig.8.11: Correlation of Co in soil and palm oil**

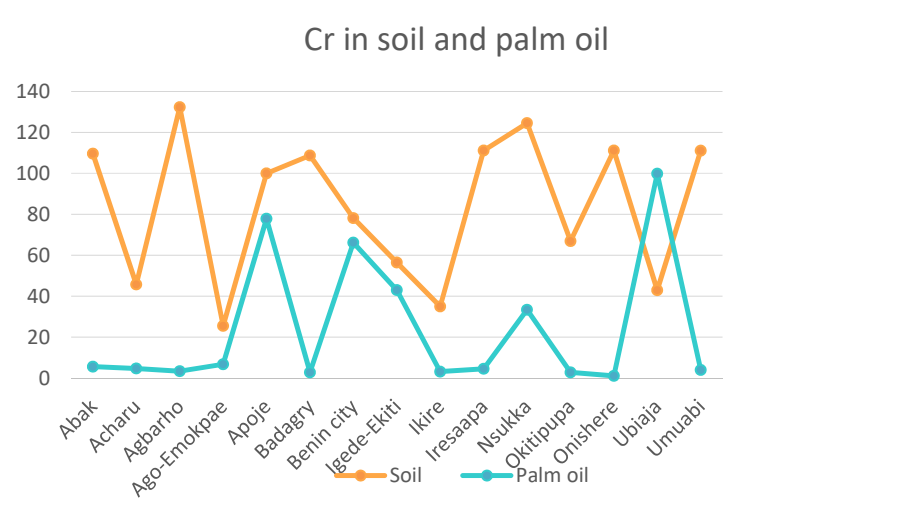



**Fig. 8.12: Correlation of Cr in soil & palm oil**

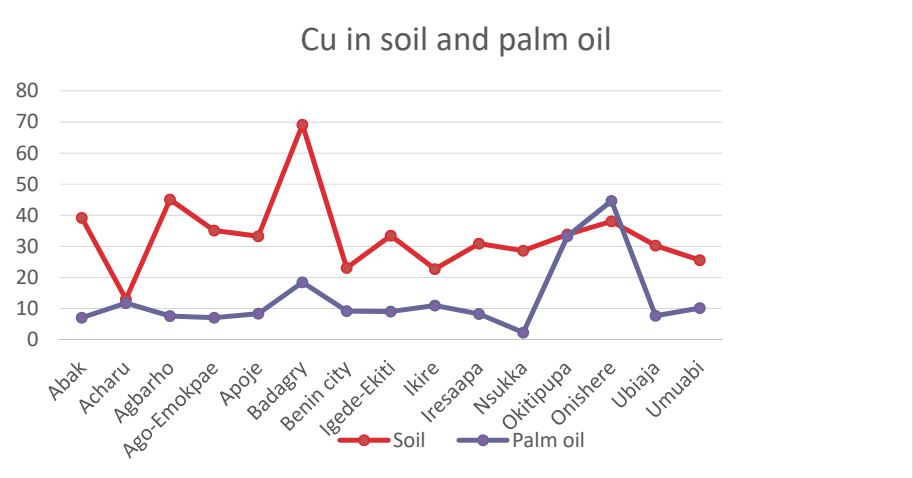


**Fig. 8.13: Correlation of Cu in soil & palm oil**

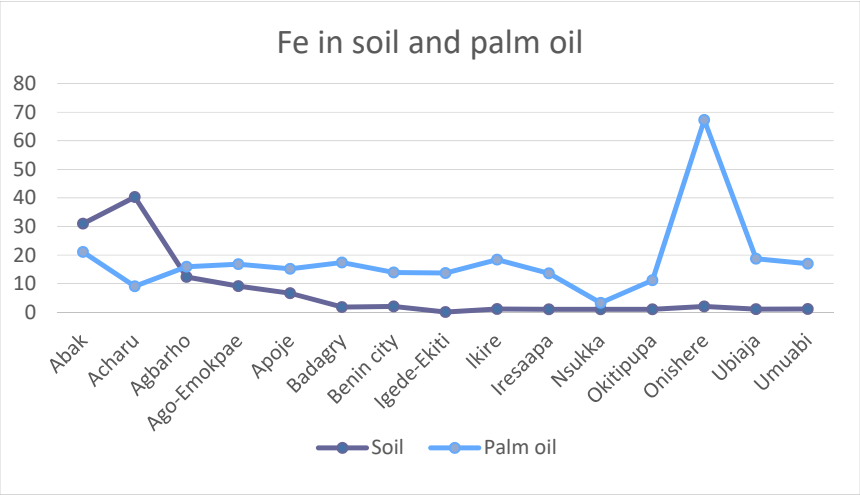



**Fig. 8.14: Correlation of Fe in soil and palm oil**

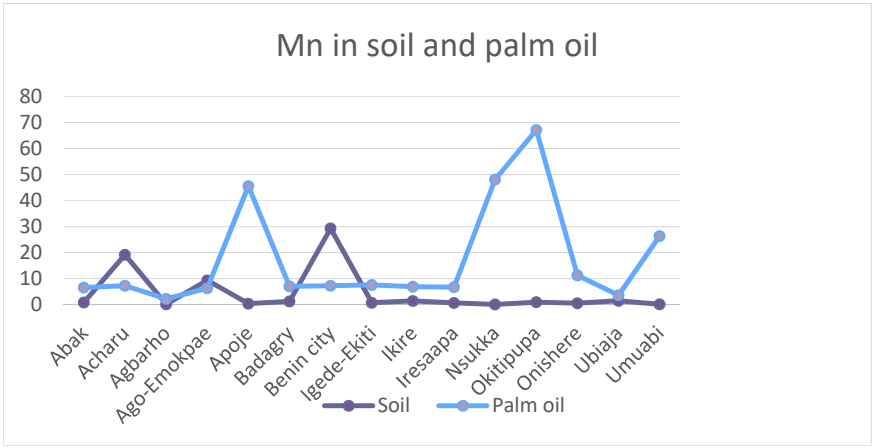



**Fig. 8.15: Correlation of Mn in soil and palm oil**

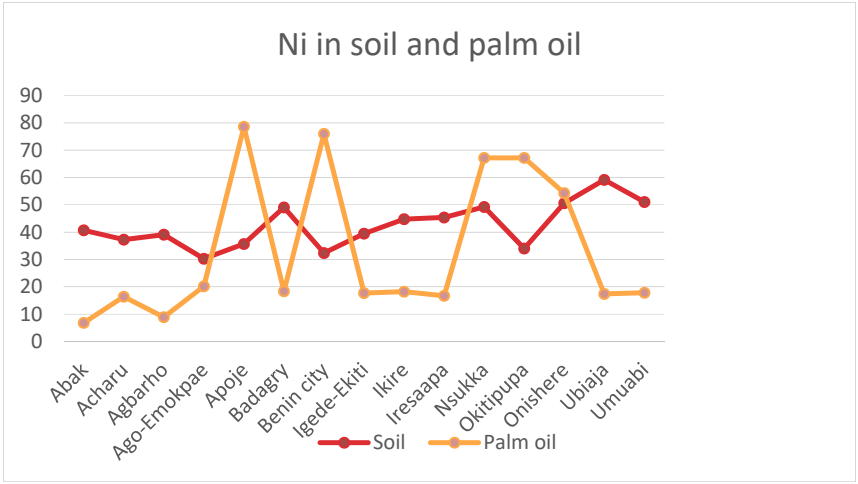



**Fig. 8.16: Correlation of Ni in soil and palm oil**

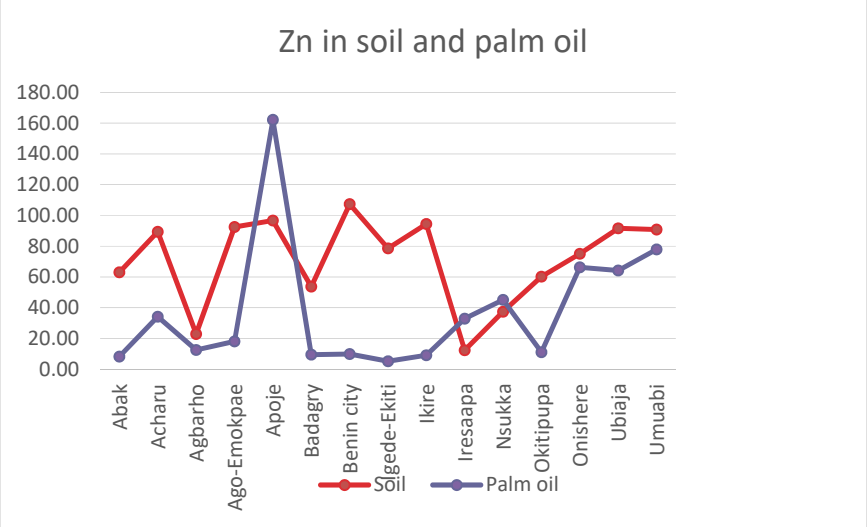



**Fig. 8.17: Correlation of Zn in soil and palm oil**

## 8.7. Conclusions

Agronomical practices such as pesticides and fertilizers use have been extensively applied in agriculture due to the quest for improved yield. Agriculture produce have always been grown on acclaimed lands such as landfills and dumpsites. The unavailability of land for agricultural purposes, leached and drained soils, and unsuitable topography has led to the quest for improved soil using sewage water, effluents, fertilizers, and pesticides on agricultural lands. Pesticides, fertilizers, sewage water, and effluents contain a relatively large concentration of metallic elements that are toxic to plants and humans when above the permissible limits. So do landfills and dumpsites. This present study assessed the concentration of palm oil pressed from oil palm fruits grown on anthropogenically contaminated oil palm plantation soils. This has led to an accumulation of metallic elements in the soil onto the palm oil. However, it was observed that the Accumulation Factor in the palm oil varied for each metal with Cadmium and Zinc being the top accumulators in palm oil. Hence, the palm oil sampled from most of the plantations was not desirable for human consumption but may be suitable for the agro allied and chemical industries and for the production of biodiesel. The plantation soils have a high concentration of metallic elements which bioaccumulated in the palm oil. The concentration of essential and non-essential metallic elements in elevated concentrations is toxic to human life and various signs and symptoms exhibit this.

To the best of the understanding of the authors, data is not available in the region for an effective risk assessment on the consumption of palm oil contaminated with metallic elements and its effect on humans. The present findings emphasize on anthropogenic contamination as the source of pollution in the palm oil. The intake of the palm oil has the potential of causing

detrimental and undesirable health issues in the present and future. The results disclose high AF and HRI values above one and close to unity for most of the plantations. The investigation proffers a concise understanding on the prevailing situation and circumstances of palm oil poisoning and pollution with imminent and impending prospective health hazard assessment. A crucial demand prevails to control the palm oil processed from the palm fruits in the region. In addition, policies and programmes must be implemented, to forestall the accumulation of the metallic elements in the palm oil. This will abate future health risks to the susceptible population of the region. The study declares anthropogenic source of pollution as the source of point and non-point pollution in the palm oil. The values arrived at in this study will furnish baseline records and data for the consumption of palm oil in the region. Recommendation is required to prevent the onset of anthropogenic pollution into the farmlands and measures be taken for clean-up of soils before the embankment of pre and post planting operations.

## 8.8 ACKNOWLEDGEMENT

The authors wish to thank the Cape Peninsula University of Technology, South Africa for funding the research and Bowen University Iwo, Nigeria for the staff Development award for Olafisoye Oladunni Bola.

## 8.9 REFERENCES


[1] R. Aziz, M.T. Rafiq, J. Yang, D. Liu, L. Lu, Z. He, M.K. Daud, T. Li, X. Yang, Impact assessment of cadmium toxicity and its bioavailability in human cell lines (Caco-2 and HL-7702), Biomed Res. Int. 2014 (2014) 1–8. doi:10.1155.

[2] K.S. Balkhair, M.A. Ashraf, Field accumulation risks of heavy metals in soil and vegetable crop irrigated with sewage water in western region of Saudi Arabia, Saudi J. Biol. Sci. 23 (2016) 32–44. doi:10.1016.

[3] S.R. Smith, K.E. Giller, Effective Rhizobium leguminosarum biovar Trifolii present in five soils contaminated with heavy metals from long-term applications of sewage sludge or metal mine spoil, Soil Biol. Biochem. 24 (1992) 781–788. doi:10.1016.

[4] A.B. Mukherjee, Chromium in the environment of Finland, Sci. Total Environ. 217 (1998) 9–19. doi:10.1016.

[5] K. Fytianos, G. Katsianis, P. Triantafyllou, G. Zachariadis, Accumulation of Heavy Metals in Vegetables Grown in an Industrial Area in Relation to Soil Environmental Contamination and Toxicology 423, Environ. Contam. Toxicol. 67 (2001) 423–430. doi:10.1007.

[6] I. Khan, A. Ghani, S.A. Awan, H. Jawed, R. Gul, The analyses of heavy metal concentrations in soil, waste water and Raphanus sativus (L.) at three different growth stages, Pyrex J. Res. Environ. Stud. 3 (2016) 42–48.

[7] O.T. Oyeku, A.O. Eludoyin, Heavy metal contamination of groundwater resources in a Nigerian urban settlement, African J. Environ. Sci. Technol. 4 (2010) 201–214. doi:10.5897.

[8] K. Asemave, S. Ubwa, B.A. Anhwange, A.G. Gbaamende, Comparative Evaluation of Some Metals in Palm Oil, Groundnut Oil and Soybean Oil from Nigeria, Int. J. Nano Mater. Sci. 1 (2012) 28–35.

[9] J.T. Ayodele, C.D. Oluyomi, Grass contamination by trace metals from road traffic, J. Environ. Chem. Ecotoxicol. 3 (2011) 60–67.

[10] H. Ullah, I. Khan, I. Ullah, Impact of sewage contaminated water on soil, vegetables, and underground water of peri-urban Peshawar, Pakistan, Environ. Monit. Assess. 184 (2012) 6411–6421. doi:10.1007.

[11] A.O.R. Ogunsola, G.O. Oluwusi, Methods of Palm Oil Processing in Ogun state, Nigeria: A Resource Use Efficiency Assessment, Am. Int. J. Contemp. Res. 4 (2014) 173–179.

[12] D. Kritchevsky, Impact of red palm oil on human nutrition and health, Food Nutr. Bull. 21 (2000) 182–188. doi:10.1177.

[13] S. Mukherjee, A. Mitra, Health Effects of Palm Oil, J. Hum. Ecol. 26 (2009) 197–203. doi:10.1080.

[14] O.J. Odia, Palm oil and the heart: A review, World J. Cardiol. 7 (2015) 144. doi:10.4330.

[15] R. Loganathan, K.M. Subramaniam, A.K. Radhakrishnan, Y.M. Choo, K.T. Teng, Health-promoting effects of red palm oil: Evidence from animal and human studies, Nutr. Rev. 75 (2017) 98–113. doi:10.1093.

[16] C. Lv, Y. Wang, C. Zhou, W. Ma, Y. Yang, R. Xiao, H. Yu: Food & Nutrition Research, Food Nutr. Res. 62 (2018) 1353. doi:10.29219.

[17] Imoisi, OB, Ilori GE, Agho I, Ekhator JO, Palm oil, its nutritional and health implications ( Review ), J. Appl. Sci. Environ. Manag. 19(1) 2015) 127-133.

[18] A. Mancini, E. Imperlini, E. Nigro, C. Montagnese, A. Daniele, S. Orrù, P. Buono, Biological and nutritional properties of palm oil and palmitic acid: Effects on health, Molecules. 20 (2015) 17339–17361. doi:10.3390.

[19] J.M. Yun, J. Surh, Fatty acid composition as a predictor for the oxidation stability of korean vegetable oils with or without induced oxidative stress, Prev. Nutr. Food Sci. 17 (2012) 158–165. doi:10.3746.
[20] A.K. Endalew, Y. Kiros, Catalytic Autoxidation of Fatty Acid Methyl Esters from Jatropha Oil, J. Fuels. 2014 (2014) 1–6. doi:10.1155.
[21] I. Ide, T, Origuchi, Physiological effects of an oil rich in γ-linoleic acid in hepatic fatty acid oxidation and serum lipid levels in genetically hyperlipidemic mice., J. Clin. Biochem. Nutr. 64 (2019) 148–157. doi:10.3164.
[22] M. Anju, D.K. Banerjee, Associations of cadmium, zinc, and lead in soils from a lead and zinc mining area as studied by single and sequential extractions, Environ. Monit. Assess. 176 (2011) 67–85. doi:10.1007.
[23] B.O. Olafisoye, O.O. Fatoki, O.O. Oguntibeju, A.O. Osibote, Determination of trace and major elements in water on oil palm plantations by inductively coupled plasma-optical emission spectrometry, Instrum. Sci. Technol. 42 (2014) 652–666. doi:10.1080.
[24] A. V. Soin, T.A. Maryutina, T. V. Arbuzova, B.Y. Spivakov, Sample preparation in the determination of metals in oil and petroleum products by ICP MS, J. Anal. Chem. 65 (2010) 571–576. doi:10.1134.
[25] E. Bulska, B. Wagner, Quantitative aspects of inductively coupled plasma mass spectrometry, Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 374 (2016) 1–18. doi:10.1098.
[26] J.A. Carter, A.I. Barros, J.A. Nóbrega, G.L. Donati, Traditional calibration methods in atomic spectrometry and new calibration strategies for inductively coupled plasma mass spectrometry, Front. Chem. 6 (2018) 1–25. doi:10.3389.
[27] G. Sylvia, T.T. Nikita, J.K. Michael, M.M. Fanyana, J.M. Sekomeng, E.P. Vusumzi, Quantification of Cd, Cu, Pb and Zn from sewage sludge by modified-BCR and ultrasound assisted-modified BCR sequential extraction methods, African J. Pure Appl. Chem. 11 (2017) 9–18. doi:10.5897.
[28] J. Malakar, S.O. Sen, A.K. Nayak, K.K. Sen, Development and Evaluation of Microemulsions for Transdermal Delivery of Insulin, ISRN Pharm. 2011 (2011) 1–7. doi:10.5402.
[29] E. Moghimipour, A. Salimi, S. Changizi, Preparation and microstructural characterization of griseofulvin microemulsions using different experimental methods: SAXS and DSC, Adv. Pharm. Bull. 7 (2017) 281–289. doi:10.15171.
[30] H.A. Tekie, R.I. McCrindle, P.J.J.G. Marais, A.A. Ambushe, Evaluation of six sample preparation methods for determination of trace metals in lubricating oils using inductively coupled plasma-optical emission spectrometry, South African J. Chem. 68 (2015) 76–84. doi:10.17159.
[31] K.V. Y Sharma, K. Kamalpreet, Analysis of pH and Electrical Conductivity of White Ash Discharge from Textile Analysis of pH and Electrical Conductivity of White Ash Discharge from Textile Industries in Barnala Region (Punjab, India): Deteriorating to Human Health, J. Chem. Chem. Sci. 7 (2017) 72–80.
[32] K.L. Sahrawat, Simple modification of the Walkley-Black method for simultaneous determination of organic carbon and potentially mineralizable nitrogen in tropical rice soils, Plant Soil. 69 (1982) 73–77. doi:10.1007.
[33] M.B. Galuch, A.F.B. Piccioli, E.S. Neto, N. Fier, N.C. Saldan, E.E. Garcia, Microemulsion as sample preparation for direct flame atomic absorption spectrometry (FAAS)

determination of total iron in crude and refined vegetable oils, J. Braz. Chem. Soc. 29 (2018) 748–756. doi:10.21577.
[34] M.E.A. Hammouda, M.A. Abu El-Enin, D.T. El-Sherbiny, D.R. El-Wasseef, S.M. El-Ashry, Microemulsion liquid chromatographic method for simultaneous determination of simvastatin and ezetimibe in their combined dosage forms, J. Anal. Methods Chem. 2013 (2013) 1–9. doi:10.1155.
[35] R. Log, Standard Operating Procedure No. 30 ICP-OES Analysis, (2008) 1–19.
[36] A. Shrivastava, V. Gupta, Methods for the determination of limit of detection and limit of quantitation of the analytical methods, Chronicles Young Sci. 2 (2011) 21. doi:10.4103.
[37] N. Saadati, M.P. Abdullah, Z. Zakaria, S.B.T. Sany, M. Rezayi, H. Hassonizadeh, Limit of detection and limit of quantification development procedures for organochlorine pesticides analysis in water and sediment matrices, Chem. Cent. J. 7 (2013) 1. doi:10.1186.
[38] C. Radulescu, C. Stihi, I. V Popescu, I.D. Dulama, E.D. Chelarescu, A. Chilian, N. Engineering, Heavy Metal Accumulation and Translocation in, Heavy Met. Accumul. Translocat. Differ. Parts Brassica Oleracea L C. 58 (2013) 1337–1354.
[39] H. Zhou, W.T. Yang, X. Zhou, L. Liu, J.F. Gu, W.L. Wang, J.L. Zou, T. Tian, P.Q. Peng, B.H. Liao, Accumulation of heavy metals in vegetable species planted in contaminated soils and the health risk assessment, Int. J. Environ. Res. Public Health. 13 (2016) 1–12. doi:10.3390.
[40] EPA, Radionuclides in Drinking Water: A Small Entity Compliance Guide, 2002.
[41] N. Abdu, A.A. Yusuf, Human health risk characterization of lead pollution in contaminated farmlands of Abare village, Zamfara State, Nigeria, African J. Environ. Sci. Technol. 7 (2013) 911-916. doi:10.5897.
[42] B. Olafisoye, O. Oguntibeju, O. Osibote, An Assessment of the Bioavailability of Metals in Soils on Oil Palm Plantations in Nigeria, Polish J. Environ. Stud. 25 (2016) 1125–1140. doi:10.15244.
[43] Q.H. Zhu, D.Y. Huang, S.L. Liu, Z.C. Luo, H.H. Zhu, B. Zhou, M. Lei, Z.X. Rao, X.L. Cao, Assessment of single extraction methods for evaluating the immobilization effect of amendments on cadmium in contaminated acidic paddy soil, Plant, Soil Environ. 58 (2012) 98–103.
[44] R.A. Wuana, F.E. Okieimen, Heavy metals in contaminated soils: A review of sources, chemistry, risks, and best available strategies for remediation, Heavy Met. Contam. Water Soil Anal. Assessment, Remediat. Strateg. 2011 (2014) 1–50. doi:10.1201.
[45] FAO/WHO, JOINT FAO/WHO Food standards programme and Codex Committee on contaminants in foods. 5th Session. The Hague, The Netherlands. March 2011, Codex Aliment. Commision. 5 (2011) 1-88.
[46] A.S. El-Hassanin, M.R. Samak, G.N. Abdel-Rahman, Y.H. Abu-Sree, E.M. Saleh. Risk assessment of lead and cadmium in maize grains cultivated in soils irrigated with low-quality water in comparison with freshwater. Toxicology Reports 7. (2020) 10-15.
[47] C.M.A. Iwegbue, F.O. Arimoro, G.E. Nwajei, O.I. Eguavoen, Concentrations and Distribution of Trace Metals in Water and Streambed Sediments of Orogodo River, Southern Nigeria, Soil Sediment Contam. 21 (2012) 382–406. doi:10.1080.
[48] R. Dungani, P. Aditiawati, S. Aprilia, K. Yuniarti, T. Karliati, I. Suwandhi, I. Sumardi, Biomaterial from Oil Palm Waste: Properties, Characterization and Applications, in: Palm Oil, 2018: pp. 31–51. doi:10.5772.

[49] R.A. Bernhoft, Cadmium toxicity and treatment, Sci. World J. 2013 (2013) 1–7. doi:10.1155.
[50] T.A. Tran, L.P. Popova, Functions and toxicity of cadmium in plants: recent advances and future prospects, Turk. J. Botany. 37 (2013) 1–13. doi:10.3906.
[51] C. Zhang, A.J. Easteal, N.R. Edmonds, G. Liang, M. Razzak, W. Leech, In vitro and mechanism study of poly(ethylene-co-vinyl acetate)-based implant for sustained release of vitamin B12, Macromol. Res. 18 (2010) 653–659. doi:10.1007.
[52] W. Xing, G. Liu, Iron biogeochemistry and its environmental impacts in freshwater lakes, Fresenius Environ. Bull. 20 (2011) 1339–1345.
[53] V.I.A.L. Onwukeme, Fractionation of Some Trace Metals in Floodplain Soil in Awka, Anambra state, Nigeria, Int. J. Plant, Anim. Environ. Sci. 2012 (2012) 163–168.
[54] H. Haase, L. Rink, The immune system and the impact of zinc during aging, Immun. Ageing. 6 (2009) 1–17. doi:10.1186.
[55] L.M. Plum, L. Rink, H. Hajo, The essential toxin: Impact of zinc on human health, Int. J. Environ. Res. Public Health. 7 (2010) 1342–1365. doi:10.3390.
[56] O.O. Oguntibeju, A.J. Esterhuyse, E.J. Truter, Journal of medicinal plant research., J. Med. Plants Res. 4 (2010) 188–196.
[57] G.U. Chibuike, S.C. Obiora, Heavy metal polluted soils: Effect on plants and bioremediation methods, Appl. Environ. Soil Sci. 2014 (2014) 12 pp. doi:10.1155.
[58] S.D. Cunningham, W.O. David, Promises and Prospects of Phytoremediation, Plant Physiol. 4 (1996).
[59] J.O. Agbenin, G. Welp, Bioavailability of copper, cadmium, zinc, and lead in tropical savanna soils assessed by diffusive gradient in thin films (DGT) and ion exchange resin membranes, Environ. Monit. Assess. 184 (2012) 2275–2284. doi:10.1007.
[60] H. Horiguchi, E. Oguma, S. Sasaki, K. Miyamoto, Y. Ikeda, M. Machida, F. Kayama, Dietary exposure to cadmium at close to the current provisional tolerable weekly intake does not affect renal function among female Japanese farmers $, Environ. Res. 95 (2004) 20–31. doi:10.1016.
[61] M. Ikeda, Z.W. Zhang, S. Shimbo, T. Watanabe, H. Nakatsuka, C.S. Moon, N. Matsuda-Inoguchi, K. Higashikawa, Urban population exposure to lead and cadmium in east and south-east Asia, Sci. Total Environ. 249 (2000) 373–384. doi:10.1016.
[62] P. Zhuang, M.B. McBride, H. Xia, N. Li, Z. Li, Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China, Sci. Total Environ. 407 (2009) 1551–1561. doi:10.1016.

# CHAPTER NINE

## Synthetic antioxidants and metallic elements as additives/contaminants in virgin palm oil

*OB Olafisoye[1], OS Fatoki[1], OO Oguntibeju[2], OA Osibote[3*]*

*[1]Faculty of Applied Sciences, Department of Chemistry, Cape Peninsula University of Technology, Cape Town, South Africa*

*[2]Faculty of Health and Wellness Sciences, Department of Biomedical Sciences, Cape Peninsula University of Technology, Bellville, South Africa*

*[3]Faculty of Applied Sciences, Department of Mathematics and Physics, Cape Peninsula University of Technology, Cape Town, South Africa*

***Corresponding author: oguntibejuo@cput.ac.za***
***Faculty of Health and Wellness Sciences, Department of Biomedical Sciences, Cape Peninsula University of Technology, Cape Town, South Africa, 8000, South Africa. +27733545569.***

***Synthetic Antioxidants and Metallic Elements as Additives/Contaminants in Virgin Palm Oil***

***Original Paper.***

***Published in the Asian Journal of Agriculture and Biology***

### Abstract

A Reverse Phase High Performance Liquid Chromatography analysis with Ultra Violet Visible detection spectrophotometry was employed for the simultaneous analysis of synthetic antioxidants in virgin palm oil. The synthetic antioxidants under study were Butylatedhydroxyanisole (BHA), Butylatedhydroxytoluene (BHT), 2-ethylhexyl 4 methoxycinnamate (EEMC) and Propyl gallate (PG). The limits of detection for BHA, BHT, EEMC and PG were 0.041, 0.057, 0.06 and 0.03 mg/L respectively. Limits of quantification for BHA, BHT, EEMC and PG were also 0.56, 0.49, 0.05 and 0.04 mg/L respectively. None of the synthetic antioxidants was detected in the real samples under investigation. This was an indication that local farmers probably preserved the oil samples prior to storage by traditional methods. In addition, the elemental analysis of virgin palm oil is necessary to decide if the oil is suitable for food, fuel or raw materials for the chemical industry. The concentrations of

metallic elements found in the oil samples analysed in this study ranged between 0.006 mg/kg in Ubiaja plantation and 161.576 mg/kg in Benin City plantation respectively. Tin recorded high concentration in Benin City plantation and Pb a low concentration in Ubiaja plantation.

***Key words: synthetic antioxidants, virgin palm oil, micro emulsion techniques, metallic elements, RP-HPLC, ICP-OES.***

## 9.1 Introduction

Elaeis guineensis is commonly known as African oil palm is the virgin palm oil, having pinnate leaves and a dense cluster of flowers, produces a thick bright red liquid. A cash crop which strives in the tropics and is native of west Africa, such as Nigeria and others like Sri Lanka, Malaysia and Indonesia. It is important in food processing and in industry (Adeniyi *et al*., 2014). It is an essential ingredient in most processed foods, non-food productions and as a raw material for the production of biodiesel. There is a growing need for this essential vegetable oil as the world population increases extensively and there is a desire for good health and improved diets (Imoisi *et al*., 2015). Being an essential crop for food and non-food uses, it becomes paramount to monitor the processing of the virgin oil from planting to storage of the finished products.

Auto-oxidation usually sets in when edible oils are stored prior to usage. This can be seen in deterioration of the aesthetics of the oil. Antioxidants may be added to the virgin palm oil, either natural or synthetic before storage to prevent the onset of auto-oxidation and oxidative degradation of the oils during storage. Mancini *et al*., (2015) defined synthetic antioxidants generally as substances added to foods/oils to prolong the shelf life of such foods/oils preventing the onset of auto-oxidation that causes rancidity, change in colour, texture, and odour of the oils. Mancini *et al*., (2015), further emphasized that synthetic antioxidants act by inhibiting reactions that catalyse oxygen through the transfer of hydrogen and hence inhibiting the chemical reactions, which favour the production of aldehydes, ketones and peroxide radicals which are major substances contributing to auto-oxidation. The applications of antioxidants range across a wide variety of products such as fruit concentrates and juices, snacks, confectionaries and meat. Usually manufacturers and local farmers may use antioxidants in the preservation of their products and this may be oblivious to the consumers. There is a possibility of synthetic antioxidants added to farm produce. Local farmers may add these additives to prolong the shelf life. This could be without adequate analytical measurements or quality control. Possible health risks are associated with the intake of synthetic antioxidants. The increased concentration of synthetic antioxidants in various analyses from various countries in foods is not strictly recognized. Synthetic antioxidants are

chemically synthesized since they do not occur naturally in nature and are more harmful than beneficial to human (Kamar, 2014). At low and permitted concentrations, synthetic antioxidants could be helpful in the prevention of spoilage of food in addition to possessing anti-inflammatory and antiviral properties. Regulatory bodies responsible for the administration and control of synthetic antioxidants have not been very effective especially in developing countries. Most manufacturer label synthetic antioxidants as dietary supplements while others especially local farmers do not give any information on the composition of a particular food additive whether singly or in combination with other antioxidants. Synthetic antioxidants in minute concentrations may not pose a threat to human health although elevated concentrations and long-term use in humans can lead to acute and chronic toxicity. Chronic toxicity is manifested in symptoms such as cancer, obesity, infertility, mutation and decreased immunity (Hamid *et al*., 2010). The choice of synthetic antioxidants by the manufacturer is dependent on many factors that range across value regulation and its efficacy (Akkbik, 2011). Other synthetic antioxidants have been banned at some point in time in various countries. Generally, the guidelines for the administration and control of synthetic antioxidants vary from country to country (Pezo *et al*., 2008). This is one of the reasons the use of synthetic antioxidants in foods be checked and kept under control; Hence the need to assess them in this study.

Trace/heavy elements are also present in palm oil due to various reasons ranging from environmental and processing processes to unwholesome agronomical methods. Ayodele and Oluyomi (2011) reported on the issue of contamination arising during cultivation of the oil palm tree and harvesting of the oil palm fruit due to pre-planting and post-planting farming practices such as the use of fungicides and fertilizers residues. Contamination may also arise from a number of factors that includes washing of the oil palm fruit with water from lead/metal pipes or rivers. In addition, mechanical stripping of the oily flesh from the oil palm fruit, cooking and sieving of the flesh to obtain the virgin oil palm, corrosion of the processing equipment and storage in large metallic vessels are sources of metallic contamination (Itumoh *et al*., 2013). Other sources of anthropogenic contamination may also arise from the oil palm plantation situated close to domestic and industrial sources of pollution (Asemave *et al.,* 2011). The determination of elements in virgin palm oil is of economic importance because palm oil is a very important cash crop for the food and chemical industry. It is essential to determine the presence of trace and major elements in palm oil as this is one of the criteria for oil quality. Metallic elements in palm oil are deleterious because this affects the shelf life and aesthetic quality of the oil. Elements in the oil enhance the oxidation of fatty acids to esters, which affects the nutritional value and the properties of the oil. Trace elements are toxic at elevated concentrations. However, trace elements are essential to man, their presence in palm oil,

which is a raw material for a variety of food, and chemical industries may not be ideal for production processes (Brandshaw and Thompson, 2007). This is particularly an issue in the production of biodiesel due to the presence of such metals that consequently affects the quality of the oil.

Hence, an analysis was initiated for the determination of four synthetic antioxidants (BHA, BHT, EEMC and PG) and metallic elements (Al, Co, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sn and Zn) in virgin palm oil from fifteen independent sampling locations. These methods were proposed to achieve high throughput and low flow rate with minimal mobile phase solvent for synthetic antioxidants and an impending problem majorly due to the dense matrix of oil samples and the presence of metallic elements in oil at very critical concentrations. Literature survey revealed that several analytical methods like HPLC, LC-MS, GC and GC-MS have been reported for the estimation of synthetic antioxidants (Guo *et al*., 2006; Mohamed *et al.,* 2012). Analytical chemists have also employed several instrumental techniques for the determination of elements in oil samples, the most common technique being Atomic Absorption Spectrometry (Ayodele and Oluyomi 2011; Asemave *et al.,* 2011; Olafisoye *et a*l., 2013). The determination of elements in oil using AAS was not adequate due to the nature of the matrix and the difficulty of the analyte to be separated from such matrix. This was also attributed to the instability of the analyte in the oil and the high organic content of the oil. The use of hazardous solvents had to be employed to destroy or dissolve the matrix as the case may be so the analyte may be free in solution. Sample separation and pre-treatment steps were long and laborious. Such sample preparation steps such as solid phase extraction, microwave assisted acid digestion and wet/dry ashing, involving hazardous acids or a mixture of both was normally employed. Another disadvantage of this process was the use of very expensive organometallic standards for instrument calibrations. There was also a need to develop a HPLC method, which could be employed for the routine analysis of virgin palm oil either singly or in combination using simple mobile phase composition. The method eradicated the use of hazardous chemicals and the use of expensive unstable organometallic standards for calibration. Micro emulsions were employed for the determination of metallic elements. They were stable thermodynamically when tested using a UV spectrometer after being observed for about three hours. The micro emulsions were composed of water, oil, and alcohol and in some instance, a surfactant such as a base in other instances. Additionally, the micro emulsion particles were homogenous and were actually in the order of 5-100nm in size suspended in a phase which is continuous (Xiu-Qin *et al.,* 2009).

The proposed ICP-OES analysis using oil-water micro emulsion as sample preparation method was not only reproducible, accurate and reliable but also equally convenient because it

provided a sample extraction capable of breaking down complex matrix in virgin palm oil for metallic element analysis (Perrin and Meyer, 2003; Maruyama et al., 2014). To the best of our knowledge, research has not been conducted on the simultaneous analysis of BHA, BHT, PG and EEMC in virgin palm oil samples using HPLC and also trace elements in virgin palm oil with micro emulsion as sample preparation method by ICP-OES; both methods using UV/Vis detection techniques. The analyses provided accelerated and precise methods for the qualitative and quantitative determination of synthetic phenolic antioxidants and trace elements in virgin palm oil sampled from 15 locations on oil palm plantations in southwestern, south eastern and south southern Nigeria.

## 9.2 Materials and methods

### 9.2.1 Sampling and chemicals

Virgin palm oil was sampled from fifteen sampling locations that included the Nigerian Institute for Oil Palm Research (NIFOR) and its substations. More samples were collected from areas in the southern states of Nigeria where the oil palm tree was extensively cultivated and received input of pollution characteristics. Sampling points were partitioned into four sections and a sample was collected from each section to make a grab sample. Sampling was also based on factors such as densely populated areas and areas receiving intense pollution stress. The sampling containers were sterilized and the samples preserved in a refrigerator prior to analysis in the laboratory. All chemicals used for the analysis were purchased from Sigma Aldrich (USA) and were of analytical grade. The chemicals included Propyl gallate (PG) 99.8 % pure, n-hexane, methanol (HPLC grade), Butylhydroxytoluene (BHT) (≥99 % pure), acetronitrile, ethanol, acetic acid, 2-ethylhexyl 4 methoxycinnamate (EEMC), Butylatedhydroxyanisole (BHA), Petroleum ether, Hydrochloric acid, propan-2-ol and metal standards

### 9.2.2 Preparation of micro emulsion for metal analysis

About 0.5 g of each of the oil samples was accurately weighed into a 100 mL polypropylene tube with lid. HCl was added (c.a 2 mL) and propan-2-ol to a final volume of 10 mL. The mixture was shaken vigorously on a shaker for 30 minutes to obtain an evenly dispersed homogenous emulsion that remained stable without dispersing when left for about four hours (Brandshaw and Thompson, 2007). This was kept in the fridge at 4 ℃ for metallic element analysis using the ICP-OES.

### 9.2.3 Extraction procedure for virgin palm oil for synthetic antioxidant analysis

The modified extraction method proposed by Capit´an-Valley et al. (2002) for the determination of BHA, BHT, PG, and EEMC method was employed. Virgin palm oil samples (0.5 g) from fifteen independent sampling locations were weighed in individual centrifuge tubes. Acetronitrile and hexane in a ratio of 3:1 were added to each tube and the contents of the tubes homogenized for about 5 minutes at 1800 rpm and further homogenized at 4000 rpm for an additional 5 minutes. Centrifuged samples were allowed to separate into two layers and the non-polar phase (acetronitrilephase) was collected and extracted thrice using the same extraction technique. The re-extracted phases were re-collected into a 10 mL sample flask and made up to the 10 mL mark with acetronitrile. This was kept in the refrigerator prior to HPLC analysis.

### 9.2.4 Preparation of stock solution standards for synthetic antioxidants and metal analysis

Quality type water (reverse phase osmosis) was used throughout the analysis. A concentration of 5000 mg/L of stock solution was employed for the analysis and was prepared by dissolving 1250 mg/L of each of the antioxidants comprising of BHA, BHT, PG and EEMC in a100 mL standard flask and made up to the mark with acetronitrile. Out of the stock solutions, working solutions of 10 µg/mL were prepared. The repeatability of the method was checked using six injections of the working standard. The linearity was determined in the range of 0.3-11 µg/mL. The recovery of the method was achieved by spiking 50 mg/kg of each antioxidant and analysed using similar methods (Capitan-Valley *et al*., 2002; Capitan-Valley *et al*., 2004; Reichenbach *et al*., 2009).

### 9.2.5 HPLC analysis and instrumentation

An ODS $C_{18}$ Chromatographic column with a particle size of 5 µL was used (4.6 x 250) cm. An Isocratic system with mobile phases of 75:25 v/v methanol: water mobile phase was employed. The Agilent Technologies (1200 series) RP-HPLC Instrument used for the analysis was equipped with UV/Vis detector and quaternary pumps. The maximum wavelength chosen was 280 nm and 1 mL/min flow rate.

### 9.2.6 ICP-OES analysis and instrumentation

The Inductively Coupled Plasma Optical Emission Spectrometer (Spectro Arcos FHS 12 ICP-OES) equipped with radial viewed plasma was used for the research. The instrumentation has been extensively discussed in Olafisoye *et al*., 2014.

## 9.3 Results and discussions

### 9.3.1 High performance liquid chromatography analysis for the determination of synthetic antioxidants Identification assignment and integration of peaks

The aim and objective of qualitative analysis is to identify what type of analyte is contained in the sample. In this analysis, this was achieved by the use of reference standards. The optimum wavelength of the UV/Vis spectrometer for BHA, BHT, EEMC and PG shows maximum absorption between 275 nm and 300 nm. The UV/Vis wavelength for the RP-HPLC was fixed at 280 nm for simultaneous determination of the four antioxidants.

The sample components to be identified were known and the peaks within the chromatogram were assigned to the known components. Hence, standards of the pure components were injected into the HPLC-UV instrument under identical conditions and peaks were assigned based on the retention times of the standards with the UV/Vis detector aiding in the identification of the spectra in assigning peaks. The retention factor and the response of the peaks in the instrument were compared with the sample chromatogram. The concentrations of the standard solutions were matched to that of the real samples as peak mis-assignment due to shape defects and were avoided as much as possible (Capitan-Valley *et al*., 2002; Capitan-Valley *et al*., 2004; Reichenbach *et al*., 2009). The analysis was carried out in the reverse order and a more vigorous peak assignment and confidence was achieved.

### 9.3.2 Spiking

The samples were spiked with standards for the confirmation of the identity of the sample component peaks. Table 9.1 presents the results of the recovery study for BHA, BHT, EEMC and PG by RP-HPLC-UV/Vis at $\lambda_{max}$ = 280nm.

### 9.3.3 Quantitative identification

Matching the recorded spectra of the standard solution with that of the sample spectrum was used as a quantitative determination of the peak assignment. Quantitative peak areas were used to calculate the concentration of the compounds in the samples. Standard solutions (10) of BHA, BHT, EEMC, and PG of multi linear concentrations of 1.5, 10, 15, 25, 50, 75, 100, 125 and 250 mg/L were prepared in acetronitrile. The peak areas of the four antioxidants standards (BHA, BHT, EEMC, and PG) were plotted against the concentrations to obtain a wide concentration range in the samples. The samples were analysed to obtain instrument response and the response was compared with the responses obtained from the four standards. The quantitative determination of the compounds in the samples was achieved using this method under identical conditions.

### 9.3.4 Requirements of the chromatogram

The accuracy of the quantification was affected strongly by the resolution of the peaks and the nature of the baseline around the peaks under investigation. Peaks well separated were easy to reproduce and integrate. In addition, measures were taken as to ensure that other interfering peaks do not affect the integration or height of the peaks of interest. The results show that some of the peaks were eluted on sloppy and noisy baseline that made reproducibility difficult. Other peaks were eluted with split or shoulders and tailings. The baseline and perpendicular method was used to resolve the abnormality. From the calibration curve, the concentration of the sample was calculated using the formula.

$$Concentration\ of\ Sample\ =\ Response\ RF\ \times\ M\ \times\ D\ \ldots\ldots\ldots\ldots(9.1)$$

where Response is the peak area; RF is the response factor got from the calibration curve, M is a multiplier, which takes into account the purity of the standard, while D is the dilution factor (Capitan-Valley *et al*., 2002; Capitan-Valley *et al.,* 2004; Reichenbach *et al*., 2009).

### 9.3.5 Information from the calibration curve

#### 9.3.5.1 LOD (Limit of Detection)

This was calculated as the minimum concentration of the analyte that can normally be detected in the sample. LOD was expressed as the concentration of the lowest measure in the analysis. The samples, standards and blanks were analysed under identical conditions.

#### 9.3.5.2 LOQ (Limit of Quantification)

This was the lowest concentration of an analyte in the sample where positive identification was measured for quantification. It is thrice the LOD. Table 9.2 shows the validation of the analytical procedure.

## 9.4 Analysis of real samples

Fifteen different virgin palm oil samples from independent palm oil plantations in the southern states of Nigeria were analysed. The samples were analysed for BHA, BHT, EEMC and PG contents. The real samples were analysed in triplicates. The retention factors and response of the peaks presented in all the samples were compared against that of the standards for BHA, BHT, EEMC and PG. The peaks of the real samples could not be assigned tentatively. This was no agreement with the peak of the samples and standards since all the antioxidants under studies were not detected in the analysis of the real samples. Hence, there was no close match between the chromatograms of the real samples and standards. Hitherto quantitative analysis

of the real sample peaks was integrated and identified for determination of sample concentrations. The response of the samples containing the unknown concentration was also matched against that of the response of standards to determine the amount of antioxidants present. This was closely observed to avoid peak mis-assignment due to peak size and shape effects. The analysis was performed under a reverse phase condition to increase the confidence of the results. None of the antioxidants under study was detected in any of the real samples under study.

### 9.5 ICP-OES analysis for the determination of metals

The results for the analysis of metallic elements are presented in Tables 9.3 - 9.7. The results revealed detectable levels of the metallic elements as most of them exceeded the WHO permissible limits for metallic elements in vegetable oils (WHO, 2011).

The application of Pb metal is numerous in industry. It is not an essential element with health importance to neither plants nor animals. The concentration of Pb recorded was highest in Onishere (0.847 mg/L) and lowest in Badagry (0.014 mg/L) respectively). WHO (2011) permissible limit for Pb in vegetable oils is 0.01 mg/L and most of the palm oil samples analysed recorded elevated levels above this limit. An exception was Ubiaja plantation that recorded 0.006 mg/L. Pb is a soluble metallic element in soil solution. Concentration of Pb in the environment is usually from anthropogenic sources such as the exhaust pipes of vehicles or machines being ran on leaded petrol and electronic waste such as leaded batteries (Chibuike and Obiora, 2014; Olafisoye *et a*l., 2014; Anju and Barnajee, 2011). Bitumen deposits, lead acid battery factories, and glass-making industries in and around the vicinity of the plantation may contribute to particulate Pb, which may get into the oil during processing. Generally, all the machineries used for processing were run on leaded petrol/diesel and could be a contributory factor of high lead concentrations on the plantations. Similar studies on soils sampled on the oil plantations have shown that Pb is a potentially mobile element and soluble in soil water and under acidic conditions of the soil, it becomes mobile and can bio-accumulate in the palm fruit (Yasmin *et al*., 2000).

A recent study on the bioavailability of metallic elements in the soil reflected the environmental quality objectives of manganese in soil solution (Olafisoye *et al*., 2016). This reflected that Mn is loosely bound to organic matter and clays in the form of precipitates in the speciation studies in soil of the oil plantation under investigation. Mn is essential to plants and animals and it is a potentially mobile metallic element in soils, which is usually bound to the organic phases. Potentially mobile elements also exist in the mobile phase as carbonate, sulphides, or organic forms. The metallic element is released into soil solution under acidic conditions and accessible for plant uptake. Mn possesses antioxidant properties and is a very active component of the

mitochondria preventing plants and animals from cellular damage and oxidative stress. This makes it an essential metallic element that may be toxic at elevated concentrations. It is also accessible to plants since it is soluble in soil solution and not bound to the crystalline lattice of soil. This has the tendency to bio accumulate in the palm oil fruits under acidic conditions. A study on plant and human health has also revealed the devastating effects of Mn in human (Levy and Nassetta, 2003; Lawrence *et al*., 2009). Previous studies on the oil palm plantation have shown that the soil has a pH of between 4 and 5 which is acidic. The oil samples analysed did not reveal elevated levels of Mn. Since the concentrations of Mn in all the oil samples under investigation were below the WHO (2011) permissible limits of Mn in vegetable oil, the bioaccumulation of Mn in this study may not pose danger to plants and humans.

Cadmium is a metallic element that is found in the exchangeable fractions of the soil. The exchangeable fraction of the soil has potential toxic and hazardous effects on man and plants. Cd is the most assessable metallic elements to pollutants because it is the most mobilisable metallic element (Aziz *et al*., 2014). This is because it is found in the soluble fraction or the non-residual fraction, it is not found in the insoluble or the residual fraction of the soil. The concentration of Cd in oil on the plantations ranged from 0.127 (Badagry/Abak plantation) to 0.762 (Igede-Ekiti plantation). All the plantations under study had elevated concentrations of Cd, which exceeded the WHO (2011) permissible limits for Cd (0.005 mg/L) in vegetable oils. Cd is not an essential element. Although Cd may be found naturally in the earth crust, possible sources of anthropogenic Cd poisoning in the oil samples may be from the use of fertilizers and insecticides in unwholesome farming practices. Other sources may be from effluents of electronic waste, mining, and metal smelting companies. Toxicity of Cd in humans includes infertility, pulmonary and renal maladies (Aiwegbue *et al*., 2011). The concentration Cd on the oil palm plantation can also be traced to the accessibility of the metal element by the plants from soil water. Previous studies of the soil water from the oil palm plantations especially recorded high concentrations of Cd due to electronic waste dump leachate in soil water from the plantations. Such oil sampled from the plantation may be rather suitable for industrial use rather than consumption because Cd is as a human/animal carcinogen. Other deleterious effects of Cd poisoning include respiratory tissue ulcers/lesions and infertility. Since Cd is a very mobile element readily available in the exchangeable fractions of the soil, it is the most bioavailable metallic element found in this fraction and easily released to soil solution hence toxic. This makes it accessible to the plants and hazardous when bio-accumulated in the fruit (Bernhoft, 2013, Tran and Popova, 2013).

Cobalt being a mobile element is fairly mobilised in the soil. It is essential for the treatment of blood disorders, foetal development, and exists in the diet as vitamin $B_{12}$ (Permenter *et al*., 2013; Zhang *et al.,* 2010). The concentrations of Co in the oil samples studied ranged between

0.098 mg/L in Abak and 0.665 mg/L in Nsukka plantation respectively. Although Co occurs naturally in the environment, anthropogenic sources may arise from the burning of fossil fuels and the smelting of metals. Cobalt may also be found in effluents of porcelain and paint industries. Cobalt being a mobile element, hence the concentration of Co in soil will be assessable to plants and may bio-accumulate in the fruits. In addition, production processes can also accumulate Co in the palm oil fruit. Elevated concentration of Co is toxic and manifested in humans as symptoms such as blood and lung disorders (Bhattacharya et al., 1995). WHO (2011) permissible limit for Cobalt in vegetable oils is 0.060 mg/L. All the oil plantations investigated revealed elevated concentrations in the palm oil. This buttresses the results from previous speciation study on the oil palm plantations that show that the concentration of Co was above the permissible limits for Cobalt in soils and this is in agreement with the bioaccumulation of the Cobalt in the fruits of the oil palm tree.

Chromium is easily found with soil organic matter when studied in speciation studies. It exists as $Cr^{3+}$ in soil solution. $Cr^{3+}$is used extensively in industry, hence it is readily available in the environment (Baralkiewicz and Siepak 1998). In the presence of elevated pH and organic matter, $Cr^{3+}$ is metabolised to $Cr^{6+}$, which is the toxic form of Chromium. Although Cr may be an essential metallic element required in trace amounts for the metabolism in plants and animals and enzyme activity, elevated concentrations especially $Cr^{6+}$ is toxic and lethal to life. WHO (2011) permissible limit for Cr in vegetable oil is 0.1 mg/L. The plantations under study revealed highest and lowest concentrations of Cr as 0.011 mg/L (Onishere plantation) and 0.998 mg/L (Ubiaja plantation) respectively. Most of the oil samples investigated showed high concentrations of Cr metallic element.

A metallic element, which possesses antioxidant properties, is Copper. It is a component of antioxidant enzyme ferroxidase. This assists in the regulation of iron and the metabolism of carbohydrate from storage. Previous speciation studies on soil on the oil palm plantations revealed Cu exists in the immobile fraction of the soil that is insoluble in soil solution and poorly oxidised or reduced. The concentrations of Cu in the palm oil samples ranged from 0.022 mg/L to 0.446 mg/L. This was above the WHO (2011) permissible levels for Cu in palm oil. Studies on the toxicity of Cu had revealed that elevated levels of Cu are toxic and causes bioaccumulation and bio-magnifications in fruits. Being a semi mobile metallic element, bio-accessibility and bioaccumulation is enhanced since its mobility is increased at lower soil pH. Adverse effects of this are seen as manifested in liver and genetic disorders and Wilson's disease (Ek et al., 2001). Anthropogenic sources of Cu on the oil palm plantation could be from effluents of coin and electrical wiring industries and pesticides containing Cu.

Anthropogenic pollution from Iron usually outweighs the natural forms in which Iron exists especially in the forms of mica and clay. Anthropogenic sources of Fe pollution may be from

casings of wells, pumps, Iron pipes, and crude oil drilling. Effluents from landfills may also leach the metallic element into soil water. Toxicity of Fe is manifested in oxidative stress, anaemia, reduced growth and death (Xing and Liu, 2001; Ajala and Onwukeme, 2012). Iron is also a semi mobile element. It is an essential element and a component of the enzyme haemoglobin. WHO (2011) permissible limit for Cr in vegetable oil is 0.2 mg/L. Onishere and Abak plantations recorded 0.211 mg/Land 0.673 mg/L elevated levels of Fe in the study. Crude oil drilling and processing near Abak plantation may be responsible for the elevated concentration of Fe in the palm oil sampled from the plantation.

Zinc, nickel and selenium are immobile elements and their concentrations in the oil samples under investigation were relatively high in the oil samples under study (Hajo and Lohar, 2009; Laura et al., 2010). Under favourable conditions, these metals may be released from their residual crystalline and immobile phases into soil solutions for absorption by plants. Zn, Ni, and Se have been considered by researchers as essential elements with great antioxidant properties protecting the body against the actions of free radicals and usually toxic when concentrations are elevated (Sieprawska et al., 2015). Human, for the proper functioning of the respiratory and cardiovascular organs requires selenium. It actively participates in the activity of the thyroid hormone. Its strength as an antioxidant enzyme is manifested in the inhibition of the HIV to AIDS (Oguntibeju *et al*., 2010). Ni and Zinc assist vitamin C and E by Enhancing fertility and the prevention of oxidative stress by free radicals. Plants take in metallic elements via the soil solution and ideally, this reflects the level of environmental pollution of the area. It is erroneous to base environmental quality of the area on the total metal concentrations rather than the availability of the metallic elements in soil solution (Chibuike and Obiora, 2014).

Environmental pollution arising from aluminium and tin are usually from utensils on dumpsites and in landfills. The leachate from such sites seeps into soil water causing environmental pollution (Roseland et al., 1990). Al and Sn are not essential elements and have no biological importance to life. Nervous system disorder and Alzheimer diseases are signs of Al toxicity (Sparling and Lowe, 1996; Vardar and Unal, 2004; Ashraf *et al*., 2012). Tin element toxicity is seen in symptoms such as intestinal and urinary tract infections. WHO (2011) permissible limits of Al and Sn in vegetable oils are 0.05 and 0.01 mg/L respectively. All the plantations under study showed elevated levels of Al and Sn. Organotin compounds have been studied to be carcinogenic. However, recently, some of the compounds are useful in agriculture as insecticides, fungicides and in the treatment of some forms of cancer (Wesdock, 2014).

Total concentration of metallic elements (mg/L) analysed in water and soil from previous findings and virgin palm oil samples presently on the oil palm plantations were presented in Tables 9.5, 9.6 and 9.7. This assessed the possible human health threats linked with the intake

of palm oil contaminated with toxic metals. Contaminated palm oil with essential metallic elements above the recommended values also become toxic. A possible route of human contact to slow poisoning is from the ingestion of contaminated food. Several sources of contamination of the oil palm plantations were identified in this study. Soil acidity and/or alkalinity are a major contributing factor to the bioavailability and accessibility of metallic elements in soils. Smith and Giller (1992) confirmed a decrease in the bioavailability and accessibility of metallic elements with increasing pH. This fact was attributed to the formation of insoluble complexes coupled with the removal of hydroxides and carbonates from soil solution. Low pH values have also been associated with a reduction on particle soil size and organic matter. Other factors, which varied significantly in the bioavailability and mobility of metallic elements in soil, were redox reactions, cation exchange capacity, soil chemistry amongst other soil properties (Mukherjee, 1998). The pH of the soil studied on the oil palm plantation ranged between 4 and 7. Under these conditions, metallic elements in the soil solution are bioavailable and accessible to the plants grown on these soils due to increased mobility. This is hazardous to humans and the food chain due to the fact the crops bio accumulates toxic metals in their edible parts especially their fruits (Wei *et al.,* 2005). Bioaccumulation and bio magnifications of metallic elements in plant tissues is influenced by factors such as pH, moisture content of the soil, soil organic matter and nutrient load. Rupa *et al.,* 2003 studied an elevation in the uptake of metallic elements such as Zn, Cr, Fe and Fe due to the occurrence of soil organic matter. In this study, the relationship between soil factors and metallic elements determined the bioaccumulation and accessibility of the toxic elements in the palm oil. The soils analysed on the plantations were acidic, an indication of elevated concentrations of the metallic element in the oil samples. This prompted an increase in mobilization and uptake of the metallic elements in the palm oil. Itanna in 2002 emphasized the influence of morphology and physiology of plants as an important factor in mobility, bioaccumulation and elimination of metallic elements in soils. Toxic metallic elements route to humans and the food chain via consumption of food crops. This is especially hazardous and a critical health risk issue when the metallic elements exceed the permissible levels in palm oil. The food chain as a pathway of toxic metallic elements is vital in risk assessment in developing countries like Nigeria since ingestion of palm oil remains deregulated. Palm oil is a stable ingredient for the preparation of most dishes in Nigeria and consumed regularly by the population at large. Scientists such as Horiguchi *et al*., 2004 implied that the intake of metallic elements does not equate the concentrations absorbed by humans. He further explained that part of the absorbed dose is eliminated through various biochemical processes. The remainder portion becomes bio accumulated and biomagnified in humans. This study can be used to assess crop pollution and prospective risk assessment.

Comparison of the concentration of metallic elements on the water and soil of the oil palm plantations from previous findings to that found in the palm oil in this study show that the concentration of the metallic elements varied considerably. Metallic elements have the ability to be translocated from soil and water to various parts of the plants. Invariably researchers have studied the oil palm tree extensively as an effective crop in remediation technology. It is a cheap choice to phytoremediation because it is low in maintenance and eco-friendly. Soils are cleaned up as the oil palm tree translocated metallic elements from soils/water to various parts of the plant such as the fruits or stems. This provides interesting tools to sites contaminated by toxic metals. Cunningham and Ow (1996) have studied the accumulation of metallic elements in parts of the oil palm tree such as the stem and the root. Research is limited in area of the virgin palm oil which is the oil palm fruit to decide if accumulation may be higher in such parts.

## 9.6 Conclusion

Auto-oxidation usually sets in when virgin palm oil is stored prior to usage. This can be seen in deterioration of the aesthetics of the oil. Antioxidants may be added to the virgin palm oil, either natural or synthetic before storage to prevent the onset of auto-oxidation and oxidative degradation of the oils during storage. Trace/heavy elements are also present in palm oil due to various reasons ranging from environmental and processing processes to unwholesome agronomical methods. High concentrations of metallic elements in virgin palm oil affect the flavour, colour, shelf life, and taste of oil used as food. Elements in the oil enhance the oxidation of fatty acids to esters, which affects the nutritional value, and the keeping properties of the oil. The research determined the simultaneous analysis of synthetic antioxidants in virgin palm oil samples using HPLC and trace elements in virgin palm oil, with micro emulsion as sample preparation method by ICP-OES. Both methods used UV/Vis detection techniques. Synthetic antioxidants were absent in the virgin palm oil in all the plantations under study. Most of the plantations recorded significant levels of the metallic elements. The virgin palm oil is not suitable for food at its present state due to the presence of elevated concentrations of the metallic elements; but can be used in the raw material/chemical industry and in the production of biodiesel. The maximum concentration of metallic elements allowed in virgin palm oil used as food is much lower than that used as biodiesel or raw material for the chemical industry. It is recommended that the level of environmental pollution on the plantation be eradicated or reduced to the barest minimum to improve the quality of the virgin palm oil for human consumption. In addition, agronomical practices, pre-planting, and post planting activities should be done under sanitary conditions. This would potentially reduce metallic elements improving the quality of virgin palm oil. Individuals and governmental bodies should address

point and non-point sources of the environmental pollution on the oil palm plantation. This is of paramount importance considering the fact that the oil palm tree is an essential crop. The analytical methods may be employed for routine laboratory analysis.

## 9.7 References


Adeniyi, O.R., Ogunsola G.O., Oluwusi D. 2014. Methods of palm oil processing in Ogun state, Nigeria. Am. Int. J. Contemp. Res. 4, 173-179.

Aiwegbue, C.M., Aromoro F.O., Iwegbue C.E., Eguavoen, O. 2011. Levels of Cd, Cu, Cr, Ni, Zn, Pb and Mn in some Species from Orogodo River. Nigeria J. Chem. Soc. Nigeria 36, 37-41.

Ajala, L.O., Onwukeme V. 2012. Speciations of some trace metals in flood plain soil of Enugu, Nigeria. J. Appl. Chem. 1, 9-13.

Akkbik, M., Assim Z., Ahmad F.B. 2011. Optimization and validation of RP-HPLC-UV Vis method for the determination of phenolic compounds in several personal care products. Int.J. Anal. Chem. 2011, 1-10.

Anju, M., Banarjee D.K. 2011. Associations of cadmium, zinc and lead in soils from a lead and zinc mining area as studied by single and sequential extractions. Environ. Monitor. Assess. 67-85.

Asemave, K., Ubwa, S.T., Anhwange, B.A., Gbaamende A.G. 2011. Comparative evaluation of some metals in palm oil. Int. J. Mod. Chem. 1, 28-35.

Ashraf, M.A., Maah, M.J., Yusoff I. 2012. Chemical speciation and potential mobility of heavy metals in the soil of former tin mining catchment. Scient. World J. 1-11.

Ayodele, J.T., Oluyomi C.D. 2011. Gas contamination by trace metals from road traffic. J. Environ. Chem. Ecotoxicol.3, 60-67.

Aziz, R., Rafiq, M.T., Yang, J.C., Liu, D., Lu, L., He. Z., Duad, M.K., Li, T., Yang X. 2014. Impact assessment of cadmium toxicity and its bioavailability in human cell lines (Caco-2 and HL-7702), a review. Biomed. Res. Int. 2014 (2014), 1-8.

Barelkiewicz, D., Siepak, J. 1998. Chromium, nickel and cobalt in environmental samples and existing legal norms, a review. Pol. J. Environ. Stud. 8, 201-208.

Bernhoft, R.A. 2013. Cadmium toxicity and treatment, a review. The Scient. World J. 2013, 1-7.

Bhattacharya S., Ubero, V., Madura, R.L., Haghighi-Podeh, M.R. 1995 Effect of cobalt on methanogenesis. Environ. Tech. 16, 271-278.

Bradshaw, D.K., Thompson L. 2007. The analysis of water and waste water by USEPA Method, 200.7 using the Optima 8300 ICP-OES and prep fast auto dilution/calibration system. USA, Perkin Elmer (2007).

Capitan-Valley, L.F., Valencia M.C., Nicholas E.A. 2004. Solid phase ultraviolet absorbance photometric multisensory for the simultaneous determination of butylated toluene and co-existing antioxidants. Analytica Chimica Acta, 503, 179-186.

Capitan-Valley, L.F., Valencia, M.C. Nicholas E.A. 2002. Flow through sensor for determination of butylatedhydroxytoluene in cosmetics. Anal Lett.35, 65-81.

Chibuike, G.U., Obiora, S.C. 2014. Heavy metal polluted soils, effect on plants and bioremediation methods. Appl. Environ. Soil Sci. 2014, 1-12.

Cunningham, S.D., Ow D.W. 1996. Promises and prospects of phytoremediation. Plant physiology, 110, 715-719.

Ek A.S., Lofgren S., Bergholm, J., Qvarfort U. 2001. Environmental effects of one thousand years of copper production at Falon, central Sweden. Ambio. 30, 96-103.

Guo, L., Xie, M.Y. Yan, A.P. Wan Y.Q. Wu Y.M. 2006. Simultaneous determination of five synthetic antioxidants in edible vegetable oil by GC-MS. Anal.Bioanal. Chem. 386, 1881-1887.

Hajo, H., Lothar R. 2009. The immune system and the impact of zinc during aging. Immun. Aging. 6, 1-17.

Hamid, A., Aielaagbe, O., Usman, L.A., Ameen, O.M., Lawal, A. 2010. Antioxidants, its medicinal and pharmacological applications: Review. Afr. J. Pure and Appl. Chem. 4, 142-152.

Horiguchi, H., Ogume, E., Sasaki, S., Miyamato, K., Ikeda, Y., Machida, M. Kayoma, F. 2004. Dietary exposure to cadmium at close to the current provisional tolerable weekly intake does not affect renal function among female Japanese farmers. Environ. Res. 95, 20-31.

Imoisi, O.B., Ilori, G.E., Agho, I., Ekhator, J.O. 2015. Palm oil, its nutritional and health implications: Review. J. Appl. Sci. Environ. Manage. 19, 127-133.

Itanna, F. 2002. Metals and leafy vegetables grown in Addis Ababa and toxicological implications. Ethiop. J. Health Dev. 16, 295-302.

Itumoh, E.J., Uraku, A.J., Omaka O.N., Nwabue F.J. 2013. Trace metal toxicity in our environment: Case studies of influx of metals in soils, crops, waters and air in Ebonyi State. Glob. J. Bio-sci. Bio-tech. 2, 33-36.

Kamar, S. 2014. The importance of antioxidant and their role in pharmaceutical science: A review. Asian J. Res. Chem. 1, 27-44.

Laura, M.P., Rink, L., Haase, H. 2010. The essential toxin, impact of zinc on human health. Int. J. Environ. Res. Public Health. 7, 1342-1365.

Lawrence, L., Fox, J., Castille F.J. Jnr. 2009. Decreased toxicity of copper and manganese ions to shrimp Nauplii in the presence of EDTA. J. World Aquacul. Soc. 12, 271-280.

Levy, B.S., Nassetta, W.J. 2003. Neurological effects of manganese in humans, a review. Int. J. Occup. Health 9, 153-163.

Mancini, A., Imperlini, E., Nigro, E., Montagnese, C., Daniele, A., Orru S., Buono, P. 2015. Biological and nutritional properties of palm oil and palmitic acid effects on health: Review. Molecules. 20, 17339-17361.

Maruyama, S.A., Claus, T. Chiavelli, L.U.R., Bertozzi, J., Pilau, E.J., Souza, N.E., Matsushita, J.V. 2014. Analysis of carotenoids and tocopherol, sterols and phenolic compounds from white bread enriched with chia (salvia hispanica. L) seeds and carrot (DaucasCarota L) leaves.J. Braz. Chem. Soc. 25, 1108-1115.

Mohammed, S.S., Batu, M.A., Mohammed, M. B. 2012. Analysis of chromium in dumpsite samples using AAS and EDXRF techniques. Res. J. of Chem. Sci. 2, 65-68.

Mukherjee, A. B. 1998. Chromium in the environment of Finland. Sci. Total Environ. 217 (1-2), 9-19.

Oguntibeju, O.O., Esterhuyse, A.J. Truter, E.J. 2010. The role of red palm oil supplementation in reducing oxidative stress in HIV/AIDS and TB patients. A Review. J. Med. Plants Res. 4, 188-196.

Olafisoye O.B., Oguntibeju. O.O., Osibote, O.A. 2016. An assessment of the bioavailability of metals in soils on oil palm plantations in Nigeria. Pol. J. Environ. Stud. 25, 1125-1140.

Olafisoye, O.B., Adefioye, T. Osibote, O.A. 2013. Heavy metals contamination of water, soil and plants around an electronic waste dumpsite. Pol. J. Environ. Stud. 22, 1431-1439.

Olafisoye, B.O., Fatoki, O.S., Oguntibeju O.O., Osibote O.A. 2014. Determination of Trace and Major Elements in Water on Oil Palm Plantations by Inductively Coupled Plasma-Optical Emission Spectroscopy, Instrumen. Sci. Tech.42, 652-666.

Permenter, M.G., Dennis, W.E., Sutto, T.E., Jackson, D.A., Lewis J.A., Stalling J.D. 2013. Exposure to cobalt causes transcriptomic and proteomic changes in two rat liver derived cell lines. PLoS ONE 8 (12), 1-11.

Perrin, C., Meyer L. 2003. Simultaneous determination of ascorbylpalmitate and nine phenolic antioxidants in vegetable oils and edible fats by HPLC. J. Am. Oil. Chem. Soc. 80, 115-118.

Pezo, D., Salafranca J., Nevin C. 2008. Determination of the antioxidant capacity of active food packaging by in situ gas-phase hydroxyl radical generation and high-performance liquid chromatography–fluorescence detection. J. Chromatogr. A. 1178, 126-133.

Reichenbach, S.E., Charr, P.W., Stoll D.R., Tao Q. 2009. Smart templates for peak pattern matching with comprehensive two-dimensional liquid chromatography. J. Chromatogr. A. 1216, 3458-3466.

Roseland B.O., Eldhuset, T.A., Staurnes, M. 1990. Environmental effects of aluminium. Environ. Geochem. Health 12 (1-2), 17-27.

Rupa, T. R., Srinivasa, R. C., Subba, R. A., Singh, M. 2003. Effects of farmland manure and phosphorus on zone transformations amd phytoavailability in two alfisols of India. Bioresour. Technol. 87, 279-288.

Schreinemachers, D.M., Ghio A.J. 2016. Effects of environmental pollutants on cellular iron homeostasis and ultimate links to human disease. Environ. Health Insights.10, 35-43.

Smith, S.R., Giller, K. E. 1992. Effective *Rhizobium leguminosarum* from long-term applications of sewage sludge or metal mine spoil. Soil Biol. Biochem. 24 (8), 781-788.

Sparling, D. W., Lowe, T.P. 1996. Environmental hazards of aluminium to plants, invertebrates, fish and wildlife. Rev. Environ. Contam.Toxicol.145, 127-128.

Tran, T.A., Popova L.P. 2013. Functions and toxicity of cadmium in plants; recent advances and future prospects, a review Turk. J. Bot. 37, 1-13.

UNESCO, WHO. 2011. Ground Water Pollution. International Hydrological Programme. Guidelines for Drinking Water Quality, 4th edition.

Vardar, F. Unal, M. 2007. Aluminium toxicity and resistance in higher plants. Adv. Mol. Bio.1, 1-12.

Wei, S., Zhou, Q., Wang, X. 2005. Identification of weed plants excluding the uptake of heavy metals. Environ. Int. 31, 829-834.

Xing, W., Liu, G. 2011. Iron biogeochemistry and its environmental impacts in fresh water lakes. Fresennius Environmental Bulletin. 20, 1339-1345.

Xiu-Qin, L., Chao, J., Yan-Yan, S., Mia-Li, Y., Xiao-Gang, C. 2009. Analysis of synthetic antioxidants and preservatives in edible vegetable oil by HPLC/TOF-MS. Food Chem. 113, 692-700.

Yasmin, S.T., Schirnding, Y.E., Prapamontol, T. 2000. Environmental lead exposure, a public health problem of global dimension, environmental and health. Bull. World Health Org. 78 (9), 1068-1077.

Zhang, M.K., Liu, X.Y. Wang, H. 2010. Use of single extraction methods to predict the bioavailability of heavy metals in polluted soils to rice. Commun. Soil Sci. Plant Anal. 4, 820-831.

**Table 9.1 BHA, BHT EEMC & PG**

| Spiked (mg/L) | BHA | BHT | EEMC | PG |
|---|---|---|---|---|
| 1 | 126.2 | 103.4 | 151.7 | 101.3 |
| 2 | 108.7 | 99.4 | 109.2 | 95.3 |
| 5 | 83.4 | 77.3 | 81.7 | 89.4 |
| 10 | 62.1 | 61.3 | 66.8 | 59.4 |
| 15 | 59.9 | 44.8 | 55.2 | 50.8 |

**Table 9.2 Analytical validation for SPA**

| Compound | Retention time (mins) | Calibration Equation | $R^2$ | RSD (%) | LOD (mg/L) | LOQ (mg/L) |
|---|---|---|---|---|---|---|
| BHA | 3.56 | y=1933x+12722 | 1 | 0.635 | 0.041 | 0.56 |
| BHT | 15.58 | y=95893x+42687 | 0.999 | 0.989 | 0.057 | 0.49 |
| EEMC | 8.55 | y=20773x+20897 | 0.999 | 0.594 | 0.006 | 0.05 |
| PG | 2.22 | y=1941x+4903 | 0.998 | 1.075 | 0.003 | 0.04 |

**Table 9.3: Concentration of metals in oil A**

| Location | Al | Co | Cd | Cr | Cu | Fe |
|---|---|---|---|---|---|---|
| Abak | 0.062±0.024 | 0.098±0.003 | 0.127±0.001 | 0.056±0.004 | 0.070±0.002 | 0.211±0.007 |
| Acharu | 0.524±0.004 | 0.104±0.001 | 0.139±0.001 | 0.047±0.001 | 0.117±0.001 | 0.091±0.004 |
| Agbarho | 0.451±0.008 | 0239±0.001 | 0.683±0.001 | 0.340±0.002 | 0.075±0.001 | 0.159±0.005 |
| Ago-Emokpae | 0.245±0.006 | 0.104±0.001 | 0.140±0.001 | 0.068±0.001 | 0.070±0.003 | 0.168±0.013 |
| Apoje | 0.390±0.001 | 0.458±0.001 | 0.266±0.002 | 0.778±0.002 | 0.083±0.002 | 0.152±0.009 |
| Badagry | 0.115±0.007 | 0.091±0.002 | 0.127±0.001 | 0.028±0.003 | 0.184±0.003 | 0.174±0.043 |
| Benin city | 0.112±0.002 | 0.332±0.001 | 0.557±0.002 | 0.661±0.002 | 0.091±0.002 | 0.139±0.005 |
| Igede-Ekiti | 0117±0.001 | 0.551±0.002 | 0.762±0.002 | 0.430±0.002 | 0.090±0.001 | 0.137±0.002 |
| Ikire | 0.833±0.010 | 0.103±0.001 | 0.138±0.001 | 0.032±0.001 | 0.109±0.001 | 0.184±0.005 |
| Iresaapa | 0.041±0.010 | 0.131±0.001 | 0.139±0.001 | 0.046±0.001 | 0.082±0.002 | 0.136±0.001 |
| Nsukka | 0.368±0.001 | 0.665±0.004 | 0.611±0.001 | 0. 334±0.002 | 0.022±0.001 | 0.033±0.002 |
| Okitipupa | 0.112±0.002 | 0.311±0.002 | 0.389±0.002 | 0.028±0.001 | 0.332±0.002 | 0.112±0.001 |
| Onishere | 0.098±0.003 | 0.887±0.002 | 0.445±0.0050 | 0.011±0.001 | 0.446±0.006 | 0.673±0.003 |
| Ubiaja | 0.018±0.001 | 0.102±0.001 | 0.137±0.001 | 0.998±0.001 | 0.076±0.005 | 0.187±0.023 |
| Umuabi | 0.074±0.002 | 0.100±0.001 | 0.131±0.001 | 0.040±0.001 | 0.101±0.007 | 0.170±0.003 |

**Table 9.4: Concentration of metals in oil B**

| Location | Mn | Ni | Pb | Se | Sn | Zn |
|---|---|---|---|---|---|---|
| Abak | 0.066±0.001 | 0.068±0.001 | 0.043±0.027 | 0.116±0.001 | 0.110±0.001 | 0.083±0.002 |
| Acharu | 0.073±0.004 | 0.164±0.003 | 0.090±0.001 | 0.699±0.048 | 114.993±1.036 | 0.342±0.001 |
| Agbarho | 0.023±0.001 | 0.089±0.005 | 0.054±0.001 | 0.011±0.003 | 0.090±0.004 | 0.126±0.001 |
| Ago-Emokpae | 0.064±0.001 | 0.202±0.004 | 0.030±0.004 | 0.810±0.081 | 7.685±4.025 | 0.182±0.002 |
| Apoje | 0.456±0.002 | 0.786±0.001 | 0.155±0.001 | 0.672±0.003 | 0.552±0.002 | 1.621±0.073 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Badagry | 0.071±0.001 | 0.184±0.003 | 0.014±0.008 | 0.374±0.105 | 145.429±4.159 | 0.096±0.001 |
| Benin city | 0.073±0.001 | 0.760±0.002 | 0.341±0.001 | 0.913±0.048 | 161.576±3.907 | 0.100±0.001 |
| Igede-Ekiti | 0.076±0.001 | 0.177±0.001 | 0.028±0.006 | 0.926±0.001 | 160.328±0.731 | 0.053±0.003 |
| Ikire | 0.070±0.001 | 0.182±0.002 | 0.020±±0.003 | 0.077±0.001 | 86.583±5.729 | 0.092±0.001 |
| Iresaapa | 0.068±0.001 | 0.167±0.001 | 0.221±0.003 | 0.440±0.027 | 109.867±3.323 | 0.329±0.001 |
| Nsukka | 0.482±0.001 | 0.672±0.003 | 0.672±0.003 | 0.672±0.003 | 23.112±0.003 | 0.452±0.001 |
| Okitipupa | 0.672±0.003 | 0.672±0.003 | 0.6720±0.003 | 0.672±0.003 | 56.444±0.001 | 0.111±0.001 |
| Onishere | 0.113±0.002 | 0.543±0.003 | 0.847±0.001 | 0.256±0.003 | 32.680±0.002 | 0.663±0.002 |
| Ubiaja | 0.037±0.002 | 0.174±0.001 | 0.006±0.001 | 0.176±0.029 | 92.272±5.215 | 0.642±0.001 |
| Umuabi | 0.264±0.003 | 0.178±0.002 | 0.175±0.001 | 0.864±0.002 | 0.682±0.001 | 0.779±0.001 |

**Table 9.5: Concentration of metals (Cd Co Cr)**

| Plantation | Cd | | Co | | Cr | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Soil | Water | Oil | Soil | Water | Oil | Soil | Water | Oil |
| Abak | 1.09 ± 0.2 | 0.26±0.01 | 0.127±0.001 | 9.42 ± 0.3 | 0.61±0.03 | 0.098±0.003 | 109.56 ± 0.1 | 0.97±0.01 | 0.056±0.004 |
| Acharu | 1.09 ± 0.2 | <0.26 | 0.139±0.001 | 2.17 ± 0.1 | 0.32±0.09 | 0.104±0.001 | 45.67 ± 0.1 | 0.96±0.03 | 0.047±0.001 |
| Agbarho | 1.09 ± 0.2 | 0.26±0.01 | 0.683±0.001 | 3.98 ± 0.2 | 0.31±0.04 | 0239±0.001 | 132.21 ± 0.1 | 0.98±0.02 | 0.340±0.002 |
| Ago-Emokpae | 1.09 ± 0.2 | 0.26±0.01 | 0.140±0.001 | 2.07 ± 0.1 | 0.30±0.02 | 0.104±0.001 | 25.50 ± 0.3 | 0.95±0.05 | 0.068±0.001 |
| Apoje | 1.28 ± 0.1 | 0.33±0.03 | 0.266±0.002 | 1.03 ± 0.1 | 0.31±0.01 | 0.458±0.001 | 99.92 ± 0.1 | 0.90±0.01 | 0.778±0.002 |
| Badagry | 4.26 ± 0.2 | 0.39±0.02 | 0.127±0.001 | 2.61 ± 0.1 | 0.31±0.06 | 0.091±0.002 | 108.67 ± 0.1 | <0.94 | 0.028±0.003 |
| Benin city | 1.33 ± 0.1 | 0.26±0.02 | 0.557±0.002 | 1.32 ± 0.2 | 0.31±0.05 | 0.332±0.001 | 78.11 ± 0.1 | 0.94±0.01 | 0.661±0.002 |
| Igede-Ekiti | 0.39 ± 0.2 | 0.26±0.01 | 0.762±0.002 | 1.45 ± 0.1 | 0.31±0.02 | 0.551±0.002 | 56.45 ± 0.1 | 0.91±0.06 | 0.430±0.002 |
| Apomu-Ikire | 0.27 ± 0.1 | 0.26±0.03 | 0.138±0.001 | 1.05 ± 0.2 | 0.44±0.06 | 0.103±0.001 | 34.99 ± 0.2 | <0.31 | 0.032±0.001 |
| Iresa-apa | 1.32 ± 0.1 | 0.27±0.01 | 0.139±0.001 | 2.55 ± 0.1 | 0.44±0.06 | 0.131±0.001 | 111.08 ± 0.1 | 0.02±0.02 | 0.046±0.001 |
| Nsukka | 1.12 ± 0.1 | 0.27±0.01 | 0.611±0.001 | 2.23 ± 0.1 | 0.31±0.05 | 0.665±0.004 | 124.42 ± 0.3 | 0.83±0.05 | 0.334±0.002 |
| Okitipupa | 0.12 ± 0.1 | 0.27±0.01 | 0.389±0.002 | 2.61 ± 0.2 | 0.34±0.03 | 0.311±0.002 | 66.89 ± 0.1 | 0.86±0.05 | 0.028±0.001 |
| Onishere | 0.37 ± 0.1 | 0.32±0.03 | 0.445±0.0050 | 0.80 ± 0.1 | 0.13±0.08 | 0.887±0.002 | 111.11 ± 0.3 | <0.21 | 0.011±0.001 |
| Ubiaja | 0.32 ± 0.1 | <0.32 | 0.137±0.001 | 2.45 ± 0.1 | 0.54±0.01 | 0.102±0.001 | 42.90 ± 0.2 | <0.02 | 0.998±0.001 |
| Umuabi | 0.32 ± 0.1 | 0.32±0.03 | 0.131±0.001 | 1.14 ± 0.1 | 0.55±0.01 | 0.100±0.001 | 111.02 ± 0.1 | 0.26±0.02 | 0.040±0.001 |

**Table 9.6 Concentration of metals (Cu Fe Pb)**

| Plantation | Cu | | | Fe | | | Pb | |
|---|---|---|---|---|---|---|---|---|
| | Soil | Water | Oil | Soil | Water | Oil | Soil | Water | Oil |
| Abak | 39.11 ± 0.2 | 1.01±0.01 | 0.070±0.002 | 30.99 ± 0.3 | 0.63±0.02 | 0.211±0.007 | 6.84 ± 0.2 | 1.13±0.04 | 0.043±0.027 |
| Acharu | 12.92 ± 0.1 | 0.99±0.02 | 0.117±0.001 | 40.34 ± 0.1 | 0.81±0.01 | 0.091±0.004 | 7.03 ± 0.1 | 1.36±0.15 | 0.090±0.001 |
| Agbarho | 45.06 ± 0.4 | 1.31±0.09 | 0.075±0.001 | 12.34 ± 0.1 | 0.09±0.01 | 0.159±0.005 | 11.01 ± 0.1 | 1.43±0.38 | 0.054±0.001 |
| Ago-Emokpae | 35.08 ± 0.1 | 0.10±0.01 | 0.070±0.003 | 9.11 ± 0.2 | 0.02±0.02 | 0.168±0.013 | 10.92 ± 0.2 | 1.39±0.24 | 0.030±0.004 |
| Apoje | 33.22 ± 0.1 | 0.12±0.01 | 0.083±0.002 | 6.63± 0.1 | 0.05±0.11 | 0.152±0.009 | 12.32 ± 0.1 | 0.85±0.04 | 0.155±0.001 |
| Badagry | 69.11 ± 0.1 | 0.12±0.01 | 0.184±0.003 | 1.81 ± 0.2 | 0.17±0.14 | 0.174±0.043 | 12.43 ± 0.2 | 1.39±0.24 | 0.014±0.008 |
| Benin city | 23.02 ± 0.2 | 0.01±0.01 | 0.091±0.002 | 2.02 ± 0.1 | 0.10±0.04 | 0.139±0.005 | 12.53 ± 0.3 | 1.15±0.23 | 0.341±0.001 |
| Igede-Ekiti | 33.41 ± 0.1 | <0.13 | 0.090±0.001 | 0.05 ± 0.1 | 0.01±0.01 | 0.137±0.002 | 11.51 ± 0.1 | 0.78±0.23 | 0.028±0.006 |
| Apomu-Ikire | 22.63 ± 0.1 | 0.10±0.01 | 0.109±0.001 | 1.10 ± 0.1 | 0.03±0.01 | 0.184±0.005 | 10.35 ± 0.1 | 5.29±0.01 | 0.020±± 0.003 |
| Iresa-apa | 30.82 ± 0.2 | 1.24±0.01 | 0.082±0.002 | 1.03 ± 0.1 | <0.01 | 0.136±0.001 | 13.61 ± 0.1 | 10.3±0.21 | 0.221±0.003 |
| Nsukka | 28.56 ± 0.1 | 1.37±0.03 | 0.022±0.001 | 1.01 ± 0.2 | 0.01±0.01 | 0.033±0.002 | 10.46 ± 0.1 | 0.17±0.05 | 0.672±0.003 |
| Okitipupa | 33.78 ± 0.2 | 1.24±0.02 | 0.332±0.002 | 1.01 ± 0.1 | 0.02±0.02 | 0.112±0.001 | 12.32 ± 0.1 | <0.09 | 0.6720± 0.003 |
| Onishere | 37.99 ± 0.1 | 0.88±0.02 | 0.446±0.006 | 2.02 ± 0.1 | 0.06±0.01 | 0.673±0.003 | 11.69 ± 0.2 | 0.27±0.21 | 0.847±0.001 |
| Ubiaja | 30.22 ± 0.1 | 1.01±0.01 | 0.076±0.005 | 1.06 ± 0.2 | 0.07±0.02 | 0.187±0.023 | 11.24 ± 0.1 | 0.30±0.11 | 0006±0.001 |
| Umuabi | 25.52 ± 0.1 | 0.56±0.01 | 0.101±0.007 | 1.13 ± 0.1 | 0.10±0.01 | 0.170±0.003 | 9.61 ± 0.1 | 10.1±0.12 | 0.175±0.001 |

**Table 9.7: Concentration of metal (Zn)**

| Plantation | Zn | | |
|---|---|---|---|
| | Soil | Water | Oil |
| Abak | 63.11 ± 0.1 | 5.06±0.01 | 0.083±0.002 |
| Acharu | 89.33 ± 0.2 | 4.07±0.02 | 0.342±0.001 |
| Agbarho | 23.01 ± 0.1 | 4.93±0.01 | 0.126±0.001 |
| Ago-Emokpae | 92.48 ± 0.1 | 4.86±0.02 | 0.182±0.002 |
| Apoje | 96.67 ± 0.1 | 6.54±0.01 | 1.621±0.073 |
| Badagry | 53.82 ± 0.2 | 6.79±0.04 | 0.096±0.001 |
| Benin city | 107.33 ± 0.2 | 4.94±0.02 | 0.100±0.001 |
| Igede-Ekiti | 78.62 ± 0.2 | 5.35±0.25 | 0.053±0.003 |
| Apomu-Ikire | 94.42 ± 0.1 | 3.10±0.29 | 0.092±0.001 |
| Iresa-apa | 12.36 ± 0.1 | 3.49±0.24 | 0.329±0.001 |
| Nsukka | 37.43 ± 0.1 | 6.09±0.09 | 0.452±0.001 |
| Okitipupa | 60.28 ± 0.1 | 6.22±0.68 | 0.111±0.001 |
| Onishere | 75.07± 0.1 | 2.36±0.03 | 0.663±0.002 |
| Ubiaja | 91.64 ± 0.3 | <0.06 | 0.642±0.001 |
| Umuabi | 90.88 ± 0.2 | 4.84±0.36 | 0.779±0.001 |

# CHAPTER TEN

## Assessment of naturally occurring radionuclides accumulation in palm oil from soil

*OB Olafisoye[1], OO Oguntibeju[2], OA Osibote[3]*

**Abstract**

Hyper Pure Germanium (HPGe) Radiation Detector was used to estimate the activity concentration of fifteen soil and palm oil samples collected from the oil palm plantations in the southwestern, southeastern, and south southern states of Nigeria, and evaluated for the risk assessments. The activity concentrations at a soil depth 0 – 15 cm ranged from 187.4 to 514.4, 2.328 to 6.571, and 1.509 to 6.121 Bq/kg for $^{40}K$, $^{238}U$, and $^{232}Th$, respectively. The activity concentrations in the palm oil ranged from 122.3 to 968.0, 1.240 to 6.651, and 1.199 to 8.061 Bq/L for $^{40}K$, $^{238}U$, and $^{232}Th$ respectively. Risk assessments for soils (0-15 cm): Absorbed Dose Rate (D) ranged from 11.5 to 24.54 nGy/h, while the Annual Effective Dose Equivalent (E) ranged from $1.4 \times 10^{-2}$ to $2.98 \times 10^{-2}$ mSv/y and the Radium Equivalent ranged between 1.4 to 2.98 Bq/kg respectively. The radium equivalent, absorbed dose rate, and the annual effective dose rate in the palm oil samples ranged from 17.23 to 88.00 Bq/L, 2.46 to 46.29 nGy/h, and $1.05 \times 10^{-2}$ to $56.90 \times 10^{-2}$ mSv/y, respectively. The activity concentrations reported for soil and palm oil samples were lower than the recommended world average values of 370 Bq/kg given by UNSCEAR for radium equivalent. The translocation factor of radionuclides from soi to palm oil was also investigated to be within safe limits. Hence, the hazard and risk assessments indicated a low radiation risk within the studied areas.

*Index Terms*—***activity concentration, Oil palm plantations, pressed -palm fruit oil, risk assessment indices***

***ORIGINAL PAPER under review in the journal; "International Journal of Environmental Science and Development".***

### 10.1 Introduction

The palm oil plantation is one of the cash producing crops in the south western, south eastern and south southern states of Nigeria supplying palm oil and palm kernel products for local farmers, chemical and allied industries. Vegetable oils or vegetable fats can be referred to as fats extracted from seeds or other parts of the fruit. They are similar to animal fats because

they contain a mixture of triglycerides, saturated acids, palmitic acids and polysaturated acids. Palm oil is an edible vegetable oil that is reddish in color. It is extracted from the fleshy mesocarp of the fruit of the oil palm tree, which is indigenous to Africa and Asia. Red virgin palm oil is mechanically pressed from the flesh mesocarp of the oil palm fruit. The red orange color of the oil is derived from its high content of beta-carotene content. It is a highly saturated vegetable oil and solid at room temperature. It is commonly used for cooking in parts of Africa, Asia, and South America [1]. It is a useful raw material for culinary purposes and also the food and chemical industry. Palm oil is favorable amongst food scientist due to its low cost and high oxidative ability and nutritional value as it contains a good amount of vitamin A and E known to cure various forms of cancer and heart disease [2] [3]. Unrefined, unbleached and un-deodorized virgin palm oil is rich in carotenes, (alpha and beta-carotenes) and lycopene. Palm oil is also used as a raw material in the production of biomass and biofuels. It is also used extensively in industry because of its medicinal value and long shelf life [1] [4-7]. Nigeria is the third largest producer of palm oil with approximately 2.3 hectares of oil palm plantations under cultivation of small and large-scale processes of palm oil. [8] [9] [10] Other countries with relatively high yields in the production of palm oil are Thailand, Malaysia, and Indonesia [1].

Naturally occurring radioactive materials are useful in medicine, research, agriculture, industry and much more. Prolong exposure to such radiation is detrimental to health and can lead to mutations and cancer, which could be fatal [11] [12]. Naturally occurring radioactive materials are seen in the environment (air, water, soil, food and even in living things such as plants and animals). The oil palm fruit can be contaminated in several ways; one of the ways involves the transfer of the radionuclides through soil and water [11] [13]. This introduces radionuclides into the food chain and possesses risk to human life. The primary route is through the ingestion of the palm oil that has been previously contaminated with the naturally occurring radioactive material through transfer from the soil. The extent and concentration of radioactive materials in a particular region is dependent on geology, climate agronomical farming practices and more [14-17]. Seepage of pollutants into ground water bodies, excessive fertilization of agricultural lands, abandoned mines, industrial sites and thermonuclear testing of nuclear power plants; increase the risk of radionuclide contamination via ground water and soil to plant. More of the effects of radiation are manifested in pulmonary and kidney cancer, leukemia and anemia [6, 18-19]. United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR, 2000) [18], stated that over one-eighth of the annual effective mean dose of radionuclides ingested by man is because of food. Contamination of palm fruits by naturally occurring radionuclides is more prominent in the rainy season when accumulation in fruits, shoots, and roots is put into consideration. This could be attributed to direct fallout or runoff from rain [11]

[12] [13]. Radionuclides are accumulated by plants via soil through a process known as translocation from the roots to other parts of the plant. A complex mechanism exist through which radionuclides are transferred from soil/ground water to man and a correlation exists between this depending on the extent of contamination and the degree of accumulation in different types of plants [20-25]. Globally studies were carried out on the determination of Naturally occurring radionuclides on various environmental samples in different areas of the world either as routine checks or baseline studies in order to update previous investigations or investigate fallouts of radionuclides [26-39]. Hence, the study aims at the estimation of the palm oil samples and evaluates the associated risk it poses. The radionuclides of interest are the naturally occurring radionuclides $^{40}K$; $^{238}U$ and $^{232}Th$ in palm oil pressed from oil palm fruits grown on fifteen independent oil palm plantations soils that may have been polluted anthropogenically by human made activities. These regions are famous for oil palm production in Nigeria. The survey carried out measurement of naturally occurring radioactivity in soils and aimed to determine dose of radiation exposure from sources and the evaluation of the health risk assessment posed by such radiation.

**Table 10.1: Previous works in agreement with present work**

| Reference | Region | Indices Investigated | Instrument Used | No of Samples | Results obtained |
|---|---|---|---|---|---|
| Alausa et al., 2017 [21] | Elere Oil Palm Plantation, Ibadan, Oyo State, Nigeria | Activity Concentration of NORM. Transfer Factor from Soil to Palm Oil. Hazard & Risk Assessment | Na(Tl) Detector | Twenty samples of Soil & palm Oil from respective Palm Oil Trees | $^{40}K$, $^{238}U$ and $^{232}Th$ in palm oil ranged from 50.48 - 112.16 $Bqkg^{-1}$; 6.35 - 12.80 $Bqkg^{-1}$ & 6.08 - 10.13 $Bqkg^{-1}$ respectively. The activity concentrations of $^{40}K$, $^{232}U$ & $^{232}Th$ in the soil samples ranged from 412.43 - 672.16 $Bqkg^{-1}$; 10.25 - 17.43 & 8.12 $^{-1}$ - 12.48 $Bqkg^{-1}$ respectively. |
| Ademola A.K, 2019 [39] | Oil Palm Plantation, Oyo State, Nigeria | Activity Concentration of NORM. Transfer Factor from Soil to Palm Oil. Hazard & Risk Assessment | HPGe | 84 soil samples, 36 food crop samples, & 48 vegetable samples | The average concentration of $^{226}Ra$, $^{228}Ra$ & $^{40}K$ in soil was 25.3 ± 7.1, 26.2 ± 5.0 & 381.8 ± 16.0 Bq/kg, respectively in Agbaaru; 25.4 ± 3.1, 39.5 ± 3.8, & 401.9 ± 25.4 Bq/kg in Abuja; 26.5 ± 3.3, 39.2 ± 7.4, & 394.9 ± 18.6 Bq/kg in Arget; and 26.5 ± 3.5, 38.8 ± 2.5, & 389 ± 18.6 Bq/kg in Igbeti. The soil-to-vegetables Transfer Factor (TF) for $^{226}Ra$, $^{228}Ra$, and $^{40}K$ is 0.123, 0.058, & 0.215, respectively, in Agbaaru; 0.065, 0.040, & 0.185 in Abuja; 0.093, 0.035, & 0.243 in Arget; and 0.080, 0.050, and 0.265 in Igbeti |
| Usikalu et al, 2014 [40] | Ewekoro Cement Factory, Ogun State, Nigeria | Activity Concentration of NORM in Soil Samples used for Construction. Hazard & Risk Assessment | HPGe | Sixty Soil Samples | The concentration of $^{238}U$ was 1.60±1.60 $Bqkg^{-1}$ and 2.56±0.08 $Bqkg^{-1}$ respectively. For $^{232}Th$, 44.78±1.83 $Bqkg^{-1}$ (east) and 56.62±1.96 $Bqkg^{-1}$ (north) were recorded respectively. $^{40}K$ recorded 261.54±12.67 $Bqkg^{-1}$ (south) & 342.08±14.17 $Bqkg^{-1}$ (east). The assessment of NORM in eastern & northern part of Owowo village was for $^{238}U$; 1.78±0.09 $Bqkg^{-1}$ & 2.62±0.08 $Bqkg^{-1}$ respectively. For the radionuclide $^{232}Th$, 50.07±1.93 $Bqkg^{-1}$ (west) & 61.69±1.89 $Bqkg^{-1}$ (north) were recorded. Values of $^{40}K$ were |

| | | | | | |
|---|---|---|---|---|---|
| | | | | | 244.11±13.38 Bqkg$^{-1}$ (north) & 296.40±14.90 Bqkg$^{-1}$ (south) respectively. |
| Chad-Umoren & Umoh, 2014 [41] | Soil samples in Abak, Nigeria | Activity Concentration of NORM in Soil Samples used for Construction. Hazard & Risk Assessment | HPGe | Ten soil samples | The activity concentration range from 14.80±1.16 Bq/kg to 150.20±11.47 Bq/kg for $^{40}$K. Values of $^{238}$U were from 14.52±3.49 Bq/kg to 42.04±8.59 Bq/kg & from 3.05±0.27 Bq/kg to 7.00±0.58 Bq/kg. Values of 18.789±3.102 nGy/h were for absorbed dose, 0.3±0.05 Bq/kg for representative level index, 39.82±6.65 Bq/kg for radium equivalent, 0.11±0.02 for external hazard index, and 0.18±0.032 for internal hazard index and 0.023±0.004 mS/yr for effective dose rate respectively. |
| Oladapo, 2012 [42] | Wasteland around Olusosun Dumpsite, Ojota, Lagos, Nigeria | Activity Concentration of NORM in Soil Samples used for Construction. Hazard & Risk Assessment | Na(Tl) Detector | Thirty Soil Samples | The mean value of $^{238}$U, $^{232}$Th and $^{40}$K concentrations determined for soil samples from the active dumpsite were 69.69 ± 19.10 Bqkg$^{-1}$, 14.49 ± 3.22 Bqkg$^{-1}$ and 409.44 ± 86.08 Bqkg$^{-1}$ respectively. For the soil samples from the dormant dumpsite, the mean value of $^{238}$U, $^{232}$Th and $^{40}$K concentrations were 61.25 ± 21.82 Bqkg$^{-1}$, 12.08 ± 1.74 Bqkg$^{-1}$ and 345.98 ± 56.92 Bqkg$^{-1}$ respectively. The mean annual effective dose for soil from active dumpsite is 0.2767 while 0.2550 was obtained for soil samples from the dormant dumpsites. |
| Jibiri & Amakom, 2010 [43] | Samples of soil waste stream in the sedimentation tanks of an oil & gas production well site Petroleum Company in Warri, Delta, State, Nigeria | Activity Concentration of NORM. Risk assessment, Cumulative Cancer Mortality & Morbidity Risk | HPGe | Samples of soil waste stream | $^{137}$Cs was not detected in the samples that proved no occurrence of such sources in the area. |
| George et al., 2018 [44] | Samples of soil in a Kaolin Deposit of the mining field of Ifonyintedo Town, Nigeria. | Activity Concentration of NORM in Soil Samples used for Construction. Hazard & Risk Assessment | HPGe | Eleven Soil Samples | The mean activity concentrations for $^{40}$K, $^{232}$Th and $^{238}$U and gamma dose were estimated as 93.9 Bq kg$^{-1}$, 65.1 Bq kg$^{-1}$, 38.2 Bq kg$^{-1}$ and 59.6 nGyh$^{-1}$ respectively. The radiological hazards estimated were Radium Equivalent, External and Internal Gamma and Alpha Indices, and Representative Level index. These were calculated as 138.5 Bq kg$^{-1}$, 0.37 mSvyr$^{-1}$, 0.48 mSvyr$^{-1}$, 0.29 mSvyr$^{-1}$, 0.48, 0.19, and 0.97 respectively. |
| Olalekan et al., 2019 [45] | A review of soil, rock, sediment, & water samples used in agriculture & construction industry in the northern and southern area of Nigeria. | Activity Concentration of NORM in Soil Samples used for Construction. Hazard & Risk Assessment | HPGe | A review of over fifty samples | The activity concentrations of the rocks determined in the study was highest when compared to other matrices. The concentration of $^{40}$K and $^{238}$U in granite rocks are higher than the recommended permissible value. All the water samples were within acceptable concentrations of radionuclides with mean activity values of 3.98±0.26, 11.00±2.58, and 17.73±5.04 BqL$^{-1}$ for $^{40}$K, $^{232}$Th, and $^{238}$U, respectively. The value of the mean absorbed dose rate for all the area is 0.123 mSvyr$^{-1}$, which is within acceptable limits recommended limit of 1 mSvyr$^{-1}$. The mean in situ measured absorbed dose rate is 232.8 ± 49.8 nGy h$^{-1}$ and the total annual effective |

| | | | | | |
|---|---|---|---|---|---|
| | | | | | ingestion dose obtained was 339.4 mSv $y^{-1}$ |

## 10.2 Materials and method

### 10.2.1 Geology of area

The study area is characterized by few mountains and steep terrains, which are rough with vegetation that is mostly rain forest. Most of the terrain is flat land with rivers. The climate is characterized into two major climates, which are the raining season and the harmattan. The raining season is between March and November and lasts for more than half the year. The soil receives a lot of rainfall all through the year and percolation of ground water into soil is to be considered in the transportation of radionuclides from water into soil and accumulation in the fruit. Hence, the transport of rainfall and the translocation from ground water to soil is of paramount importance [19]. The selected sampling locations (Table 10.2) in states of Nigeria are home to rocks and sediments enclosing valleys and mountains from the south to the western regions of Nigeria. The geology of Nigeria was formed in the Archean and Proterozoic eras. Its province and more than half of the surface is igneous and metamorphic rocks with a crystalline and sedimentary basement. Massive sedimentation was under way in these basins as it returned to its terrestrial conditions within the Pan African mobile belt. The western and southern states lie between eight degrees North latitude and ten degrees' south longitude. The terrain is mostly swampy, forest and some marshy areas with various rivers, landscapes, meadows, springs, peninsulas, and islands adorning the regions. The vegetation of the area is mostly forest, shrub land, and wetland, which support the growth of a lot of plantation and cash crops such as the oil palm, rubber, and cocoa tree plantations.

### 10.2.2 Description of sampling areas

Figure 10.1 is the map of Nigeria showing all the fifteen sampling points. A brief description of some of the major cities and towns is given. Acharu is a town in Dekina local government area of Kogi state. Kogi state is popularly called the confluence state because of the confluence of river Niger and Benue. Flora Shaw coined the name Nigeria out of the river Niger in Lokoja. The Acharu town is blessed with reserves of oil palm. Agbarho is a town in the Ughelli North local government area of Delta state, Nigeria. This area is called the Niger delta and it is affected by oil spillages. In the Niger Delta – oil spillages/leakages are constant features of oil production, and have caused physical damage. Benin City is famous for its bronzes and carved works. Deposits of bronze, tin and zinc are scattered around the metropolis. Agriculture is the main occupation of the locality that provides income and employment for about 75 % of the population.

### 10.2.3 Translocation factor (Tf)

The entry of radionuclides that are present in the terrestrial environment and find entry into the food chain is controlled in the long term by their uptake by plant roots known as the transfer factor; Tf [13]. This is empirically addressed, and modelled in an equation as seen below. For the radionuclide '$i$' in the edible part of the plant '$p$', it is assumed that:

$C_i^p$ (BqL$^{-1}$ dry weight) is linearly related to its concentration in soil within the rooting zone $C_i^s$ (15-30 cm) depth. This is to say:

$$Tf = \frac{activity\ concentration\ of\ nuclide\ per\ liter}{activity\ concentration\ in\ dry\ soil\ within\ the\ rooting\ zone} \ldots\ldots\ldots Equation\ 1 \text{ [13]}$$

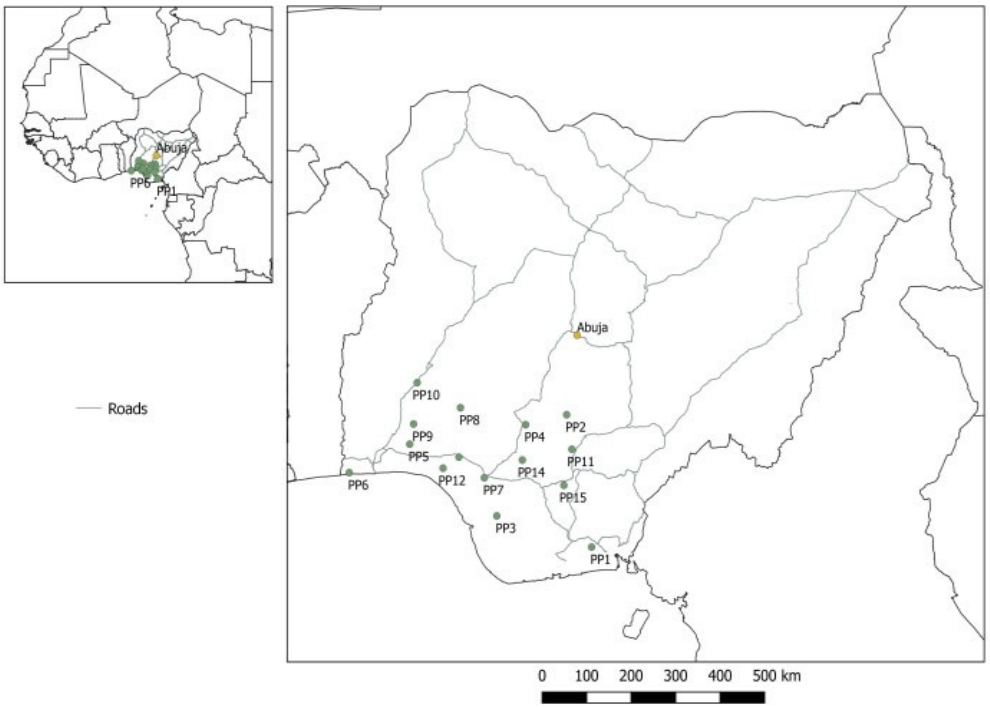



**Fig 10.1: Map of Nigeria showing sampling points**

**Table 10.2: Sampling locations**

| Code | Location | Latitude | Longitude | Elevation above sea level (m) |
|---|---|---|---|---|
| PP1 | Abak | 4.9833 | 7.7833 | 174 |
| PP2 | Acharu | 7.5320 | 7.2792 | 210 |
| PP3 | Agbarho | 5.5833 | 5.8667 | 111 |
| PP4 | Ago-Emokpae | 7.3400 | 6.4500 | 200 |
| PP5 | Apoje | 6.9644 | 4.1064 | 24 |
| PP6 | Badagry | 6.4166 | 2.8833 | 36 |
| PP7 | Benin city | 6.3176 | 5.6145 | 88 |

| | | | | |
|---|---|---|---|---|
| PP8 | Igede-Ekiti | 7.6667 | 5.1321 | 576 |
| PP9 | Ikire | 7.3533 | 4.1833 | 207 |
| PP10 | Iresa-apa | 8.1504 | 4.2567 | 118 |
| PP11 | Nsukka | 6.8667 | 7.3833 | 552 |
| PP12 | Okitipupa | 6.5025 | 4.7795 | 305 |
| PP13 | Onishere | 6.7150 | 5.1001 | 68 |
| PP14 | Ubiaja | 6.6597 | 6.3822 | 255 |
| PP15 | Umuabi | 6.17 36 | 7.2233 | 221 |

### 10.2.4 Sampling Procedure

Fifteen samples (S1-S15) were collected from topsoil (0-15 cm) and furthermore from a depth of soil (15-30 cm) by conventional methods of diagonal systematic sampling using an auger. Diagonal sampling was performed for each sampling point and the samples mixed for homogeneity to give a sample per location. The soil samples were left to dry in a cool airy cupboard for a month. Palm oil samples were taken from the same sampling points as soil samples. Palm oil was collected in 1L plastic bottles and the containers were labeled PO1-PO15 with respect to the fifteen sampling points as revealed in Table 10.2. After the drying period for the soils, the previously dried samples were pulverized, crushed, and sieved using a 2 mm mesh sieve size to obtain soils with definite and homogeneous fine sizes. Sieved samples of soils were dried in an oven set at 100 ºC for 24 hours then transferred to previously cleaned Marinelli beakers. This was properly sealed with paraffin film to prevent any escape of radon gas. Palm oil samples were treated similarly and, sealed accordingly. The soil and palm oil samples were kept for a month for the radon gas and its progeny to attain secular equilibrium after which, gamma spectrometry measurements of the samples were carried out. The sampling locations, elevation, and coordinates are listed in Table 10.2.

## 10.3 Gamma Spectrometry

The gamma-counting equipment was a Canberra vertical high-purity coaxial germanium (HPGe) crystal detector, model GC2018-7500, series number b 87063 enclosed in a 100 mm thick lead shield and coupled to a Canberra Multichannel Analysing (MCA) computer system. Calibration of the energy and efficiency of radionuclides was performed with the aid of a well-calibrated standard soil reference standard source supplied by the International Atomic Energy Agency (IAEA), Vienna. The MCA was calibrated to display gamma photo peaks in the energy range of 200—1500 KeV, this being the energy range covering all the gamma energies of radionuclides of interest. The detector chamber was shielded with three layers of copper, cadmium, and lead of 30 mm, 3 mm and 100 mm thick, respectively. The photo-peaks observed with regularity in the samples were identified to belong to the natural radioactive decay series headed by $^{238}U$ and $^{232}Th$, and a third non-series natural radionuclide, $^{40}K$, for a

counting time of 36,000-seconds. The activity of the natural radionuclides was calculated using Equation 2.

$$As = \frac{Ca}{EPrMs} \ldots\ldots\ldots\ldots\ldots 2$$

where $Ca$ is the net counting rate of gamma ray (counts per second), $E$ is the detector efficiency of the specific gamma ray, $Pr$ is the absolute transition probability of gamma decay and $Ms$ the mass of the sample (kg).

### 10.3.1 Radium Equivalent ($Ra_{eq}$)

Radium Equivalent was used to describe the gamma radiation from the varying mixtures of the radionuclides in the soil and is calculated using the relation

$$Raeq = CRa + 1.43CTh + 0.077CK \ldots\ldots\ldots 3$$

Where: $CRa, CTh$ and $CK$ are the activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K respectively. The index represents a weighted total of the above-mentioned radionuclides' *activity* concentrations because of an assumption that states that 1 Bq/Kg of $^{226}$Ra, 0.7 Bq/Kg of $^{232}$Th and 13 Bq/Kg of $^{40}$K produce an equal amount of gamma radiation dose [19].

### 10.3.2 Absorbed Dose (D)

Absorbed dose rate is defined by United Nations Scientific Committee on the Effects of Atomic Radiation and provide the characteristic of the external gamma ray. This was calculated using the equation 4.

$$D\left(\frac{nGy}{h}\right) = 0.462CRa + 0.604CTh + 0.0417CK \ldots\ldots\ldots 4$$

This is the absorbed dose rate in air outdoor at 1 m above the ground surface due to specific activity concentrations of $^{238}$U, $^{232}$Th and $^{40}$K (UNSCEAR, 2000) [18].

### 10.3.3 Annual Effective Dose Equivalent (E)

Annual effective dose equivalent, $E$ is the parameter to determine the overall effects of the radiation on health due to the absorbed dose rate and calculated by the equation

$$E\ (mSv/y) = D\ (nGy/h)\ x\ 8760\ (h/y)\ x\ 0.2\ x\ 0.7\ (Sv/Gy)\ x\ 10^{-6} \ldots\ldots\ldots\ldots 5$$

Where the values 0.7 $SvGy^{-1}$ is the conversion coefficient from absorbed dose in the air 1m above ground to effective dose received by adults, 8760 is the time taken in hours in a particular year, 0.2 represents the outdoor occupancy factor and is the observed dose rate [19].

### 10.3.4 Excess Lifetime Cancer Risk

The results of the statistics of cancer in Nigeria revealed that the age normalized occurrence estimate for all intrusive cancers was 66.4 per 100 000 men and 130.6 per 100,000 women. Data was based on the Population Based Cancer Registry (IBCR) and the Abuja Population Based Cancer Registry (ABCR) covering a 2 year period which was from 2009–2010 [46]. The term excess lifetime cancer risk describes the risk of death of cancer in excess of the natural background risk existing from a lifetime of exposure to carcinogenicity. Excess Life Time Cancer Risk $(ELCR)$ was computed from the calculated values of the Annual Effective Doses as seen in equation 6 [20][46].

$$ELCR = E\ X\ D_L\ X\ R_F \ldots\ldots\ldots Equation\ 6$$

Where $D_L$ and $R_F$ are the life time duration (70 years) and fatal cancer risk factor for the stochastic effect (0.055 $Sv^{-1}$ for the general public respectively).

## 10.4 Spectrochemical Analysis

The prepared samples were analysed by gamma ray spectroscopy with the use of a Hyper Pure Germanium (HPGe) Detector. The counting time for the analysis was 36,000 seconds and the soil reference material IAEA-375 was prepared in the same way as the sample and counted in triplicates alongside the sample. The photo peak, of the gamma ray for the ($^{214}$Bi) 1764 keV; ($^{228}$Ac) 911.21 keV; ($^{40}$K) 1461 keV. The Absolute Full Energies were 0.02, 0.001, and 0.04 respectively. These were used to determine the activity of the naturally occurring radionuclides $^{238}$U, $^{232}$Th, and $^{40}$K. Their percentage emission probabilities corresponded to 14.9, 62.8, and 12.4 respectively. The detector was calibrated using the standard source which was a mixture of $^{22}$Na, $^{57}$Co, $^{60}$Co. Spectra analysis was performed using Genie software 2000 developed by CANBERRA. The background contribution was removed by subtracting this from the result of the analysis. The Detection Limit (DL) is the net signal above which a signal can be considered to have been reliably detected. In this study, the Detection Limit (DL) and the Minimum Detectable Activity (MDA) was achieved by modelling the Curies Model formula that presents the background counts, branching ratio, sample mass and detector efficiency.

$$DL = 2.71 + 4.66\sqrt{N_B} \ldots\ldots 7 \quad and$$

$$MDA = DL/T\varepsilon Bm \ldots\ldots\ldots 8$$

$M$ is the mass the sample (kilograms) and $N_B$ is the background counts (counts per second). For the photo peak of the gamma ray ($^{214}$Bi) 1764 keV; ($^{228}$Ac) 911.21 keV and ($^{40}$K) 1461 keV. The Detection Limit (DL) and Minimum Detectable Activity (MDA), was calculated using equation [18].

### 10.5 Results and discussion

Table 10.3 presents the concentrations (mean±SD) of radionuclides (Bq/kg) of $^{40}$K, $^{238}$U and $^{232}$Th in soil and palm oil samples collected from the various plantations. An unusual variation is seen in the sampling location. The activity concentrations at a soil depth 0 – 15 cm ranged from 187.4 to 514.4, 2.328 to 6.571, and 1.509 to 6.121 Bq/kg for $^{40}$K, $^{238}$U, and $^{232}$Th, respectively. The activity concentrations in the palm oil ranged from 122.3 to 968.0, 1.240 to 6.651, and 1.199 to 8.061 Bq/L for $^{40}$K, $^{238}$U, and $^{232}$Th respectively. Meanwhile, variations of activity concentrations values of radionuclides are better explained by the properties of the soil and accumulation of humus. In the uppermost layer, due to decay and mobility distribution, will require more advanced techniques and studies to determine if an area is safe or unsafe as far as health hazards is concerned. The values for Palm oil were in a similar pattern [41-43].

**Table 10.3 Concentration values for NORM in soil (Bq/kg) and Palm Oil (Bq/L)**

| | 40K | 238U | 232Th | 40K | 238U | $^{232}$Th | $^{40}$K | $^{238}$U | $^{232}$Th |
|---|---|---|---|---|---|---|---|---|---|
| | Soil Depth (0-15) | | | Soil Depth (15-30) | | | Palm Oil | | |
| 1 | 430.9±0.07 | 4.905±0.02 | 4.929±0.06 | 343.2±0.03 | 2.467±0.01 | 4.935±0.09 | 236.1±0.02 | 2.677±0.98 | 6.881±0.01 |
| 2 | 444.66±0.01 | 3.228±0.07 | 1.820±0.01 | 421.6±0.01 | 2.392±0.02 | 4.365±0.01 | 214.3±0.01 | 4.790±0.34 | 5.432±0.02 |
| 3 | 345.0±0.17 | 5.176±0.19 | 3.148±0.05 | 463.2±0.02 | 4.877±0.03 | 5.041±0.02 | 150.4±0.54 | 4.790±0.11 | 2.156±0.03 |
| 4 | 389.7±0.08 | 5.778±0.02 | 3.426±0.02 | 653.4±0.03 | 6.575±0.04 | 4.770±0.02 | 187.5±0.02 | 1.705±0.12 | 4.243±0.01 |
| 5 | 434.6±0.01 | 4.153±0.04 | 1.777±0.09 | 219.2±0.01 | 4.680±0.05 | 1.476±0.13 | 367.0±0.03 | 3.757±0.45 | 3.461±0.24 |
| 6 | 193.9±0.67 | 3.812±0.45 | 2.732±0.04 | 211.4±0.02 | 1.802±0.02 | 4.007±0.22 | 122.3±0.01 | 2.890±0.01 | 3.443±0.33 |
| 7 | 187.4±0.34 | 6.173±0.23 | 4.816±0.01 | 281.1±0.02 | 9.410±0.09 | 6.275±0.34 | 347.2±0.02 | 3.924±0.39 | 4.311±0.07 |
| 8 | 411.5±0.05 | 5.030±0.01 | 6.121±0.02 | 467.5±0.05 | 6.579±0.02 | 4.237±0.98 | 327.8±0.01 | 2.960±0.11 | 6.378±0.21 |
| 9 | 514.4±0.04 | 3.471±0.13 | 4.237±0.03 | 169.0±0.01 | 1.726±0.01 | 1.829±0.22 | 266.7±0.12 | 3.192±0.15 | 4.109±0.17 |
| 10 | 455.8±0.03 | 6.571±0.23 | 4.121±0.09 | 163.4±0.03 | 1.345±0.03 | 3.613±0.12 | 212.5±0.15 | 2.661±0.41 | 1.199±0.03 |
| 11 | 309.2±0.01 | 2.328±0.11 | 4.760±0.01 | 318.8±0.02 | 1.789±0.03 | 3.500±0.32 | 128.2±0.12 | 2.475±0.08 | 5.249±0.02 |
| 12 | 302.7±0.04 | 3.189±0.02 | 5.988±0.03 | 602.7±0.04 | 3.788±0.12 | 4.239±0.11 | 179.4±0.09 | 1.240±0.01 | 8.060±0.01 |
| 13 | 405.5±0.08 | 5.462±0.11 | 3.855±0.21 | 507.4±0.05 | 5.775±0.99 | 5.472±0.01 | 968.0±0.02 | 6.030±0.02 | 5.200±0.01 |
| 14 | 458.5±0.01 | 3.106±0.03 | 5.476±0.02 | 451.7±0.02 | 5.064±0.34 | 2.343±0.01 | 229.8±0.02 | 1.996±0.01 | 5.042±0.02 |
| 15 | 475.6±0.03 | 2.884±0.01 | 1.509±0.02 | 281.3±0.01 | 2.327±0.15 | 4.264±0.02 | 238.6±0.01 | 6.651±0.03 | 1.509±0.01 |

### 10.5.1 Risk assessment

Risk assessment indices can be used in the calculation of radionuclide dose in soils and palm oil. Tables 10.4 represents the risk assessment results for soil and palm oil obtained in the present study. For the risk assessments, the Absorbed Dose Rate (D) ranged from 11.5 to 24.54 nGy/h, while the Annual Effective Dose Equivalent (E) ranged from $1.4 \times 10^{-2}$ to $2.98 \times 10^{-2}$ mSv/y and the Radium Equivalent ranged between 21.72 to 49.14 Bq/kg. The radium equivalent, absorbed dose rate, and the annual effective dose rate in the palm oil samples ranged from 17.23 to 88.00 Bq/L, 2.46 to 46.29 nGy/h, and $1.05 \times 10^{-2}$ to $56.90 \times 10^{-2}$ mSv/y, respectively.

**Table 10.4: Values for Ra, D, & E in Soils and Palm Oil**

| | $Ra_{(eq)}$ (Bq/kg) | D (nGy/h) | E (mSv/y) ($\times 10^{-2}$) | $Ra_{(eq)}$ (Bq/kg) | D (nGy/h) | E (mSv/y) ($\times 10^{-2}$) |
|---|---|---|---|---|---|---|
| | Soil | | | Palm Oil | | |
| Abak | 45.13 | 23.21 | 2.82 | 30.70 | 15.24 | 1.87 |
| Acharu | 38.07 | 18.54 | 2.25 | 29.06 | 14.43 | 1.77 |
| Agbarho | 36.25 | 21.12 | 2.56 | 19.45 | 9.787 | 1.20 |
| Ago-Emokpae | 40.69 | 20.99 | 2.55 | 22.22 | 11.17 | 1.44 |
| Apoje | 40.15 | 21.11 | 2.56 | 36.97 | 18.18 | 2.23 |
| Badagry | 22.65 | 11.50 | 1.40 | 17.23 | 8.514 | 1.05 |
| Benin City | 27.49 | 13.58 | 1.65 | 36.82 | 18.90 | 2.23 |
| Igede Ekiti | 45.47 | 23.18 | 2.81 | 37.32 | 18.90 | 2.23 |
| Ikire | 49.14 | 23.17 | 2.81 | 29.61 | 15.08 | 1.86 |
| Iresa Apa | 47.56 | 24.54 | 2.98 | 20.74 | 10.81 | 1.33 |
| Nsukka | 37.19 | 16.85 | 2.04 | 19.853 | 31.94 | 39.17 |
| Okitipupa | 21.72 | 17.71 | 1.41 | 26.58 | 12.92 | 1.60 |
| Onishere | 42.20 | 21.76 | 2.64 | 88.00 | 46.29 | 56.9 |
| Ubiaja | 46.25 | 23.87 | 2.90 | 26.90 | 13.55 | 1.67 |
| Umuabi | 41.66 | 22.07 | 2.68 | 27.18 | 13.93 | 1.71 |

The estimated average value of Radium equivalent ($Ra_{eq}$) in soils and palm oils were lower than the recommended value of 370 Bq/kg (UNSCEAR, 2010) [19]. The gamma absorbed dose rates (D) in air in the present study were lower than the worldwide average limit value. The values for the Annual Effective Dose Rates (E) followed a similar trend. It was observed that decrease in these values was attributed to rainfall. Transport by rainfall is expectantly high due to changes in the elevation of the region. Radionuclides may be transported to new regions and values varied amongst different sampling locations due to the geographic structures, degree of rainfall and elevations of the region. Regions receiving higher degree of fertilizers, pre planting and post planting activities also contributed significantly to the level of radionuclide in the area. Values were generally lower than the global average limit value. Table 5, show that the Transfer factor (Tf) in the pressed all palm oil was a little greater than unity/very close to unity.

**Table 10.5: Tf and ELCR values for NORM in Soil and Palm Oil**

| Sampling Location | Transfer factor | | | Excess Life Time Cancer Risk | | |
|---|---|---|---|---|---|---|
| | $^{40}K$ | $^{238}U$ | $^{232}Th$ | ELCR | | |
| | Soil Depth (15-30 cm) | | | Soil Depth (0-15 cm) | Soil Depth (15-30 cm) | Palm Oil |
| Abak | 0.688 | 1.085 | 1.394 | 0.1086 | 0.0947 | 0.0720 |
| Acharu | 0.508 | 2.003 | 1.244 | 0.0866 | 0.0997 | 0.0682 |
| Agbarho | 0.325 | 0.982 | 0.428 | 0.0986 | 0.1151 | 0.0462 |
| Ago-Emokpae | 0.287 | 0.259 | 0.890 | 0.0982 | 0.1783 | 0.0554 |
| Apoje | 1.674 | 0.803 | 2.345 | 0.0986 | 0.0569 | 0.0859 |
| Badagry | 0.579 | 1.604 | 0.859 | 0.0539 | 0.0562 | 0.0404 |
| Benin City | 1.235 | 0.417 | 0.687 | 0.0635 | 0.0928 | 0.0859 |
| Igede Ekiti | 3.278 | 0.450 | 1.474 | 0.0861 | 0.0882 | 0.0859 |
| Ikire | 1.578 | 1.849 | 2.247 | 0.1082 | 0.0416 | 0.0716 |
| Iresa Apa | 1.301 | 1.978 | 0.332 | 0.1147 | 0.0451 | 0.0513 |
| Nsukka | 0.031 | 1.384 | 1.500 | 0.0785 | 0.6349 | 0.0157 |
| Okitipupa | 1.794 | 0.327 | 1.901 | 0.0836 | 0.1375 | 0.0616 |
| Onishere | 1.908 | 1.044 | 0.950 | 0.0264 | 0.1267 | 2.1907 |
| Ubiaja | 0.509 | 0.394 | 2.152 | 0.1117 | 0.1055 | 0.0643 |
| Umuabi | 0.848 | 2.858 | 0.354 | 0.1032 | 0.2518 | 0.0658 |

This is an indication of low concentration of NORM from soil to pressed palm oil. Factors responsible include rhizospheres and bioavailability of NORM supported by soil factors and pore size of soils [47]. Rhizospheres can be defined as the section or area around the plant root. Environmental scientists define bioavailability of metals in soil solution as the concentration of that particular metal or compound that is accessible for the plant or organism. For uptake by plants, bioavailability is related to the abundance of nutrients or contaminants such as heavy metals and trace metals, persistent organic pollutants, soil water, soil organic matter, oxygen in soils and water available for plant uptake [48]. Risk assessment can also be determined by the bioavailability of such elements in soils and factors, which influence the uptake. These factors include pH, cation exchange capacity, soil size and texture, soil organic matter, sorption, diffusion and fractions of the soils. The bioavailability of the metals and radionuclides from soil to the edible part of the plant also depends on the competing ions [49-54].

## 10.6 Conclusion

All the naturally occurring radionuclides were detected in all samples of the soil and palm oil on the oil palm plantation, but they did not exceed the recommended guidance levels for the ingestion of radionuclides in food. The concentration of $^{40}K$ was found to be high in comparison to other radionuclides due to transfer from soils and high transfer ratio. Potassium is found readily in soils especially due to preplanting and post planting operations and the use of pesticides and phosphate fertilizer. The high concentration of potassium in soil samples may be due to the tiny potassium ions trapped inside the clay particle composition of the soil attributed to the crystalline forces that hold these potassium ions uptake [54]. In addition, soil

characteristics may favor its mobilization and translocation into plant tissues of a micronutrient. However, radioactive potassium, $^{40}K$ concentration must be monitored closely as it transports and translocate to fruits through roots/shoot and ingested by humans, although radionuclide $^{40}K$ is regulated by the human body.

### 10.7 Conflict of Interest

The authors declare no conflict of interest.

### 10.8 Author Contributions

Olafisoye OB performed data collection, the experiment, and data analysis, conceptualized part of the research and wrote the manuscript. Oguntibeju O.O and Osibote OA conceptualized the research, supervised the study and edited the manuscript.

### 10.9 Acknowledgment

The authors wish to thank Cape Peninsula University of Technology, Cape Town, South Africa for funding the research and Bowen University Iwo for the Staff Development Fund for Olafisoye Oladunni Bola.

### 10.10 References

[1] V. Varsha, L.P. Stuart, N.J. Clinton, &J.S. Sharon, 2016. The Impacts of Oil Palm on Recent Deforestation and Biodiversity. *PLoS ONE*, 11(7): 1–19.

[2] R. Loganathan, K.M. Subramaniam, A.K. Radhakrishnan, Y. Choo, Health-promoting effects of red palm oil: evidence from animal and human studies, Nutr. Rev. 75 (2017) 98–113. doi:10.1093/nutrit/nuw054.

[3] C.Y. May, K. Nesaretnam, Highlight Article Research advancements in palm oil nutrition Ã, Eur. J. Lipid Sci. Technollogy. 116 (2014) 1301–1315. doi:10.1002/ejlt.201400076.

[4] O.B Imoisi, G,E Ilori, I, E.J. Agho, 2015. Palm oil, its nutritional and health implications (A Review). *Journal Applied Science Environmental Management*, 19(1) 127-: 127.

[5] Chawla, S., Saxena, S., Division, E.B., Sciences, A. & Road, L. 2013. Red Palm Oil - Health Benefits and Their Molecular Executors. *International Journal of Bioassays*, 2(09): 1223–1231.

[6] Olafisoye, O.B., Oguntibeju, O.O. & Osibote, O.A. 2017. Trace elements and radionuclides in palm oil, soil, water, and leaves from oil palm plantations: A review. *Critical Reviews in Food Science and Nutrition*, 57(7): 1295–1315.

[7] Joel, E.S., Maxwell, O., Adewoyin, O.O., Olawole, O.C., Arijaje, T.E., Embong, Z. & Saeed, M.A. 2019. Investigation of natural environmental radioactivity concentration in soil of

coastaline area of Ado-Odo/Ota Nigeria and its radiological implications. *Scientific Reports*, 9(1): 1–8.

[8] European Commission, 2018. Study on the environmental impact of palm oil consumption and on existing sustainability standards.2018

[9] A. Baudoin, P. Bosc, P. Levang, Review of the diversity of palm oil production systems in Indonesia, 2017.

[10] E.M. Ordway, R.L. Naylor, R.N. Nkongho, E.F. Lambin, Oil palm expansion and deforestation in Southwest Cameroon associated with proliferation of informal mills, Nat. Commun. (2015) 1–11. doi:10.1038/s41467-018-07915-2.

[11] N. R Eugenio, M. McLaughlin, Daniel Pennock, Soil pollution, 2018.

[12] IAEA, 2010. Handbook of Parameter Values for the Prediction of Radionuclide Transfer in Terrestrial and Freshwater, 2010.

[13] IAEA, 2003. Modelling the transfer of radionuclides to fruit. Report of the Fruits Working Group.2003.

[14] Papastefanou, C. 2009. Radioactivity of tobacco leaves and radiation dose induced from smoking. *International Journal of Environmental Research and Public Health*, 6(2): 558–567.

[15] Tchokossa, P., Olomo, J.B., Balogun, F.A. & Adesanmi, C.A. 2013. Radiological study of soils in oil and gas producing areas in Delta state, Nigeria. *Radiation Protection Dosimetry*, 153(1): 121–126.

[16] Itoh, S., Eguchi, T., Kato, N. & Takahashi, S. 2014. Radioactive particles in soil, plant, and dust samples after the Fukushima nuclear accident. *Soil Science and Plant Nutrition*, 60(4): 540–550..doi.org/10.1080.

[17] Dieguez-Elizondo, P.M., Gil-Lopez, T., O'Donohoe, P.G., Castejon-Navas, J. & Galvez-Huerta, M.A. 2017. An analysis of the radioactive contamination due to radon in a granite processing plant and its decontamination by ventilation. *Journal of Environmental Radioactivity*, 167: 26–35. http://dx.doi.org/10.1016.

[18] United Nations Scientific Committee on the Effects of Atomic Radiation. 2000. *Sources and Effects of Ionizing Radiation: Volume* I

[19] Gruca, M., van Andel, T.R. & Balslev, H. 2014. Ritual uses of palms in traditional medicine in sub-Saharan Africa: A review. *Journal of Ethnobiology and Ethnomedicine*, 10(1): 24 pp.

[20] Chad-Umoren, Y. & Umoh, I. 2014. Baseline Radionuclide Distribution Patterns in Soil and Radiation Hazard Indices for Abak, Nigeria. *Advances in Physics Theories and Applications*, 32: 69–80.

[21] Alausa, S.K., Odunaike, K. & Adeniji, I.A. 2017. Transfer Factor of Radionuclides From Soil-To-Palm Oil Produced From Elere Palm Tree Plantation Near Ibadan Oyo State, Nigeria. *Nigeria Journal of Pure and Applied Physics*, 7(1): 7–12.

[22] IAEA. 2014. Radiation protection and safety of radiation sources: international basic safety standards general safety: No GSR part 3. In *IAEA safety standards*. 436.

[23] Blundell, M. 2015. Naturally occurring radioactive materials. *Proceedings of the American Gas Association, Operating Section*, 490–502.

[24] Harlow, K. 2017. Naturally occurring radioactive materials and the regulatory challenges to the zircon industry. *Journal of the Southern African Institute of Mining and Metallurgy*, 117(5): 409–413.

[25] Krane, K.S. 1988. *The Radioactive Decay Law*.

[26] Cooper, M.B. 2005. *Naturally Occurring Radioactive Materials (NORM) in Australian Industries - Review of Current Inventories and Future Generation*.

[27] Fujii, K., Ikeda, S., Akama, A., Komatsu, M., Takahashi, M. & Kaneko, S. 2014. Vertical migration of radiocesium and clay mineral composition in five forest soils contaminated by the Fukushima nuclear accident. *Soil Science and Plant Nutrition*, 60(6): 751–764. doi.org/10.1080

[28] Todorović, N., Hansman, J., Mrđa, D., Nikolov, J., Kardos, R. & Krmar, M. 2017. Concentrations of 226Ra, 232Th and 40K in industrial kaolinized granite. *Journal of Environmental Radioactivity*, 168: 10–14.

[29] Durusoy, A. & Yildirim, M. 2017b. Determination of radioactivity concentrations in soil samples and dose assessment for Rize Province, Turkey. *Journal of Radiation Research and Applied Sciences*, 10(4): 348–352. doi.org/10.1016

[30] Ji, K., Wang, Y., Du, L., Xu, C., Liu, Y., He, N., Wang, J. & Liu, Q. 2019. Research Progress on the Biological Effects of Low-Dose Radiation in China. *Dose-Response*, 17(1): 1–16.

[31] Degerlier, M. 2013. Assessment of natural radioactivity and radiation hazard in volcanic tuff stones used as building and decoration materials in the Cappadocia region, Turkey. *Radioprotection*, 48(2): 215–229.

[32] Amanjeet, Kumar, A., Kumar, S., Singh, J., Singh, P. & Bajwa, B.S. 2017. Assessment of natural radioactivity levels and associated dose rates in soil samples from historical city Panipat, India. *Journal of Radiation Research and Applied Sciences*, 10(3): 283–288..doi.org/10.1016

[33] Adewoyin, O.O., Omeje, M., Joel, E.S., Akinwumi, S.A., Ehi-Eromoseled, C.O. & Embong, Z. 2018. Radionuclides proportion and radiological risk assessment of soil samples collected in Covenant University, Ota, Ogun State Nigeria. *MethodsX*, 1419–1426. doi.org/10.1016.

[34] Kumar, A., Kumar, S., Singh, J. & Singh, P. 2019. Assessment of natural radioactivity levels and associated dose rates in soil samples from historical city Panipat, India. *Journal of Radiation Research and Applied Sciences*, 10(3): 283–288. doi.org/10.1016

[35] United Nations Scientific Committee on the Effects of Atomic Radiation. 2010. *Summary of low-dose radiation effects on health. UNSCEAR 2010*.

[36] Calmon, P., Fesenko, S., Voigt, G. & Linsley, G. 2009. Quantification of radionuclide transfer in terrestrial and freshwater environments. *Journal of Environmental Radioactivity*, 100(9): 671–674.

[37] Lema, M.W., Ijumba, J.N., Njau, K.N., Ndakidemi, P.A., Arusha, P.O.B.N. & Republic, U. 2014. Environmental Contamination by Radionuclides and Heavy Metals Through the Application of Phosphate Rocks During Farming and Mathematical Modeling of Their Impacts to the Ecosystem. International Journal of Engineering Research and General Science, 2(4): 852–863.

[38] FAO/WHO. 2011. JOINT FAO/WHO Food standards programme and Codex Committee on contaminants in foods. 5th Session. The Hague, The Netherlands. March 2011. Codex Alimentarius Commision, 5(1): 88 pp.

[39] Ademola, A.K. 2019. Natural radionuclide transfer from soil to plants in high background areas in Oyo state, Nigeria. Radiation Protection and Environment, 42(3): 112.

[40] Usikalu, M.R., Akinyemi, M.L. & Achuka, J.A. 2014. Investigation of Radiation Levels in Soil Samples Collected from Selected Locations in Ogun State, Nigeria. IERI Procedia, 9: 156–161.

[41] Chad-Umoren, Y.E. & Umoh, I.J. 2014. Baseline radionuclide distribution pattern in soil and radiation hazard indices for Abak, Nigeria. Advances in Physics Theories and Applications, 32: 69-80.

[42] Oladapo, O. 2012. Assessment of Natural Radionuclides Level in Wasteland Soils around Olusosun Dumpsite Lagos, Nigeria. IOSR Journal of Applied Physics, 2(3): 38–43.

[43] Jibiri, N.N. & Amakom, C.M. 2011. Radiological assessment of radionuclide contents in soil waste streams from an oil production well of a petroleum development company in Warri, Niger Delta Nigeria. Indoor and Built Environment, 20(2): 246–252.

[44] Adagunodo, T.A., George, A.I., Ojoawo, I.A., Ojesanmi, K. & Ravisankar, R. 2018. Radioactivity and radiological hazards from a kaolin mining field in Ifonyintedo, Nigeria. MethodsX, 5(April): 362–374.

[45] Ifayefunmi, O., Kupriyanov, V., Mirzeabasov, O. & Synzynys, B. 2019. Review of Distribution of Natural Radiation in Some Parts of Nigeria. Nuclear Science, 4(4): 52.

[46] E. Jedy-Agbaa, M. P. Curadob, O. Ogunbiyi, E. O., Fabowale, F. Igbinobad, G. Osubord, T. Otue, H. Kumaie, A. Koechlinb, P. Osinubif, P. Dakuma, W. Blattnerg, 2013. NIH Public Access. *Cancer Epidemiology*, 36(5): 1–17.

[47] Ebbs, S.D., Brady, D.J. & Kochian, L. V. 1998. Role of uranium speciation in the uptake and translocation of uranium by plants. *Journal of Experimental Botany*, 49(324): 1183–1190.

[48] Sheppard, S.C. 2011. Review of "Handbook of Parameter Values for the Prediction of Radionuclide Transfer in Terrestrial and Freshwater Environments". *Journal of Environmental Radioactivity*, 102(2): 217.

[49] Shtangeeva, I. & Ayrault, S. 2004. Phytoextraction of thorium from soil and water media. *Water, Air, and Soil Pollution*, 154(1–4): 19–35.

[50] Ehlken, S. & Kirchner, G. 2002. Environmental processes affecting plant root uptake of radioactive trace elements and variability of transfer factor data: A review. *Journal of Environmental Radioactivity*, 58(2–3): 97–112.

[51] Asaduzzaman, K., Khandaker, M.U., Amin, Y.M. & Mahat, R. 2015. Uptake and distribution of natural radioactivity in rice from soil in north and west part of peninsular malaysia for the estimation of ingestion dose to man. *Annals of Nuclear Energy*, 76: 85–93.doi.org/10.1016/j.anucene.2014.09.036.

[52] Adedokun, M.B., Aweda, M.A., Maleka, P.P., Obed, R.I., Ogungbemi, K.I. & Ibitoye, Z.A. 2019. Natural radioactivity contents in commonly consumed leafy vegetables cultivated through surface water irrigation in Lagos state, Nigeria. *Journal of Radiation Research and Applied Sciences*, 12(1): 147–156. ttps://doi.org/10.1080/16878507.2019.1618084.

[53] Njinga, R.L., Jonah, S.A. & Gomina, M. 2015. Preliminary investigation of naturally occurring radionuclides in some traditional medicinal plants used in Nigeria. *Journal of Radiation Research and Applied Sciences*, 8(2): 208–215. doi.org/10.1016/j.jrras.2015.01.001.

[54] Bian, H., Wang, Y., Chen, W., Zhang, Y., Zhuang, Z., Xia, R., Dai, H., Feng, J., Pu, W., Chen, L., Cai, W., Hu, W. & Liu, Y. 2018. Multiple Organ Lesions in a Case of Contamination With Multiple Radionuclides After 38 Years. *Dose-Response*, 16(4): 1–7

## CHAPTER ELEVEN

## Radioactivity in drinking water on oil palm plantation communities

***OB Olafisoye[1], OO Oguntibeju[2], OA Osibote[3*]***

*[1]Faculty of Applied Sciences, Department of Chemistry, Cape Peninsula University of Technology, P.O. Box 652, Cape Town, South Africa 8000.* oladunniolafisoye@gmail.com.

*[2]Faculty of Health and Wellness Sciences, Department of Biomedical Sciences, Cape Peninsula University of Technology, P.O. Box 1906, Bellville, South Africa 7535.* oguntibejuo@cput.ac.za.

*[3*]Faculty of Applied Sciences, Department of Mathematics and Physics, Cape Peninsula University of Technology, P.O. Box 652, Cape Town, South Africa 8000.* osibotea@cput.ac.za

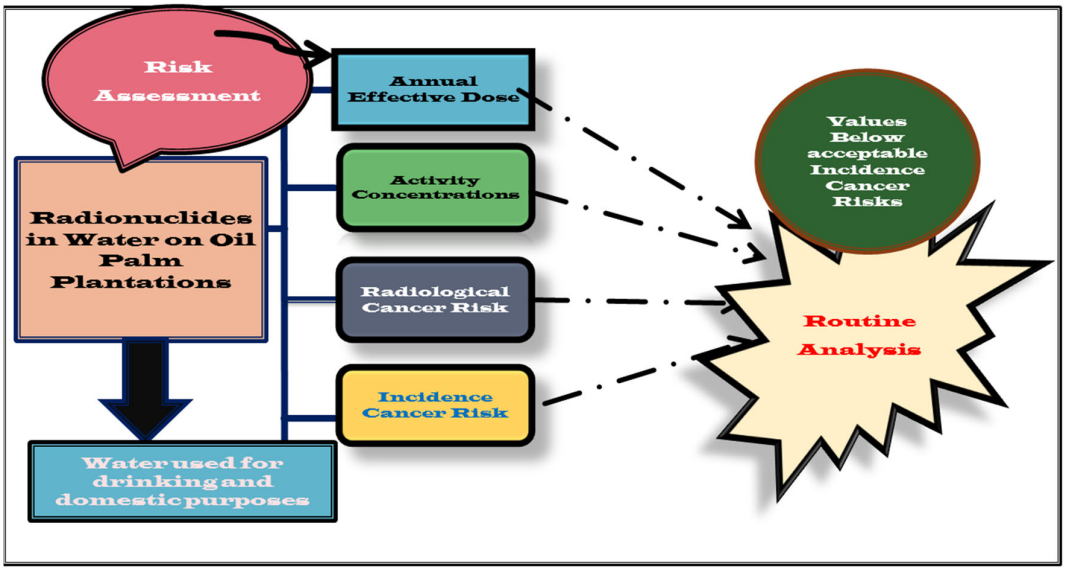
Corresponding Author: *osibotea@cput.ac.za; +27214609092*

### Abstract:

The study presents an assessment of the Annual Effective Dose and Cancer Risk from groundwater sampled in oil palm plantation communities in Nigeria. Groundwater was sampled from fifteen independent sampling locations where palm oil is extensively cultivated. The activity concentration of $^{40}K$, $^{238}U$ and $^{232}Th$ were assessed. Annual effective Dose for different age groups and cancer risk were estimated. The values for the Annual Effective Dose Estimation ($E_w$) ($mSvy^{-1}$) for $^{40}K$, $^{238}U$ and $^{232}Th$ revealed that $E_W$ for $^{40}K$ was elevated in infants, children, and adults in the order; $3.51 \times 10^{-4}$, $8.21 \times 10^{-4}$, and $11.72 \times 10^{-4}$ at W4 plantation respectively. The calculation of cancer risks based on the radium isotopes ranges from $5.91 \times 10^{-4}$ - $21.10 \times 10^{-4}$ for $^{226}Ra$. For $^{228}Ra$, the values were from $5.87 \times 10^{-4}$ - $1.64 \times 10^{-4}$. The estimation of the Annual Effective Dose for all the individual populations were below the recommended reference value of 0.1 mSv from a year intake of drinking water in accordance with the WHO, IAEA and UNSCEAR regulated guideline values. The values are within the acceptable Incidence Cancer Risks of the recommended guidelines for drinking water quality reference levels for radionuclides in drinking water.

***Keywords:*** *Activity concentrations, palm oil plantations, ground water, radiological consideration, annual effective dose estimation, cancer risk*

***ORIGINAL PAPER under review in the Elsevier journal; "HELIYON (Cell Press)".***




**Graphical abstract**

## 11.1 Introduction

Naturally Occurring Radioactive Materials (NORM) include the isotopes of uranium and thorium in addition to their daughters/progenies and potassium-40. NORM can be found in drinking water. Table 1 summarises the external and internal average radiation dose due to NORM. Drinking water and household water are potentially important pathways, directly or through their use in food preparation and processing, although dilution, time delays, and water treatment can reduce the contamination levels markedly (Tchokossa et al., 1999). Waterways from streams, lakes, and ponds could be a source of contamination when they seep into groundwater. Radium is considered as a highly toxic element in water and requires attention for human health (Tchokossa et al., 1999). Two natural radium isotopes are a cause of worry in public water supplies; $^{226}$Ra, which is daughter series of $^{238}$U, and $^{228}$Ra, which is daughter series of $^{232}$Th decay.

The largest percentage of NORM exposure from radon gas is decay of radium found in underground rocks and soils. This releases the gas in the surrounding water, air, and buildings due to the use of such materials for constructions (Tchokossa et al., 1999). Radon is produced from the isotopes of radium during the decay of naturally occurring radioactive elements, uranium, and thorium. Radon is a gas found underneath the ground and is inert which easily dissolves with ground water and can be translocated over long distances. The longest-lived isotope of radon, radon-222 is abundantly found in ground water supplies though it readily

disintegrates with a radioactive half-life of 3.8 days (IAEA, 2010). Radon concentration in ground water has higher concentration than surface water since surface water is usually aerated (Chen et al., 2018; Aieta et al., 2019; Olise et al., 2016). Figure 1 provides a description of NORM and TENORM sources in water.

**Table 11.1: Average dose of NORM radiation**

| Source | Worldwide average annual effective dose | Typical range (mSv) |
|---|---|---|
| External exposure<br>Cosmic rays<br>Terrestrial gamma rays[a] | <br>0.4<br>0.5 | <br>0.3 – 1.0<br>0.3 – 0.6 |
| Internal exposure<br>Inhalation (mainly radon)<br>Ingestion (food and drinking water) | <br>1.2<br>0.3 | <br>0.2 – 10[b]<br>0.2 – 0.8 |
| Total | 2.4 | 1 – 10 |

[a.] ***Terrestrial exposure is due to radionuclides in soil and building materials***
[b.] ***Dose from inhalation of radon may exceed 10 mSvy$^{-1}$ in certain residential areas (UNSCEAR, 2000).***

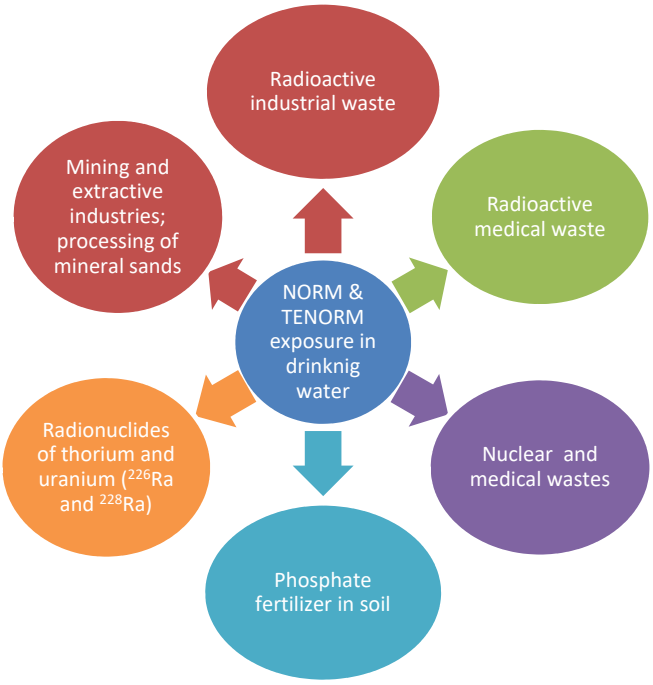



**Fig. 11.1: NORM and TENORM sources**

The value of potassium-40 is not as significant as radon to the assessment of radionuclides in drinking water when compared to radon. This is because potassium is a major element in the

regulation of the body physicochemical and biological functions and this is kept constant by the bodies' physiological processes (Tchokossa et al., 1999). The toxicity of NORM greatly depends on physicochemical properties such as pH, and redox reactions, electrical conductivity, bioavailability and bio accessibility in soil solution. Thorium is generally immobile and insoluble while uranium is very mobile in neutral and alkaline soil water (WHO Geneva, 2009; WHO Geneva, 2018). Drinking water is not a global hazard but other environmental contributions may lead to a radiological hazard. The dose, which results from the ingesting of radionuclides, is dependent on chemical and biological points to consider such as the absorbed dose by the tissues or visceral organs and their sensitivity, nature and persistence in the body before disintegration. The World Health Organization (WHO) in a book, "the management of radioactivity in drinking water", and International Atomic Energy Agency (IAEA) has recorded data coefficients in relation to ingestion of radionuclides for age groups (IAEA, 2013; WHO Geneva, 2018). WHO handbook on indoor radiation and the Management of Radioactivity in drinking-water sets a compliance level for radon concentrations in indoor air (100 - 300 Bq $m^{-3}$). This is due to the volatility of radon in dissolved water used in homes. Inhalation and ingestion are two key factors to consider when assessing radon concentrations in indoor air and ground water used in homes. Ingestion of radon is minimal in comparison to inhalation (WHO Geneva, 2009; WHO Geneva, 2018). Degassing of water and aeration in water treatment, distribution, and storage removes the greater percentage of radon in drinking water (IAEA, 2010; WHO Geneva, 2009; WHO Geneva, 2018).

A major concern is the tendency of radon exposure in water used for domestic purposes from ground water bodies such as springs boreholes and wells, which have relatively a short time between water extraction and usage of water (WHO Geneva, 2018; El-Gamal *et al.*, 2019). There is generally no guideline level for radon since it is more logical to measure the concentration of air as indoor radon rather than radon in domestic or drinking water. Hence, an average of the dose from radon in water is actually from inhaling rather than ingesting dissolved radon (UNSCEAR, 2000; WHO Geneva, 2009; WHO Geneva, 2009). The concentration and dose of radon in indoor air is mainly from domestic activities such as heating, agitating, showering, bathing, and toilet flushing. The value of 0.1 $mSvy^{-1}$ consumption of drinking water holds independent of the age group. Uranium is assessed based on its chemical toxicity and the WHO guideline value for the overall concentration of uranium in drinking water is 30 $\mu gL^{-1}$ (0.37 $BqL^{-1}$) of $^{238}U/^{234}U$. Due to the toxicity of uranium to the visceral organs and tissues, the guideline for the determination of uranium in drinking water is 15 $\mu gL^{-1}$. Studies have shown the health effects caused by radiation on the population and cancer related effects occurs when the probability coefficient for radiation exceeds 0.1 mSv per year from

inhaling/ingesting radionuclides in water which is minimal when compared to other health related issues (WHO Geneva, 2009; IAEA, 2010; WHO Geneva, 2018; Lema et al., 2014; Edition et al., 2017). United Nations Scientific Committee on the Effect of Atomic Radiation (UNSCEAR) reviewed levels of NORM in drinking water globally and this varied with respect to the geology of the area. For instance, mean uranium concentrations in water bodies used for portable water showed variability for groundwater and the concentration were between 1.0 $\times 10^{-5}$ $BqL^{-1}$ to 200 $BqL^{-1}$. Less than 3 % of samples analyzed exceeded the guidelines for uranium in drinking water (UNSCEAR, 2015) and the data compiled show that NORM is usually low in drinking water. The concentration of NORM in drinking water can be reviewed, by a past data of the geology and hydrology of an area. This is in the management of radiology in water especially in non-emergency cases (WHO Geneva, 2009; El-Gamal et al., 2019; Mohammed & Mazunga, 2013). Globally humans receive a radiation dose of an average of 0.3 $mSvyr^{-1}$ from ingesting NORM and a dose of 0.01 mSv is from drinking water. The remainder dose comes from radon, cosmic rays and food (UNSCEAR, 2015).

The IAEA and WHO therefore, drew upon experts and specialists in the radio analytical field, to provide guidelines for collecting, preparing and analyzing relevant environmental material, and basic food for radionuclides of interest. For water samples, an assessment of annual effective dose and cancer risk for different age groups were determined. During a radionuclide assessment, several radionuclides are usually identified and the sum of all the radionuclides needs to be considered to ascertain they do not exceed unity (WHO Geneva, 2018). Hence, the aim and objective of the study and the significance of the present work was to investigate groundwater samples taken from fifteen independent sampling locations on oil palm plantations producing areas in states in the south eastern, south western and south southern areas/states of Nigeria. The ground water samples were investigated for the annual effective dose and cancer risk for different age groups. If there is an exposure of radionuclides in the proximity of the oil palm plantation, its concentration in the water will provide far more meaningful information than its concentration in air. Different age groups in the oil palm plantation for drinking and domestic purposes, use the ground water. The oil palm plantation community is of paramount importance in the provision of a source of revenue and livelihood. The ground water was sampled and the radionuclides analyzed in view of the consumption of the ground water which may contribute to the population exposure.

## 11.2 Materials and Methods

### 11.2.1 Geology of the sampling area

The study areas are the substations of Nigeria Institute for Oil Palm Research Headquarters (NIFOR) and its Headquarters in Benin City, Nigeria. The headquarters of NIFOR is an establishment of hectare of land situated in Benin City about 29 km from the city center. More samples were collected in the southern states of Nigeria where oil palm is greatly cultivated. These states include Edo state, Enugu state, Delta state, Akwa-Ibom state, Ondo state, Ekiti state, Kogi state, Oyo state, Osun state, Ogun state and Lagos state. Figure 2 provides the map of Nigeria showing the sampling points.

### 11.2.2 Sampling procedure and preparation

A composite sample was used for analysis, which was achieved by partitioning the sampling area into four parts. This was based on factors such as population density and areas where pollution was suspected to be high. Fifteen water samples were collected from ground water in polyethylene containers labelled W1-W15 using automatic samplers. The ground water samples were collected at the water plant just after sedimentation and filtration. They were properly stored to avoid degradation, spoiling, decomposition of the radionuclides and contamination. Proper care was taken to avoid the loss of volatile radionuclides. The ground water samples were transferred to plastic containers, which have been pre-cleaned with hydrochloric acid. Prior to storage of the water in the refrigerator, 11 mol/L hydrochloric acid was added at the groundwater at the rate of 10 mL per litre after sampling to avoid adsorption of radionuclides on the walls of the container (IAEA, 2010; WHO Geneva, 2009; WHO Geneva, 2018; UNSCEAR, 2000). The water samples were hermetically sealed in Marinelli beakers. They were then stored for a minimum of 28 days to attain secular equilibrium. The sealed samples were placed on the shielded High Purity Germanium detector (HPGe) and counted for 36,000 seconds. Sample preparation and gamma spectroscopy was performed at the Centre for Energy and Research Development (CERD), Obafemi Awolowo University, Ile Ife, Osun State, Nigeria according to standard procedure (IAEA, 2010; WHO Geneva, 2009; WHO Geneva, 2018).

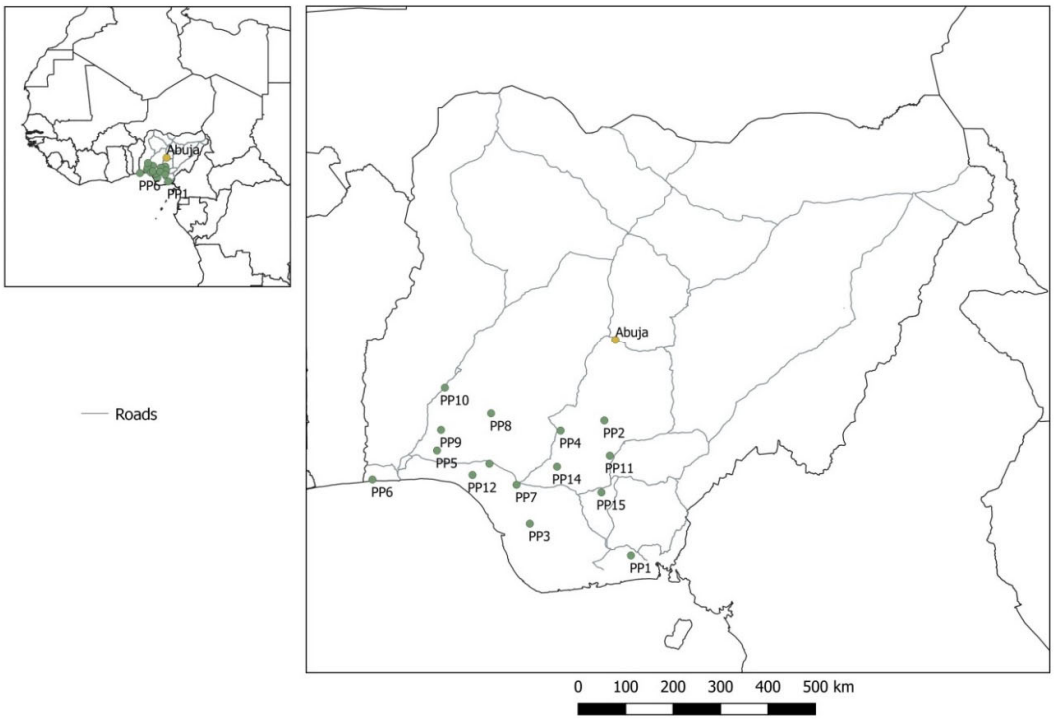



**Fig 11.2: Map of Nigeria showing sampling points**

### 11.2.3 Instrumentation

The HPGe detector enclosed in a 100-mm thick lead shield was connected to a Genie 2000 acquisition and analysis software that matched gamma energies to a library of possible isotopes was used for the analysis. The photo-peaks observed with regularity in the water samples were identified to belong to the natural radioactive decay series headed by $^{238}$U and $^{232}$Th, and a third non-series natural radionuclide, $^{40}$K. The $^{226}$Ra concentration was calculated by averaging over the measured concentrations for $^{214}$Pb and $^{214}$Bi. The $^{232}$Th activity was determined from the gamma peaks of 238.6 (43.6 %) keV from $^{212}$Pb and 338.4 (12 %), 911.2 (29 %) and 969 (17 %) keV from $^{228}$Ac and 583.0 (86 %) keV gamma rays from $^{208}$Tl. The $^{40}$K activity concentration was calculated from the energy 1460 (10.7 %) keV gamma ray line

The activity of the natural radionuclides $(As)$ was calculated using the software formula.

$$As = \frac{Ca}{EPrMs} \ldots\ldots\ldots Equation\ 1$$

Where:

$Ca$ is the net count rate of gamma ray (counts per second)

$E$ is the detector efficiency of the specific gamma ray

$Pr$ is the absolute transition probability of gamma decay

$Ms$ the mass of the sample (kg)

The prepared samples were analysed by gamma ray spectroscopy with the use of a Hyper Pure Germanium (HPGe) Detector. The counting time for the analysis was 36,000 seconds and the soil reference material IAEA-375 was prepared in the same way as the sample and counted in triplicates alongside the sample. The photo peak of the gamma ray for the ($^{214}$Bi) 1764 keV; ($^{228}$Ac) 911.21 keV; ($^{40}$K) 1461 keV were used to determine the activity of the naturally occurring radionuclides $^{238}$U, $^{232}$Th, and $^{40}$K. Their percentage emission probabilities corresponded to 14.9, 62.8 and 12.4 respectively. The detector was calibrated using the standard source which was a mixture of $^{22}$Na, $^{57}$Co, $^{60}$Co. Spectra analysis was performed using Genie software 2000 developed by CANBERRA. The background contribution was removed by subtracting this from the result of the analysis. The Detection Limit (DL) is the net signal above which a signal can be considered to have been reliably detected. In this study, the and the Minimum Detectable Activity (MDA) was achieved by modelling the Curies Model formula, which presents the background counts, branching ratio, and sample mass and detector efficiency.

$$DL = 2.71 + 4.66\sqrt{N_B} \ldots\ldots Equation\ .2 \qquad and$$

$$MDA = \frac{DL}{T\varepsilon Bm} \ldots\ldots Equation\ 3$$

$M$ is the mass the sample (kilograms) and $N_B$ is the background counts (counts per second).

### 11.2.4 Radiological considerations

It is appropriate to use guidance levels in the determination of the radiological quality of water. Though this may be conservative because it is assumed that drinking water is consumed and the activity is based at a rate of 2 liters per day. This assumption is used in the calculation of the radiation dose estimation of more vulnerable groups such as infants and children. Drinking water consumption rates may vary between countries and ages of the population, habits, and climate. If local data exist, this can be used for the calculation of radiological doses. If they do not exist, data from neighboring countries may be used. Ground water for use in the preparation of infant food should also be put into consideration (IAEA, 2013; WHO Geneva, 2018; El-Gamal *et a*l., 2019).

### 11.2.5 Radiation Dose Estimation

The total annual effective doses were measured for the Environmental Protection Agency (EPA), USA, which introduced different age groups according to the equation (WHO Geneva, 2018; El-Gamal *et al*., 2019).

$$Ew = A(W)X\ q(W)X\ Cf(W) \ldots\ldots\ldots Equation\ 4$$

Where

$Ew$ is the annual effective dose in water(mSvy$^{-1}$).
$A(W)$ is the radionuclide activity concentration in water (BqL$^{-1}$).
$q(W)$ is the water consumption rate for a person in one year, which is 150, 350 and 500 L for infants, children and adults respectively.
$Cf(W)$ is the effective dose equivalent conversion factor (mSvBq$^{-1}$).

### 11.2.6 Cancer Risk Estimation

The radiological risk related to the radium isotope can be determined by calculating the lifetime cancer risk (R) using the following equation (WHO Geneva, 2018; El-Gamal *et al*., 2019).

$$R = MCL\ X\ RC\ X\ TWI \ldots\ldots\ldots Equation\ 3$$

where
$MCL$ is the contaminant level of the activity concentration of the radionuclide in water with unit BqL$^{-1}$ (activity concentration of uranium-238 in water at each sampling site), $RC$ is the mortality risk coefficient (7.17 × 10$^{-9}$ and 2.0 × 10$^{-8}$ Bq$^{-1}$ for $^{226}$Ra and $^{228}$Ra respectively, $TWI$ is the total water intake (2Ld$^{-1}$× 365.4 dyear$^{-1}$ × 70 years). (El-Gamal *et al*., 2019).

### 11.3.0 Results and discussion

Table 2 show the Ingestion dose coefficients for different age groups. The average and effective dose equivalents are presented in Tables 1 and 3 were used in the calculation of radiation doses. Table 4 show the activity of NORM in water. Activity concentration of $^{40}$K (Bq/L) were least in Okitipupa plantation (171.7 ± 0.01 Bq/L) and the highest activity was recorded in Ago-Emokpae plantation (468.9 ± 0.01 Bq/L) respectively. 274.8 BqL$^{-1}$, 3.8142 BqL$^{-1,}$ and 4.927 BqL$^{-1}$ are the activity concentrations of $^{40}$K, $^{238}$U, and $^{232}$Th respectively. The activity concentrations of $^{238}$U (Bq/L) ranged between 1.611 ± 0.01 Bq/L – 5.750 ± 0.01 Bq/L and the concentrations were least in Ikire plantations and highest in Ago-Emokpae plantations

respectively. Activity concentrations values (Bq/L) for $^{232}$Th in water were highest in Ikire plantation (9.619 ± 0.26 Bq/L) and lowest in Apoje plantation (1.554 ± 0.62 Bq/L) respectively. Table 5 presents the values for the Annual Effective Dose Estimation ($E_w$) (mSvy$^{-1}$) for $^{40}$K, $^{238}$U and $^{232}$Th respectively. The highest $E_w$ recorded at W4 were 3.51 × 10$^{-4,}$ 8.21 × 10$^{-4}$, and 11.72 × 10$^{-4}$ mSvy$^{-1}$ for infants, children, and adults respectively. The highest $E_W$ recorded at W4 was 3.51 × 10$^{-4}$, 8.21 × 10$^{-4}$, and 11.72 × 10$^{-4}$ mSvy$^{-1}$ for infants, children, and adults respectively. The $E_w$ or $^{40}$K was highest in infants, children, and adults (3.51 × 10$^{-4}$, 8.21 × 10$^{-4}$, and 11.72 × 10$^{-4}$) at W4 plantation respectively. Lowest values of $E_w$ (mSvy$^{-1}$) were recorded in the same order at W12 plantation respectively (1.29 × 10$^{-4}$, 3.01 × 10$^{-4}$, and 4.29 × 10$^{-4}$). $E_w$ values (mSvy$^{-1}$) for $^{232}$Th were negligible at W1 and W12 plantations. Highest and lowest values were recorded as 6.49 × 10$^{-4}$ (W9), 9.76 × 10$^{-4}$ (W9) and 9.17 × 10$^{-4}$ (W2) for infants, children, and adults respectively. Lowest values of $^{232}$Th $E_W$ values (mSvy$^{-1}$) in the sampled ground water were recorded (1.12 × 10$^{-4}$, 1.68 × 10$^{-4}$, and 1.12 × 10$^{-4}$) for infants, children, and adults in W5 and W9 plantations respectively. The radionuclide $^{238}$U recorded $E_W$ values (mSvy$^{-1}$) in the range of 0.77 × 10$^{-4}$ mSvy$^{-1}$ – 11.06 × 10$^{-4}$ mSvy$^{-1}$, 1.04 × 10-4 mSvy$^{-1}$ – 16.10 × 10$^{-4}$ mSvy$^{-1}$ and 2.25 × 10$^{-4}$ mSvy$^{-1}$ – 8.05 × 10$^{-4}$ mSvy$^{-1}$ for infants, children, and adults respectively. The values were generally low for infants. Radionuclide $^{232}$Th was not detected in Abak and Nsukka plantations.

**Table 11.2 : Ingestion dose coefficients**

| Radionuclide | Dose coefficient (mSv/Bq$^{-1}$)[a,b] | | | |
|---|---|---|---|---|
| | Adults | Infants (< than 6 months old)[c] | Children (1 year old) | Children (10 year old) |
| Tritium | 1.8 × 10$^{-8}$ | 6.4 × 10$^{-8}$ | 4.8 × 10$^{-8}$ | 2.3 × 10$^{-8}$ |
| Carbon-14 | 5.8 × 10$^{-7}$ | 1.4 ×10$^{-6}$ | 1.6 × 10-$^{6}$ | 8.0 × 10$^{-7}$ |
| Strontium-90 | 2.8 × 10$^{-5}$ | 1.3 × 10$^{-4}$ | 7.3 × 10$^{-4}$ | 6.0 × 10$^{-4}$ |
| Iodine-131 | 2.2 × 10-$^{5}$ | 4.8 × 10$^{-4}$ | 1.8 × 10$^{-4}$ | 5.2 × 10$^{-5}$ |
| Caesium-134 | 1.9 × 10$^{-5}$ | 2.6× 10$^{-5}$ | 1.6 × 10$^{-5}$ | 1.4 × 10$^{-5}$ |
| Caesium-137 | 1.3 × 10$^{-5}$ | 1.1 × 10$^{-5}$ | 1.2 × 10$^{-5}$ | 1.0 × 10$^{-5}$ |
| Lead-210 | 6.9 × 10$^{-4}$ | 2.4 × 10$^{-3}$ | 3.6 × 10$^{-3}$ | 1.9 × 10$^{-3}$ |
| Polonium-210 | 1.2 × 0$^{-3}$ | 5.6 × 10$^{-2}$ | 8.8 × 10$^{-3}$ | 2.6 × 10$^{-3}$ |
| Radium-226 | 2.8 × 10$^{-4}$ | 5.7 × 10$^{-3}$ | 9.6 × 10$^{-4}$ | 8.0 × 10$^{-4}$ |
| Radium-228 | 6.9 × 10$^{-4}$ | 3.0 × 10$^{-2}$ | 5.7 × 10$^{-3}$ | 3.9 × 10$^{-3}$ |
| Uranium-234 | 4.9 × 10$^{-5}$ | 1.7 × 10$^{-4}$ | 1.3 × 10$^{-4}$ | 7.4 × 10$^{-5}$ |
| Uranium-238 | 4.5 × 10$^{-5}$ | 1.4 × 10$^{-4}$ | 1.2 × 10$^{-4}$ | 6.8 × 10$^{-5}$ |
| Thorium-228 | 7.2 × 10$^{-5}$ | 3.7 × 10$^{-3}$ | 3.7 × 10$^{-4}$ | 1.4 × 10$^{-4}$ |
| Thorium-230 | 2.1 × 10$^{-4}$ | 4.1 × 10$^{-3}$ | 4.1 × 10$^{-4}$ | 2.4 × 10$^{-4}$ |
| Thorium-232 | 2.3 × 10$^{-4}$ | 1.6 × 10$^{-3}$ | 4.5 × 10$^{-4}$ | 2.9 × 10$^{-4}$ |
| Plutonium-239/240 | 2.5 × 10$^{-4}$ | 5.2 × 10$^{-3}$ | 4.2 × 10$^{-4}$ | 2.7 × 10$^{-4}$ |
| Americium-241 | 2.0 × 10$^{-4}$ | 4.7 × 10$^{-3}$ | 3.7 × 10$^{-4}$ | 2.2 × 10$^{-4}$ |

***a Taken from WHO (2018)***
***b Taken from IAEA (2013)***
***c Values to be used for bottle-fed infants where tap water is used for making bottled milk (IAEA, 2013; WHO, 2018)***

**Table 11.3: Conversion Factor Cf(W) of $^{40}K$, $^{232}Th$ and $^{238}U$ for age groups**

| Age groups | $^{226}Ra \times 10^{-7}$ ($SvBq^{-1}$) | $^{232}Th \times 10^{-7}$ ($SvBq^{-1}$) | $^{40}K \times 10^{-7}$ ($SvBq^{-1}$) |
|---|---|---|---|
| Infants | 9.6 | 4.5 | 5 |
| Children | 8 | 2.9 | 5 |
| Adults | 2.8 | 2.3 | 5 |

***(WHO Geneva, 2018)***

Hazards may not be acute or immediate compared to other sources of radiation. The level of the radionuclide $^{40}K$ is not a hazard when considering radiological cancer health risks associated with radiological dose as the $^{40}K$ is a major element in the regulation of various physiological processes in the human systems. These physiological processes keep the concentration of $^{40}K$ constant (Chen *et al*., 2018). The activity concentrations of the radionuclides in ground water sampled for this study were from sources in rocks and soils. Some of the sampling areas had tailings from mining and crude oil drilling activities. These activities did not elevate the concentration of NORM as they were still within the background levels according to WHO guidelines (WHO Geneva, 2018). The activity concentrations of the $^{40}K$, $^{238}U$ and $^{232}Th$ varied across the sampling states due to the underlying geology of the rocks and parent material. The results of the study show that the water sampled for radiological testing of NORM contributed to a minor extend to the total value of the annual background radiation. The activity concentration of NORM in the water were below the recommended safety limits for the cancer risk estimation and the radiation dose guidelines given by WHO and UNSCEAR (WHO Geneva, 2018; UNSCEAR, 2000). The calculation of the children dose was most relevant making them the targeted population. Children are more sensitive to exposure from some radionuclides as reflected in different dose coefficients, although they typically consume smaller quantities of drinking water when compared to adults. The estimation of the assessed annual effective dose for all the individual populations were below the recommended reference value of 0.1 mSv resulting from a year intake of drinking water in accordance with the WHO, IAEA and UNSCEAR regulated guideline values (UNSCEAR, 2000; IAEA, 2013; WHO Geneva, 2018). The consumption of ground water of the study location does not pose any radiological hazard. Drinking water and household water are potentially important pathways for radionuclide ingestion and radium is considered as a highly toxic element in water and requires attention for human health. Although drinking water is not a global hazard, other environmental contributions may lead to a radiological hazard. The dose, which results from the ingesting of radionuclides, is dependent on chemical and biological points to consider such as the absorbed dose by the tissues or visceral organs and their sensitivity, nature and persistence in the body before disintegration. The oil palm plantation community depends on the source of ground water for drinking and other domestic uses.

**Table 11.4: Activity concentration of $^{40}K$, $^{232}Th$, and $^{238}U$ in water samples**

| Code Water | | Activity ($BqL^{-1}$) of $^{40}K$ | Activity ($BqL^{-1}$) of $^{238}U$ | Activity ($BqL^{-1}$) of $^{232}Th$ |
|---|---|---|---|---|
| W1 | Abak | 225.8±0.03 | 3.722±0.01 | ND |
| W2 | Acharu | 377.0±0.02 | 4.738±0.05 | 7.977±0.02 |
| W3 | Agbarho | 189.7±0.43 | 4.764±0.02 | 3.543±0.01 |
| W4 | Ago-Emokpae | 468.9±0.01 | 5.750±0.01 | 5.170±0.02 |
| W5 | Apoje | 213.4±0.01 | 5.058±0.05 | 1.654±0.62 |
| W6 | Badagry | 343.2±0.03 | 5.058±0.03 | 5.621±0.91 |
| W7 | Benin City | 422.3±0.02 | 2.844±0.04 | 5.778±0.73 |
| W8 | Igede Ekiti | 382.3±0.02 | 2.309±0.06 | 3.368±0.22 |
| W9 | Ikire | 190.0±0.01 | 1.611±0.01 | 9.619±0.26 |
| W10 | Iresa Apa | 196.3±0.03 | 1.713±0.02 | 7.293±0.02 |
| W11 | Nsukka | 259.4±0.03 | 3.046±0.24 | ND |
| W12 | Okitipupa | 171.7±0.01 | 4.773±0.03 | 2.015±0.01 |
| W13 | Onishere | 183.0±0.35 | 4.585±0.01 | 5.157±0.03 |
| W14 | Ubiaja | 226.7±0.43 | 3.330±0.01 | 2.937±0.01 |
| W15 | Umuabi | 248.2±0.06 | 3.912±0.01 | 3.912±0.01 |

**Table 11.5: Annual Effective Dose Estimation ($E_w$)**

| Sample codes | | | | $E_w \times 10^{-4}$ ($^{40}K$; $mSvy^{-1}$) | | | $E_w \times 10^{-4}$ ($^{232}Th$; $mSvy^{-1}$) | | | $E_w \times 10^{-4}$ ($^{238}U$; $mSvy^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Infant | Children | Adults | Infant | Children | Adults | Infant | Children | Adults | Infant | Children | Adults |
| W1 | 1.69 | 3.95 | 5.65 | ND | ND | ND | 1.79 | 1.04 | 5.21 | | | |
| W2 | 2.83 | 6.60 | 9.43 | 5.39 | 8.10 | 9.17 | 2.27 | 1.33 | 6.63 | | | |
| W3 | 1.42 | 3.32 | 4.74 | 2.31 | 3.60 | 4.08 | 2.89 | 13.27 | 6.70 | | | |
| W4 | 3.52 | 8.21 | 11.72 | 3.49 | 5.25 | 5.96 | 2.76 | 16.10 | 8.05 | | | |
| W5 | 1.60 | 3.74 | 5.34 | 1.12 | 1.68 | 1.92 | 2.43 | 14.16 | 7.08 | | | |
| W6 | 2.57 | 6.01 | 8.58 | 3.80 | 5.71 | 6.46 | 2.43 | 14.16 | 7.08 | | | |
| W7 | 3.17 | 7.39 | 10.56 | 3.90 | 5.89 | 6.65 | 1.37 | 7.96 | 3.98 | | | |
| W8 | 2.87 | 6.69 | 9.56 | 2.28 | 3.42 | 3.87 | 11.06 | 6.47 | 3.23 | | | |
| W9 | 1.43 | 3.33 | 4.75 | 6.49 | 9.76 | 1.12 | 0.77 | 4.51 | 2.25 | | | |
| W10 | 1.47 | 3.44 | 4.91 | 4.92 | 7.40 | 8.39 | 0.82 | 4.80 | 2.40 | | | |
| W11 | 1.95 | 4.54 | 6.49 | ND | ND | ND | 1.46 | 8.53 | 4.26 | | | |
| W12 | 1.29 | 3.01 | 4.29 | 1.36 | 2.05 | 2.32 | 2.29 | 13.36 | 6.68 | | | |
| W13 | 1.37 | 3.20 | 4.58 | 3.48 | 5.23 | 5.93 | 2.20 | 12.84 | 6.42 | | | |
| W14 | 1.70 | 3.97 | 5.67 | 1.98 | 2.98 | 3.38 | 1.60 | 9.32 | 4.66 | | | |
| W15 | 1.86 | 4.34 | 6.21 | 2.64 | 3.97 | 4.50 | 1.88 | 10.95 | 5.48 | | | |

**Table 11.6: Radiological cancer risk for Radium isotopes**

| Sample code | Radiological risk × $10^{-4}$ | Radiological risk × $10^{-3}$ |
|---|---|---|
| | $^{226}Ra$ | $^{228}Ra$ |
| W1 | 13.65 | 3.80 |
| W2 | 17.39 | 4.83 |
| W3 | 17.48 | 4.85 |
| W4 | 21.10 | 5.87 |
| W5 | 18.56 | 5.16 |
| W6 | 18.56 | 5.16 |
| W7 | 10.44 | 2.90 |
| W8 | 8.47 | 2.36 |

| | | |
|---|---|---|
| W9 | 5.91 | 1.64 |
| W10 | 6.29 | 1.75 |
| W11 | 11.18 | 3.11 |
| W12 | 17.52 | 4.87 |
| W13 | 16.83 | 4.68 |
| W14 | 12.22 | 3.40 |
| W15 | 14.36 | 3.99 |
| | | |
| SUM | 209.96 | 58.37 |
| Average | 26.25 | 3.891 |
| Maximum value | 21.10 | 5.87 |
| Minimum value | 5.91 | 1.64 |

### 11.4.0 Conclusion

The result of the annual effective dose and cancer risk estimation in the present study proves that the NORM in the ground water samples from all the plantations under study do not pose any significant health risk to the public. The oil palm plantation community depends on the source of ground water for drinking and other domestic uses. Studies have shown the health effects caused by radiation on the population and cancer related effects occurs when the probability coefficient for radiation exceeds 0.1 mSv per year from inhaling/ingesting radionuclides in water which is minimal when compared to other health related issues. In the present study, the hazard indices were below permissible limits provided by regulatory bodies such as WHO and UNSCEAR. The research provides a foundation and procedure for the establishment of national regulatory standards and risk assessment information for safety in the use of water on the oil palm plantations especially in non-emergencies. The present work revealed that the dose received by children by drinking the ground water sampled on the plantation was higher than infants and adults. Adults also received higher dose compared to infants. Children are more sensitive to exposure from some radionuclides as reflected in different dose coefficients, although they typically consume smaller quantities of drinking water when compared to adults. The ingestion of the radionuclides from different age groups and cancer risk from the ingestion over a prolong period was estimated. The research will assist in the implementation of drinking water standards for the management of risks and for provision of support from radiological agencies, water suppliers in emergency and non-emergency situations. Palm oil being a cash crop and the plantation a source of revenue to the inhabitants of the selected areas were palm oil is extensively cultivated may have such areas receiving pollution characteristics. Hence, the plantation is a community and the water needs to be assessed for radioactivity concentration levels from sources of NORM or/and TENORM. The study could also be modified for utilization in emergencies and aimed at consciousness on relevant international criteria and standards in the management of water for drinking and domestic use, on the oil palm plantations in the southern states of Nigeria. It is intended for

organizations to set and/or enforce standards. This is in relation to the management of risks from the consumption and use of water at local and international levels. This is beneficial to agencies, regulators on radiation protection measures. It includes the information on radon assessment and the management of risks associated with radon inhalation and ingestion. Routine monitoring of radionuclides is necessary when there is a suspicion of a significant source of radionuclides such as oil spillage and mining activities in the sampling area and high level of NORM in rocks and soils.

### 11.5.0 Conflict of Interest

The authors declare no conflict of interest.

### 11.6.0 Acknowledgment

The authors wish to thank Cape Peninsula University of Technology, Cape Town, South Africa for funding the research and Bowen University Iwo for the Staff Development Fund for Olafisoye Oladunni Bola. We also wish to acknowledge Andrew Rand for providing the Map of Nigeria showing the sampling points.

### 11.7.0 References

Aieta, E.M., Singley, J.E., Trussell, A.R., Kathryn, W., Journal, S., Water, A., Association, W., April, R., Aieta, E.M., Singley, J.E., Trussell, A.R., Thorbjarnarson, K.W. & Mcguire, M.J. 2019. Radionuclides in Drinking Water : An Overview. *American Water works Association*, 79(4): 144–152.

Chen, J., Cooke, M.W. & Mercier, J. 2018. A review of natural radionuclides in canadian drinking water ( 1975 – 16 ). *Radiation Protection Dosimetry*, 179(1): 26–36.

WHO, 2017. Guidelines for drinking water quality 4th edition .Incorporating the first addendum.

El-Gamal, H., Sefelnasr, A. & Salaheldin, G. 2019. Determination of natural radionuclides for water resources on the west bank of the nile river, assiut governorate, Egypt. *Water*, 11(2): 1–13.

Gruca, M., van Andel, T.R. & Balslev, H. 2014. Ritual uses of palms in traditional medicine in sub-Saharan Africa: A review. *Journal of Ethnobiology and Ethnomedicine*, 10(60): 1-24.

IAEA. 2010. Naturally Occurring Radioactive Material. In *Naturally Occuring Radioactive material (NORM VI). Proceedings of an International Symposium, Marrakesh, Morocco. International Atomic Energy Agency*. 22–26.

IAEA. 2013. Naturally Occurring Radioactive Material (NORM VII). *Proceedings of an International Symposium*, (March): 22–26.

Lema, M.W., Ijumba, J.N., Njau, K.N., Ndakidemi, P.A., Arusha, P.O.B.N. & Republic, U. 2014. Environmental contamination by radionuclides and heavy metals through the application of phosphate rocks during farming and mathematical modeling of their impacts to the ecosystem. *International Journal of Engineering Research and General Science*, 2(4): 852–863.

Mohammed, N.K. & Mazunga, M.S. 2013. Natural Radioactivity in Soil and Water from Likuyu Village in the Neighborhood of Mkuju Uranium Deposit. *International Journal of Analytical Chemistry*, 2013: 1–5.

Mukherjee, S. & Mitra, A. 2009. Health Effects of Palm Oil. *Journal of Human Ecology*, 26(3): 197–203.

Olise, F.S., Akinnagbe, D.M. & Olasogba, O.S. 2016. Radionuclides and radon levels in soil and ground water from solid minerals-hosted area ,. *Cogent Environmental Science*, 1(1): 1–12. doi.org/10.1080/23311843.2016.1142344.

Tchokossa, P., Olomo, J.B., & , Osibote, O.A., 1999. Radioactivity in the community water supplies of Ife-Central and Ife-East local government areas of Osun State, Nigeria. Nuclear Instruments and Methods in Physics Research. Section A: Accelerators, Spectrometers, Detectors and Associated Equipments, 422 (1 - 3); 784-789

United Nations Scientific Committee on the Effect of Atomic Radiation. 2015. Developments since the 2013 UNSCEAR report on the level and effects of radiation exposure due to the nuclear accident following the great east-japan earthquake and Tsunami. *New York*.

UNSCEAR. 2000. *2000-Sources and Effects of Ionizing Radiation: Volume I*.

WHO Geneva. 2018. *Management of Radioactivity in Drinking-Water*.

WHO Geneva. 2009. *WHO handbook on indoor Radon, A public health perspective*.

# CHAPTER TWELVE

## 12.1 General discussion

The PhD study focused on trace and essential elements, radionuclides and antioxidants in palm oil sampled from fifteen independent sampling locations in the south west, south east and south south states in Nigeria. The study was aimed to examine the quality of the palm oil that is pressed from the mesocarp of the oil palm fruit. Palm oil differs in chemical and physical composition when compared to the palm kernel oil. The palm kernel oil is oil derived from the kernel of the oil palm fruit. Palm oil is important due to its suitability for various culinary, domestic, and industrial applications. A cure for various ailments, and a raw material for the food and chemical industry (May & Nesaretnam, 2014; Ismail *et al*., 2018; Zwolak *et al.,* 2019).

Various scientists have investigated the accumulation of toxins in vegetables and have deduced and inferred that the safety of food is endangered by the pollution of soil and water. Soil pollution constitutes a serious challenge to human physical health and the environment by damaging plant and human metabolism and making crops hazardous for use (Thompson & Darwish, 2019). Several metals were investigated in the course of the study. The metals include trace, essential and toxic metals. Toxic metals such as Lead, Cadmium, Arsenic, Mercury etc. have the potential to cause damage to the nervous system, kidney, and liver as declared by the Food and Agricultural Organization (FAO) of the United Nations (Hashim *et al.,* 2014; Rai *et al.,* 2019 ). Most of the health hazards associated with humans are linked to the pollution of the soil through soil water especially, Lead, Arsenic, Cadmium, and Mercury. An accumulated concentration of toxic metals is detrimental to the food chain. Metals are accumulated in plants and enter the food chain through absorption by plants. Other exposures to toxicity may be from ingestion and atmospheric deposition.

The study on the analysis of water on the plantation by ICP-OES revealed the water sample had elevated levels of metals from pollution caused by human activities such as the burning of fuels, mining activities, and effluents from industry and fertilizer application on farmland. Plants generally absorb nutrients and toxic metals from soil water. The ICP-OES was a better option to determine trace and toxic elements because it was able to measure the entire spectrum with reliable sensitivity (Tangahu *et al.,* 2011). The results obtained were compared with standards set down by the World Health Organization (WHO Geneva, 1998; Chochorek *et al*., 2010). Toxicity of drinking water and its assimilation in human cells depended on factors such as pH, electrical conductivity, total dissolved solids, which are the physicochemical parameters. The ground water was acidic, an indication of trace/major element contamination. Major elements such as Calcium, Sodium, Magnesium, and Potassium recorded higher concentration. Lead

(Pb) (0.09-10.3 mg/L) had the highest concentration for all elements and Cadmium (0.12-0.39 mg/L) the least on all the plantations under study. The result of the study was extensively explained in the chapter Four of the thesis alongside instrumentation and method development. The published paper is entitled “Determination of trace and major elements in water on oil palm plantations by Inductively Coupled Plasma Optical Emission Spectrometry”. The section expatiates on the benefits, toxicity, and deficiencies of the intake of the elements through water. At elevated concentrations, essential metals become toxic. The method developed for the analysis was relatively cheap and it was able to measure a wide range of spectrum of metals. Generally, elevated concentration of metals was found in the water. The results of the analysis confirmed that the source of point and non-point pollution was from anthropogenic sources. A list of the various elements detected in the oil palm plantation were Aluminium, Chromium, Copper, Zinc, Cobalt, Iron, Selenium, Tin, and Lead and macro elements such as Potassium, Calcium, Sodium and Magnesium (Satarug *et al.,* 2010; Alfrey, 1984; Kowalczyk *et al*., 1986; Klotz *et al*., 2017; Rahimzadeh *et al*., 2017). The application of Lead (Pb) metal is numerous in industry. It is not an essential element with health importance to neither plants nor animals. The permissible limit for Pb in vegetable oils is 0.01 mg/L and most of the palm oil samples analysed recorded elevated levels above this limit. An exception was Ubiaja plantation that recorded 0.006 mg/L. Pb is a soluble metallic element in soil solution. Concentration of Pb in the environment is usually from anthropogenic sources such as the exhaust pipes of vehicles or machines being ran on leaded petrol and electronic waste such as leaded batteries (Adedeji *et a*l., 2013). Bitumen deposits, lead acid battery factories, and glass-making industries in and around the vicinity of the plantation may contribute to particulate Pb, which may get into the oil during processing. Generally, all the machineries used for processing were run on leaded petrol/diesel and could be a contributory factor of high lead concentrations on the plantations. Similar studies on soils sampled on the oil plantations have shown that Pb is a potentially mobile element and soluble in soil water and under acidic conditions of the soil, it becomes mobile and can bio-accumulate in the palm fruit (Anju & Banerjee, 2011). The concentrations of the elements were generally elevated in water sampled on the plantation when the values obtained were compared with permissible levels set down by regulatory bodies.The pH of the water sampled, generally acidic facilitated the dissolution and uptake of the metals by plant roots (WHO, Genewa 1998; Hout, 2012; Hashim *et al*., 2014).

This section of the thesis expatiates on the bioavailability, uptake, and toxicity of metals in soils. Total metal concentrations and sequential metal analysis were performed on soils on the oil palm plantations. The uptake and mobility of metals in soils depends on properties and soil factors, which include but are not limited to pH soil organic matter, pore size of the soil etc.

(Sharma & Kamalpreet, 2017). There was a decrease in the bioavailability and accessibility of metals with increasing pH. Low pH values have also been associated with a reduction on particle soil size and organic matter. The pH of the soil ranged between four and six. Acidic soil pHs favours the bioavailability and uptake of metals to plants due to a higher degree of mobility. This is hazardous to humans and the food chain due to the fact the crops bio accumulates toxic metals in their edible parts especially their fruits. This is not beneficial in the agricultural point of view since plants accumulate toxic metals especially in their consumable parts (Zhu *et al.,* 2012). An elevation in the uptake of highly mobile metals such as Zn, Cr and Fe due to the occurrence of soil organic matter and several soil factors have the potential of contributing to the bioaccumulation and accessibility of the toxic metals in edible plant parts. (Zhu *et al*., 2012). Chemical extraction procedures were used for the sequential extraction and based on the assumption that a relationship exists between the bioavailable fractions in the soil and the soil properties. The soil pH obtained in the study ranged from 4.96 to 7.01. Toxicity and accessibility of metals for plant uptake is favoured by a decrease in pH due to precipitations of hydroxides ions, carbonyls and/formation of insoluble complexes of organic compounds. Heavy metals are more mobile at pH less than 7 than greater. Soil pH is a useful indication of toxic elements in soil and plants have difficulty in absorbing some elements such as Cu, Zn, Mg, and Fe in basic soils (Bucher *et al*., 1999; Weinberg, 2009; Catalani *et al*., 2011; Mohan & Kasprowicz, 2016). The values of the pH from the study areas indicated the tendency of the availability of the heavy metals and high metal uptake by plants. The soil pH serves as a useful hint to the presence of nutrients and the potency of toxic substances present in soils sampled from the plantations. Electrical conductivity is a measure of the salinity of the soil. The results for the electrical conductivity in the study ranged from 22 to 229 $Scm^{-1}$. A measure of the electrical conductivity is important as it influences major key processes in the mobility and uptake of metals and nutrients by plant root hairs (Anju & Banerjee, 2011). The values of the soil electrical conductivity and the pH obtained in the Ph.D. research study could be due to the content of available soluble salts. Electrical conductivity has been correlated to the concentration of elements in soils. High values of soil organic content could be attributed to arable and cultivated soils, the presence of vegetation cover and decomposition of organic matter. Low organic matter content in soils indicates low electrical conductivity. Interactions among these factors appear to be an unavoidable influence in the allotment of the metals among the different plantation sites. The heavy metal distribution in the sample under study was used to assess their mobility and bioavailability. The mean and standard deviation results got from each extraction and residual step by applying the BCR sequential extraction procedure were expatiated for soils. Maximum limits for concentrations of metals in soils are usually based on the concentrations of their total amount. It is the bioavailable metal fractions

that gives scientist the environmental concern (Ono *et a*l., 2016). These factors are also insufficient since they are related to the soils physicochemical characteristics and the forms in which the metals exist. The presence of heavy metals in soils was identified through speciation studies on all sampling locations. Furthermore, this may cause uptake of heavy metals by the trees on the plantations that can cause serious environmental problems due to bioaccumulation and bioaccumulation in the food chain and consequently affect human and animal health. The research work shows the application of sequential extraction procedures for the process of controlling and influencing the speciation of heavy metals in soils (Agbenin & Welp, 2012). It provides details on the hazardous effects of these metals as the mobility and eco toxicity depends on their chemical forms, and they tend to be easily mobilized and dispersed. The uptake and toxicity of metals in soils acknowledges the fraction that is phyto-available to them. The heavily soluble fractions that are generally the exchangeable and the fractions bound to organic matter are generally considered phytoavailable. The accurate evaluation of the concentration of the phytoavailability of heavy metals in soils is becoming a useful tool for risk assessment and remediation studies. The study acknowledges the fact that total metal concentration may not be a very important tool for predicting metal phyto-availability on the plantations (Olaniran *et al.,* 2013). The average concentration of metals in soils and the sequence of their distribution have been discussed extensively in Chapter Five of the thesis. This is in addition to the toxicity, speciation, and mobility of the metals and the conditions that favour plant uptake and bioaccumulation. Metal levels were elevated in soil samples and hence translocated to the palm oil (Weinberg, 2009; Catalani *et` al*., 2011). The outcome of the PhD study revealed that the elements concentration in the soils in a study on the oil palm plantation were a bit lower than those in the palm oil samples when compared with soil samples due to bioaccumulation and bio magnifications in the tissues of the plant. The mean concentrations of metals in palm oil in this study were highest in Zinc (162.1 mg/L; Benin City) and Chromium (99.8 mg/L; Ubiaja) respectively. The average value of metals in palm oil in this study was lowest in Manganese and Copper and these were sampled from Agbarho and Nsukka plantations respectively. The sequence of metals in palm oil and soil were Cd>Fe>Co>Ni>Zn>Cr>Mn >Cu and Zn>Cr>Cu>Ni>Fe>Mn>Co >Cd respectively. Nearly all the concentrations of the metals exceeded the permissible limits in palm oil and soils analysed from the plantations. Palm oil samples analysed did not reveal elevated levels of Manganese (Mn). The concentrations of Mn in all the oil samples under investigation were below the World Health Organization (WHO) permissible limits of Mn in vegetable oil (WHO Geneva, 1998). The bioaccumulation of Mn in this study may not pose danger to plants and humans. The soils analysed on the plantations were acidic, an indication of elevated concentrations of the metals in the oil samples (Hepworth & Mark Heron, 1997; Badiye *et al*., 2013; Green *et al.,* 2017;

Lopez, 2019). This prompted an increase in mobilization and uptake of the metals in the palm oil. The influence of morphology and physiology of plants as an important factor in mobility, bioaccumulation, and elimination of metals in soils indicated the possible transfer of these metals from soil water to the palm oil. Soil factors affect the available ions for plant uptake of heavy metals in soils. Cadmium (Cd) is the most assessable metal to pollutants because it is the most mobilized metal in soil solution. The concentration Cd on the oil palm plantation can also be traced to the accessibility of the metals by the plants from soil water. Previous studies of the soil from water on an oil palm plantations recorded high concentrations of Cd due to electronic waste dump leachate in soil water from the plantations (Zhou *et a*l., 2016). Such oil sampled from the plantation may be rather suitable for industrial use rather than consumption because Cd is known as a human/animal carcinogen. The mobility of Cadmium is high hence, released into soil solution and this makes it toxic and easily accumulated in the oil palm fruit (Pelikan & Černy, 1970; Kimbrough, 1976; Tinggi, 2008; Olmedo *et al.,* 2013; Kieliszek & Błazejak, 2016). Cobalt being a mobile metal is fairly mobilised in the soil. Cobalt concentration in soil will be available to plants and may bio-accumulate in the fruits. In addition, effluents from industries may be a source of increased cobalt concentration. All the oil plantations investigated revealed elevated concentrations in the palm oil. Speciation studies on soil on the oil palm plantations revealed that Copper (Cu) exists in the immobile fraction of the soil that is insoluble in soil solution and poorly oxidised or reduced (Fytianos *et al.,* 2001). Toxicity of Cu had revealed that elevated levels of Cu are toxic and causes bioaccumulation and bio-magnifications in fruits. Anthropogenic pollution from Iron usually outweighs the natural forms in which Iron (Fe) exists as Fe is also a semi mobile metal. It is an essential metal and a component of the enzyme haemoglobin. Crude oil drilling and processing near Abak plantation may be responsible for the elevated concentration of Fe in the palm oil sampled from the plantation. Zinc (Zn) and Nickel (Ni) are immobile metals and their concentrations in the oil samples under investigation were relatively high in the palm oil samples under study (White & Brown, 2010). (Soetan *et a*l., 2010). (Vargas *et al*., 2018). Under favourable conditions, these metals may be released from their residual crystalline and immobile phases into soil solutions for absorption by plants. Researchers as essential metals with antioxidant values have appraised Zinc and Nickel and acting as a defence mechanism against infection but toxic when concentrations are elevated. Plants take in metals via the soil solution and ideally, this reflects the level of environmental pollution of the area (Zheng *et al.,* 2016). It is erroneous to base environmental quality of an area on the concentration of metals in samples. Importance must be stressed on the bioavailability, mobility and the factors that affect the accessibility of the metals in soil water and translocation to the edible parts of the plant. Environmental pollution arising from metals could also be from discarded utensils on dumpsites and in landfills. The

leachate from such sites seeps into soil water causing environmental pollution. Non-essential metals have no biological importance to life. Nervous system disorder and Alzheimer diseases are few signs of such toxicity. In addition, toxicity is seen in symptoms such as intestinal and urinary tract infections. Metals have the ability to be translocated from soil to various parts of the plants. Invariably researchers have studied the oil palm tree extensively as an effective crop in remediation technology. It is a cheap choice to phytoremediation because it is low in maintenance and eco-friendly (Jiang *et al*., 2013).

Soils are cleaned up as the oil palm tree translocated metals from soils to parts of the plant such as fruits and stems. This provides interesting tools to sites contaminated by toxic metals on the oil palm tree with emphases on the fruits. Toxic metals are transported to humans and the food chain through the consumption of food crops on contaminated sites. This is especially hazardous and a critical health risk issue when the metals exceed the permissible levels in palm oil. The food chain as a pathway of toxic metals is vital in risk assessment in developing countries like Nigeria since ingestion of palm oil remains deregulated (Jia *et al.,* 2018). Palm oil is a stable ingredient for the preparation of most dishes in Nigeria and consumed regularly by the population at large. The intake of metals does not equate the concentrations absorbed by humans as implied by some reported research work. A part of the absorbed dose is usually eliminated through various biochemical processes. The remainder portion becomes bio accumulated and biomagnified in humans. The results for the analysis of metallic elements in virgin palm oil in the PhD study results revealed detectable levels of the metallic elements as most of them exceeded the WHO permissible limits for metallic elements in vegetable oils.

Accumulation Factors (AF) in the palm oil can best be used to describe the degree in which the palm oil accumulates in the biological system. The value of AF in this study was between 324.20-0.78 and was greatest for Cd (324.20) in Okitipupa and Ni (141.3) in Igede-Ekiti plantations respectively. The AF value of 0.78 was obtained in Apoje oil palm plantation, which was the least AF value, investigated. The sequence of accumulation was described using the bioaccumulation factor as Cr<Cu< Ni<Zn<Fe<Cr<Mn <Co<Cd with Cd being the greatest bio accumulator in the palm oil. The AF values for Cd, Co, Fe and Mn was greater than unity in most of the palm oil sampled from the plantations (Tangahu *et al*., 2011 ; Zhou *et al*., 2016). This is an indication of bioaccumulation in the edible part of the oil palm tree, the fruit. AF factors lesser than one and very close to unity were recorded for Nickel, Chromium, Zinc, and Copper. Lower AF values show low transfer of metallic elements and a lower risk of contamination. Risk assessment can be reported by calculating the Metals Daily Intake (DIM) and Health Risk Index (HRI) values. This is particularly risky and hazardous to the food chain. Risk assessment is of paramount significance in developing countries like Nigeria where the

disposal of waste on agricultural lands is largely unregulated (Fytianos *et al.,* 2001). Although several pathways of exposure such as the air, water, and soil may contribute to contamination, food is significantly a higher route of exposure. The consumption of palm oil as the stable ingredient in most foods is the pathway to the ingestion of metals in the study. The index that describes the average consumption of the palm oil is the DIM and HRI value. The DIM values of the contaminated palm oil were highest for Zn and the sequence of intake was Zn>Cd>Cr>Cu>Co>Mn>Ni >Fe. The DIM and HRI values were close to unity and greater than unity in most of the plantations indicating a high risk to the food chain. The RfD was earlier defined as a tool quantitatively used in risk assessment to evaluate the ingestion of a non-carcinogenic contaminant per milligram per kilogram per day (Zheng *et al.,* 2016). The RfD values obtained for the metals Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn in the study were $1.02E^{-3}$, $2.50E^{-3}$, $1.40E^{-2}$, $1.5E^{0}$, $2.0E^{-2}$, $1.4E^{-2}$, $2.0E^{-2}$ and $1.33E^{0}$ respectively. The present study revealed that the metals Cd, Co, Cr and Fe had HRI values above unity and very close to unity on all the plantations analysed. Much lower values of HRI were found in metals such as Cu, Mn, and Zn. HRI values above unity signifies an indication of future toxicity to humans via the food chain (Inengite *et al*., 2015). Elevated concentrations of THQ values were observed. THQ is essential for the assessment of toxic metals in food crops. In the present study, it was observed that THQ values were high and this poses a risk to the food chain. Although biochemical and redox processes are available for the reduction of toxic metals in biological systems, such processes emphasize that ingested metals from food is not only absorbed into tissues as the skin and kidneys may excrete some toxins in sweat and urine (Inengite *et al*., 2015 ; Taghvaei & Jafari, 2015)

Local farmers, prior to use store palm oil for longer shelf life. To preserve the freshness and aesthetics of the palm oil, preservatives in the form of synthetic phenolic antioxidants may be added to prolong the shelf life of the palm oil (Taghvaei & Jafari, 2015). An aspect of this study determined fifteen different virgin palm oil samples from independent palm oil plantations in the south west, south east and south south states of Nigeria. The samples were analysed for BHA, BHT, EEMC, and PG contents. The real samples were analysed in triplicates. The retention factors and response of the peaks presented in all the samples were compared against that of the standards for BHA, BHT, EEMC, and PG. The peaks of the real samples could not be assigned tentatively. This was no agreement with the peak of the samples and standards since all the antioxidants under studies were not detected in the analysis of the real samples (Perrin & Meyer, 2003; Goulart *et al*., 2014). Hence, there was no close match between the chromatograms of the real samples and standards. Hitherto quantitative analysis of the real sample peaks was integrated and identified for determination of sample

concentrations. The response of the samples containing the unknown concentration was also matched against that of the response of standards to determine the amount of antioxidants present. This was closely observed to avoid peak mis-assignment due to peak size and shape effects. The analysis was performed under a reverse phase condition to increase the confidence of the results. None of the antioxidants under study was detected in any of the real samples under study (Perrin & Meyer, 2003; Seneviratne *et al.,* 2016).

Radionuclides also present itself as contaminants in the palm oil and hence needed to be studied. There is the likely transport and accumulation of such Naturally Occurring Radioactive Materials being accumulated from the soil water to the fruit of the palm tree. An aspect of the Ph.D. study focused on radionuclides as a contaminant in the soil, water and palm oil and the need to access the hazards posed by the utilization of the product, which is palm oil. Hence, levels of radioactivity were determined in soils, water, and palm oil from selected plantations. Naturally occurring radionuclide activity was investigated on soils from oil palm plantations using a Hyper-Pure Germanium detector with appropriate shielding coupled to a Canberra Multichannel Analyzer. The radioactivity concentrations of $^{238}U$, $^{232}Th$ and $^{40}K$ were obtained from averaging out the radioactivity concentrations of their respective progenies. With the assumption of secular equilibrium being attained, the dose rate in air 1m above ground and the effective annual dose rates were determined. Activity concentrations of the radionuclides $^{238}U$, $^{232}Th$ and $^{40}K$ were obtained from the activity concentrations of their respective daughter radionuclides. The activity concentrations of $^{40}K$ from soil depth of (0 – 15 cm) ranged from 187.4 – 514.4 Bq/kg. The activity concentrations of $^{238}U$ from soil depth of (0 – 15) cm ranged from 2.328 - 6.571 Bq/kg. The activity concentrations of $^{232}Th$ from soil depth of (0 - 15 cm) ranged from 1.509 - 6.121 Bq/kg. This was based on the analysis of the soil within the range of 0 -15 cm. For the risk assessments, the Absorbed Dose Rate (D) ranged from 11.5 to 24.54 nGy/h, while the Annual Effective Dose Equivalent (E) ranged from $1.4 \times 10^{-2}$ to $2.98 \times 10^{-2}$ mSv/y and the Radium Equivalent (Raeq) ranged between 21.72 to 49.14 Bq/kg in soils of depth 0-15 cm. Values were lesser than worldwide average values of 370 $Bqkg^{-1}$ recommended for radium equivalent by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). The calculated values for external hazard index range from 0.032 – 0.133 on soils (0-15 cm) in Okitipupa and Umuabi plantations. The Values for Internal Hazard index and representative index were 0.043-0.153 (0-15 cm; Okitipupa/Iresa-apa) and 0.081-1.345 (0-15 cm; Okitipupa/Badagry) repectively. Most of the values of hazard and gamma index in the soil samples obtained in the study were below the critical value of unity and this is below the reccommended safe limit of 1 mSv/y [14-16]. None of the samples exceeded the permissible levels of 370 $Bqkg^{-1}$ recommended by the United Nations Scientific

Committee on the Effects of Atomic Radiation (UNSCEAR) for the Radium Equivalent. In addition, the calculated values of hazards in terms of Internal and External hazard indices and Representative hazard index were determined and found to be within safe limits.

Palm oil is a useful vegetable fat for the oil and chemical industry and Nigeria is a third world producer of such oil. Hence, the oil palm plantation is an economic cash crop in such a region. Nigerian soils may be contaminated with radionuclides from natural and anthropogenic means. This motivated an aspect of the study to be conducted on palm oil sampled from fifteen regions on oil palm plantations in the south western, south eastern and south southern states of Nigeria. Pressed oil palm samples were selected from these regions using grab sampling methods and the pressed palm fruit oils analysed for their radioactivity concentrations using gamma ray spectrometry and the Hyper pure germanium detector. Radioactivity and risk assessment indices were determined in the oils. The activity concentrations in the palm oil for $^{40}K$, $^{238}U$ and $^{232}Th$ ranged from 122.3-968.0, 1.240-6.651 and 1.199-8.061 $BqL^{-1}$ respectively. The risk assessment indices for Radium equivalent activities (Ra (eq), Gamma absorbed dose rate (D) and Annual Effective Dose Rate (E) was highest in sampling point L1 (Abak) due to a high transfer of radionuclides from crude oil spills from a crude oil drilling area of the region. Translocation factor (Tf) in the all pressed palm oil was greater than unity/very close to unity.

The section of this study assessed the annual effective dose and cancer risk in water polluted with Naturally Occurring Radioactive Materials (NORM) sampled from fifteen independent sampling locations in the southeast, southwest, and south south regions of Nigeria where palm oil is extensively cultivated. The ground water in the community is used as a source of drinking water and for domestic use in the community. The activity concentration of $^{40}K$, $^{238}U$ and $^{232}Th$ were discussed and the annual effective dose for different age groups and cancer risk was estimated in the ground water samples. Activity concentration of $^{40}K$ (Bq/L) were least in Okitipupa plantation (171.7 ± 0.01 Bq/L) and the highest activity was recorded in Ago-Emokpae plantation (468.9 ± 0.01 Bq/L) respectively. The activity concentrations of $^{238}U$ (Bq/L) ranged between 1.611 ± 0.01 Bq/L – 5.750 ± 0.01 Bq/L and the concentrations were least in Ikire plantations and highest in Ago-Emokpae plantations respectively. Activity concentrations values (Bq/L) for $^{232}Th$ in the ground water was highest in Ikire plantation (9.619 ± 0.26 Bq/L) and lowest in Apoje plantation (1.554 ± 0.62 Bq/L) respectively. The values for the Annual Effective Dose Estimation (E) ($mSvy^{-1}$) for $^{40}K$, $^{238}U$ and $^{232}Th$ reveal that E for $^{40}K$ was highest in infants, children, and adults in this order; $3.51 \times 10^{-4}$, $8.21 \times 10^{-4}$, and $11.72 \times 10^{-4}$ at W4 plantation respectively. Lowest values of E ($mSvy^{-1}$) were recorded in the same order at W12 plantation respectively as $1.29 \times 10^{-4}$, $3.01 \times 10^{-4}$, and $4.29 \times 10^{-4}$). E values ($mSvy^{-1}$) for $^{232}Th$ were negligible at W1 and W12 plantations. Highest and lowest values were recorded as 6.49

$\times 10^{-4}$ (W9); $9.76 \times 10^{-4}$ (W9) and $9.17 \times 10^{-4}$ (W2) for infants, children, and adults respectively. Lowest values of $^{232}$Th EDW values ($mSvy^{-1}$) in the sampled ground water were recorded ($1.12 \times 10^{-4}$, $1.68 \times 10^{-4}$, and $1.12 \times 10^{-4}$) for infants, children, and adults in W5 and W9 plantations respectively. The radionuclide $^{238}$U recorded E values ($mSvy^{-1}$) in the range of $0.77 \times 10^{-4}$ $mSvy^{-1}$ – $11.06 \times 10^{-4}$ $mSvy^{-1}$, $1.04 \times 10^{-4}$ $mSvy^{-1}$ – $16.10 \times 10^{-4}$ $mSvy^{-1}$ and $2.25 \times 10^{-4}$ $mSvy^{-1}$ – $8.05 \times 10^{-4}$ $mSvy^{-1}$ for infants, children, and adults respectively. The values were generally low for infants. Radionuclide $^{232}$Th was not detected in Abak and Nsukka plantations. The calculation of cancer risks based on the radium isotopes ranges from $5.91 \times 10^{-4}$ to $21.10 \times 10^{-4}$ for $^{226}$Ra. For $^{228}$Ra, the values were from $5.87 \times 10^{-4}$ to $1.64 \times 10^{-4}$. Mean estimations were calculated as $26.25 \times 10^{-4}$ and $3.891 \times 10^{-4}$ for $^{226}$Ra and $^{228}$Ra respectively. The estimation of the assessed annual effective dose for all the individual populations were below the recommended reference value of 0.1 mSv resulting from a year intake of drinking water in accordance with the WHO, IAEA and UNSCEAR regulated guideline values (UNSCEAR, 2000; IAEA, 2013; WHO Geneva, 2018). The mean values for values $^{226}$Ra and $^{228}$Ra obtained in this study for both isotopes were $3.891 \times 10^{-4}$ and $26.25 \times 10^{-3}$ for $^{226}$Ra and $^{228}$Ra respectively. The mean estimation of the radiological cancer risk for radium isotope for both $^{226}$Ra and $^{228}$Ra in this study is acceptable within the guideline limits of $1 \times 10^{-4}$ to $1 \times 10^{-6}$. The values are within the acceptable incidence cancer risks of the recommended guidelines for drinking water quality and reference levels for radionuclides in drinking water.

Based on the results, with respect to the radium equivalent, internal and external hazard indices, as well as the representative level index, there is no evidence of any threat of a health hazard from the soil on all palm plantations studied concerning gamma radiation. All the naturally occurring radionuclides were detected in all samples of the soil and palm oil on the oil palm plantation but below permissible limits. Nevertheless, the activity concentrations did not exceed the recommended guidance levels for the ingestion of radionuclides in food. The concentration of $^{40}$K was found to be relatively higher in palm oil in comparison to other concentrations of NORM due to transfer from soils and high transfer ratio. Potassium is found readily in soils especially due to preplanting and post planting operations and the use of pesticides and phosphate fertilizer. In addition, soil characteristics may favor its mobilization and translocation into plant tissues of a micronutrient. However, radioactive potassium, $^{40}$K is radioactive hence, its concentration must be monitored closely as it transports and translocate to fruits through roots/shoot uptake (Bian et al., 2018; Ji et al., 2019).

The result of the annual effective dose and cancer risk estimation in the present study proves that the NORM in the ground water samples from all the plantations under study do not pose any significant health risk to the public. The research provides a foundation and procedure for

the establishment of national regulatory standards and risk assessment information for safety in the use of water on the oil palm plantations especially in non-emergencies. The results of the study revealed that the dose received by children by drinking the ground water sampled on the plantation was higher than infants and adults. Adults also received higher dose compared to infants. Children are more sensitive to exposure from some radionuclides as reflected in different dose coefficients, although they typically consume smaller quantities of drinking water when compared to adults. The result of the study could also be modified for utilization in emergencies. It is aimed at consciusness on relevant international criteria and standards in the management of water for drinking and domestic use on the oil palm plantations in the southern states of Nigeria and for organizations to set and/or enforce standards.

## 12.2 References


Abdu, N. & Yusuf, A.A. 2013. Human health risk characterization of lead pollution in contaminated farmlands of Abare village, Zamfara State, Nigeria. *African Journal of Environmental Science and Technology*, 7(9): 911-916–916.

Adedeji, O.H., Olayinka, O.O. & Oyebanji, F.F. 2013. Assessment of traffic related heavy metals pollution of roadside soils in emerging urban centres in Ijebu-North area of Ogun State, Nigeria. *Journal of Applied Sciences and Environmental Management*, 17(4): 509–514.

Agbenin, J.O. & Welp, G. 2012. Bioavailability of copper, cadmium, zinc, and lead in tropical savanna soils assessed by diffusive gradient in thin films (DGT) and ion exchange resin membranes. *Environmental Monitoring and Assessment*, 184(4): 2275–2284.

Alfrey, A.C. 1984. Aluminum toxicity. *Bulletin of the New York Academy of Medicine: Journal of Urban Health*, 60(2): 210–212.

Anju, M. & Banerjee, D.K. 2011. Associations of cadmium, zinc, and lead in soils from a lead and zinc mining area as studied by single and sequential extractions. *Environmental Monitoring and Assessment*, 176(1–4): 67–85.

Badiye, A., Kapoor, N. & Khajuria, H. 2013. Copper Toxicity: A Comprehensive Study. *Research Journal of Recent Sciences*, 2: 58–67.

Bian, H., Wang, Y., Chen, W., Zhang, Y., Zhuang, Z., Xia, R., Dai, H., Feng, J., Pu, W., Chen, L., Cai, W., Hu, W. & Liu, Y. 2018. Multiple Organ Lesions in a Case of Contamination With Multiple Radionuclides After 38 Years. Dose-Response, 16(4): 1–7.

Bucher, J.R., Hailey, J.R., Roycroft, J.R., Haseman, J.K., Sills, R.C., Grumbein, S.L., Mellick,

P.W. & Chou, B.J. 1999. Inhalation toxicity and carcinogenicity studies of cobalt sulfate. *Toxicological Sciences*, 49(1): 56–67.

Catalani, S., Leone, R., Rizzetti, M.C., Padovani, A. & Apostoli, P. 2011. The Role of Albumin in Human Toxicology of Cobalt: Contribution from a Clinical Case. *ISRN Hematology*, 2011: 1–6.

Chochorek, A., Bobrowski, A., Kiralyova, Z. & Mocak, J. 2010. ICP-OES determination of select metals in surface water - A metrological study. *Polish Journal of Environmental Studies*, 19(1): 59–64.

Fytianos, K., Katsianis, G., Triantafyllou, P. & Zachariadis, G. 2001. Accumulation of Heavy Metals in Vegetables Grown in an Industrial Area in Relation to Soil Environmental Contamination and Toxicology 423. *Environ. Contam. Toxicol*, 67(3): 423–430.

Goulart, L.A., Teixeira, A.R.L., Ramalho, D.A., Terezo, A.J. & Castilho, M. 2014. Development of an analytical method for the determination of tert-butylhydroquinone in soybean biodiesel. *Fuel*, 115: 126–131. doi.org/10.1016

Green, B., Griffiths, E. & Almond, S. 2017. Neuropsychiatric symptoms following metal-on-metal implant failure with cobalt and chromium toxicity. *BMC Psychiatry*, 17(1): 1–5..doi.org/10.1186.

Hashim, R., Song, T.H., Muslim, N.Z.M. & Yen, T.P. 2014. Determination of heavy metal levels in fishes from the lower reach of the kelantan river, Kelantan, Malaysia. *Tropical Life Sciences Research*, 25(2): 21–39.

Hepworth, J.D. & Mark Heron, B. 1997. Chapter 6.4 Six-membered ring systems: With O and/or S atoms. *Progress in Heterocyclic Chemistry*, 9(C): 289–317.

Hout, J.J. 2012. Lead in drinking water. *Journal of Environmental Health*, 75(1): 56.

IAEA. 2013. Naturally Occurring Radioactive Material (NORM VII). Proceedings of an International Symposium, (March): 22–26.

Inengite, A., Abasi, C. & Walter, C. 2015. Application of Pollution Indices for the Assessment of Heavy Metal Pollution in Flood Impacted Soil. *International Research Journal of Pure and Applied Chemistry*, 8(3): 175–189.

Ismail, S.R., Maarof, S.K., Ali, S.S. & Ali, A. 2018. Systematic review of palm oil consumption and the risk of cardiovascular disease. *PLoS ONE*, 13(2): 1–16.

Ji, K., Wang, Y., Du, L., Xu, C., Liu, Y., He, N., Wang, J. & Liu, Q. 2019. Research Progress

on the Biological Effects of Low-Dose Radiation in China. Dose-Response, 17(1): 1–16.

Jia, Z., Li, S. & Wang, L. 2018. Assessment of soil heavy metals for eco-environment and human health in a rapidly urbanization area of the upper Yangtze Basin. *Scientific Reports*, 8(1): 1–14.

Jiang, M., Zeng, G., Zhang, C., Ma, X., Chen, M., Zhang, J., Lu, L., Yu, Q., Hu, L. & Liu, L. 2013. Assessment of Heavy Metal Contamination in the Surrounding Soils and Surface Sediments in Xiawangang River, Qingshuitang District. *PLoS ONE*, 8(8).

Kieliszek, M. & Błazejak, S. 2016. Current knowledge on the importance of selenium in food for living organisms: A review. *Molecules*, 21(5): 16 pp.

Kimbrough, R.D. 1976. Toxicity and health effects of selected organotin compounds: A review. *Environmental Health Perspectives*, vol.14(April): 51–56.

Klotz, K., Weistenhöfer, W., Neff, F., Hartwig, A., Van Thriel, C. & Drexler, H. 2017. The health effects of aluminum exposure. *Deutsches Arzteblatt International*, 114(39): 653–659.

Kowalczyk, D.F., Gunson, D.E., Shoop, C.R. & Ramberg, C.F. 1986. The effects of natural exposure to high levels of zinc and cadmium in the immature pony as a function of age. *Environmental Research*, 40(2): 285–300.

Lopez, J.S., Lee, L. & Mackey, K.R.M. 2019. The toxicity of copper to Crocosphaera watsonii and other marine phytoplankton: A systematic review. *Frontiers in Marine Science*, 6(JAN): 1–13.

Manigandan, P.K. & Chandar Shekar, B. 2014. Evaluation of radionuclides in the terrestrial environment of Western Ghats. *Journal of Radiation Research and Applied Sciences*, 7(3): 310–316.doi.org/10.1016.

May, C.Y. & Nesaretnam, K. 2014. Research advancements in palm oil nutrition. *European Journal of Lipid Science and Technology*, 116(10): 1301–1315.

Mohan, N. & Kasprowicz, E. 2016. Identification and Management of Cobalt Toxicity: A Case Report of Rapidly Progressing Toxicity after Hip Arthroplasty Revision. *The Medicine Forum*, 17(1): 17–20.

Olaniran, A.O., Balgobind, A. & Pillay, B. 2013. Bioavailability of heavy metals in soil: Impact on microbial biodegradation of organic compounds and possible improvement strategies. *International Journal of Molecular Sciences*, 14(5): 10197–10228.

Olmedo, P., Pla, A., Hernández, A.F., Barbier, F., Ayouni, L. & Gil, F. 2013. Determination of

toxic elements (mercury, cadmium, lead, tin and arsenic) in fish and shellfish samples. Risk assessment for the consumers. *Environment International*, 59: 63–72.doi.org/10.1016.

Ono, F.B., Penido, E.S., Tappero, R., Sparks, D. & Guilherme, L.R.G. 2016. Bioaccessibility of Cd and Pb in tailings from a zinc smelting in Brazil: implications for human health. *Environmental Geochemistry and Health*, 38(5): 1083–1096.

Pelikan, Z. & Černy, E. 1970. Toxic effects of some 'mono-n-butyl-tin compounds' on white mice. *Archiv für Toxikologie*, 27(1): 79–84.

Perrin, C. & Meyer, L. 2003. Simultaneous determination of ascorbyl palmitate and nine phenolic antioxidants in vegetable oils and edible fats by HPLC. *JAOCS, Journal of the American Oil Chemists' Society*, 80(2): 115–118.

Rahimzadeh, M.R., Rahimzadeh, M.R., Kazemi, S. & Moghadamnia, A.A. 2017. Cadmium toxicity and treatment: An update. *Caspian Journal of Internal Medicine*, 8(3): 135–145.

Rai, P.K., Lee, S.S., Zhang, M., Tsang, Y.F. & Kim, K.H. 2019. Heavy metals in food crops: Health risks, fate, mechanisms, and management. *Environment International*, 125(February): 365–385.

Satarug, S., Garrett, S.H., Sens, M.A. & Sens, D.A. 2010. Cadmium, environmental exposure, and health outcomes. *Environmental Health Perspectives*, 118(2): 182–190.

Seneviratne, K.N., Prasadani, W.C. & Jayawardena, B. 2016. Phenolic extracts of coconut oil cake: A potential alternative for synthetic antioxidants. *Food Science and Technology*, 36(4): 591–597.

Soetan, K.O., Olaiya, C.O. & Oyewole, O.E. 2010. The importance of mineral elements for humans, domestic animals and plants - A review. *African Journal of Food Science*, 4(5): 200–222.

Taghvaei, M. & Jafari, S.M. 2015. Application and stability of natural antioxidants in edible oils in order to substitute synthetic additives. *Journal of Food Science and Technology*, 52(3): 1272–1282.

Tangahu, B.V., Sheikh Abdullah, S.R., Basri, H., Idris, M., Anuar, N. & Mukhlisin, M. 2011. A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. *International Journal of Chemical Engineering*, 2011(2011): 31 pp.

Thompson, L.A. & Darwish, W.S. 2019. Environmental Chemical Contaminants in Food: Review of a Global Problem. *Journal of Toxicology*, 2019: 14 pp.

Tinggi, U. 2008. Selenium: Its role as antioxidant in human health. *Environmental Health and Preventive Medicine*, 13(2): 102–108.

UNSCEAR. 2000. *2000-Sources and Effects of Ionizing Radiation: Volume I*.

Vaiserman, A., Koliada, A., Zabuga, O. & Socol, Y. 2018. Health Impacts of Low-Dose Ionizing Radiation: Current Scientific Debates and Regulatory Issues. *Dose-Response*, 16(3): 1–27.

Vargas, R.L. de, Schuch, L.O.B., Barros, W.S., Rigo, G.A., Szareski, V.J., Carvalho, I.R., Pimentel, J.R., Troyjack, C., Jaques, L.B.A., Souza, V.Q. de, Rosa, T.C. da, Aumonde, T.Z. & Pedó, T. 2018. Macronutrients and Micronutrients Variability in Soybean Seeds. *Journal of Agricultural Science*, 10(4): 209.

Weinberg, E.D. 2009. Iron toxicity New conditions continue to emerge. *Oxidative Medicine and Cellular Longevity*, 2(2): 107–109.

White, P.J. & Brown, P.H. 2010. Plant nutrition for sustainable development and global health. *Annals of Botany*, 105(7): 1073–1080.

WHO Geneva. 2018. Management of Radioactivity in Drinking-Water

WHO Genewa 1998. Guidelines for Drinking-Water Quality-Second Edition - Volume 2 - Health Criteria and Other Supporting Information - Addendum. *Health Criteria and Other Supporting Information*, 2(1930128): 1–283.

Y Sharma, K. Kamalpreet, K.V. 2017. Analysis of pH and Electrical Conductivity of White Ash Discharge from Textile Analysis of pH and Electrical Conductivity of White Ash Discharge from Textile Industries in Barnala Region (Punjab, India): Deteriorating to Human Health. *Journal of Chemistry and Chemical Sciences*, 7(2): 72–80.

Zheng, X., Xu, X., Yekeen, T.A., Zhang, Y., Chen, A., Kim, S.S., Dietrich, K.N., Ho, S.M., Lee, S.A., Reponen, T. & Huo, X. 2016. Ambient air heavy metals in PM 2.5 and potential human health risk assessment in an informal electronic-waste recycling site of China. *Aerosol and Air Quality Research*, 16(2): 388–397.

Zhou, H., Yang, W.T., Zhou, X., Liu, L., Gu, J.F., Wang, W.L., Zou, J.L., Tian, T., Peng, P.Q. & Liao, B.H. 2016. Accumulation of heavy metals in vegetable species planted in contaminated soils and the health risk assessment. *International Journal of Environmental Research and Public Health*, 13(3): 1–12.

Zhu, Q.H., Huang, D.Y., Liu, S.L., Luo, Z.C., Zhu, H.H., Zhou, B., Lei, M., Rao, Z.X. & Cao, X.L. 2012. Assessment of single extraction methods for evaluating the immobilization effect of

amendments on cadmium in contaminated acidic paddy soil. *Plant, Soil and Environment*, 58(2): 98–103.

Zwolak, A., Sarzyńska, M., Szpyrka, E. & Stawarczyk, K. 2019. Sources of Soil Pollution by Heavy Metals and Their Accumulation in Vegetables: a Review. *Water, Air, and Soil Pollution*, 230(7): 164–172.

# CHAPTER THIRTEEN

## 13.1 Conclusion

Metals, radionuclides and synthetic antioxidants may be present in palm oil as additives or contaminants. Hence, characterization, clean-up and remediation of such soils is necessary. Several inorganic species present themselves as additives or contaminants in edible parts of plants. The source of contamination may be via soil water transfer to plants via translocation and transportation. Information on the availability and concentration of metals and radionuclides in soils, toxicity, risk, mobility, and remediation technologies are very important tools to the environmental toxicologist.

Metals are persistent in the environment. Radionuclides with very short half-life are dangerous and fatal. Both radionuclides and metals can be complexed in soils or soil solutions. Long-term biodegradable methods are possible solutions to reduce and remediate such soils. Radionuclide risks may reduce overtime depending on the duration it takes to decay. Uranium, Thorium and their progeny half-lives is very long, hence they persistent and are of particular concern to the toxicologist; although their toxicity depends on their oxidation states in soil solution, effect on food chain, mobility and transfer. Agronomical practices such as pesticides and fertilizers use has been extensively applied in agriculture due to the quest for improved yield. Agriculture produce has always been grown on acclaimed lands such as landfills and dumpsites. The unavailability of land for agricultural purposes, leached and drained soils, and unsuitable topography has led to the quest for improved soil through the use of sewage water, effluents, fertilizers and pesticides on agricultural lands. However, it was observed that the Accumulation Factor in the palm oil varied for each metal, so also is the translocation factor. Hence, the palm oil sampled from most of the plantations was not desirable for human consumption but may be suitable for the agro allied and chemical industries and for the production of biodiesel. The results disclose high AF and HRI values above one and close to unity for most of the plantations. The investigation profers a concise understanding on the prevailing situation and circumstances of palm oil poisoning and pollution with imminent and impending prospective health hazard assessment. A crucial demand prevails to control the palm oil processed from the palm fruits in the region. In addition, policies and programmes must be put in place to forestall the accumulation of the metals in the palm oil that will abate future health risks to the susceptible population of the region. All the naturally occurring radionuclides were detected in all samples of the oil on the oil palm plantation with reasonable activity levels. Radiation dose results from intake through drinking water as well as from the inhalation of radioactive gases such as radon and is progenies were within safe limits. Ingestion is the primary exposure of NORMS through the mouth and lungs to the viscera

organs. Effects are mostly manifested in nephrotoxicity especially in bones and bronchial epithelium. Causes may also be associated with natural background radiation and nuclear electricity generators. It was pertinent to address the overall concentration of radionuclide concentration activity and profer routine monitoring in the oil palm plantation as a whole due the economic important of the cash crop. Naturally, occurring radioactive materials have biological effects on man as manifested in cancer and tumours. The oil palm plantations in Nigeria are situated in historical towns and the implications of migration, settlement and resettlement of plantation owners has a huge impact on the economic development of the nation. The palm oil tree products have been used in traditional medicine since time immemorial without checks or baseline literature on the level of contamination on the leaves or oil palm fruit. Ground water has also been utilized for domestic and industrial purpose and the soils used in the production of building materials in homes and offices. The baseline results will review current inventories on radionuclide plant uptake, accumulation, regulation, and application on the oil palm plantations and other similar works. The baseline report values will be used to access the lifetime cancer risks and dose assessment as the towns were the oil palm plantations are situated are historical towns and for the overall benefit of the oil palm tree as an economic crop. The values arrived at in this study will furnish baseline records and data on the concentration of metals and radionuclides for the consumption of palm oil in the region. The study was able to establish baseline records for protection and safety of radiation dose, metal toxicity and the application of synthetic phenolic antioxidant in the preservation of the palm oil.

### 13.2 Recommendations and further study

Further study will focus on the speciation of radionuclides since radionuclides are not biodegradable except by radioactive decay. Radioecology is another aspect of interest where the ability of microorganisms such as fungi and rhizospheres enhance translocation of NORM into plant roots, tissues, and fruits. Scientist may have looked at the reclamation of the land as a way of enhancing the aesthetics of the environment after drilling or mining of the precious mineral; but at what cost? Future studies will also concentrate on the impact of the contaminants to the environment as the present study was essentially on impact on human health. However, routine study of the area is recommended to monitor human health. This study is useful as a monitoring tool for baseline studies of radionuclides, synthetic phenolic antioxidants, and metal accumulation in the region.

# APPENDIX

## I Permission to undertake research studies at NIFOR


**NIGERIAN INSTITUTE FOR OIL PALM RESEARCH**
(An Institute under Federal Ministry of Agriculture and Water Resources)
**Benin-Akure Road, Private Mail Bag 1030, Benin City, Nigeria.**

All correspondence to be
Addressed to the Executive Director.

BENIN CITY CONTACT OFFICE:
206, Benin-Lagos Road,
Benin City, Nigeria.
Telephone: 052-602485, Fax: 052-602486
E-mail: info@nifor.org
nifor@infoweb.com.ng
Website:www.nifor.org


Our Ref: Adm/233/Vol.15/254

13th March, 2013

**Olafisoye Oladunni Bola,**
D Tech Student,
Department of Chemistry,
Faculty of Applied Sciences,
Cape Peninsula University of Technology,
Cape Town,
South Africa.

**CONFIDENTIAL**

**RE: PERMISSION TO UNDERTAKE RESEARCH STUDIES**

With reference to your letter dated 12th March, 2013 on the above subject, I am directed to convey the approval of the Executive Director for you to carry out your research studies in our oil palm stations located at Abak, Agbarho, Ubiaja, Onishere, Acharu, Umuabi and the NIFOR Demonstration Farm at Ohosu.

2. You are to first report to the Officers in-charge of these stations who will properly direct you before engaging in your task therein.

3. I wish you success in your studies, please.

**E. I. Ujadughele Esq.**
For Executive Director

# II SECU 2020 online conference poster

## Evaluation Of Radioactivity Concentration and Associated Risks in Pressed Virgin Oil Palm Fruit Oil

OB Olafisoye*, OO Oguntibeju**, OA Osibote***
Department of Chemistry*, Department of Biomedical Sciences**, Department of Mathematics and Physics***
Cape Peninsula University of Technology, Cape Town, South Africa

Cape Peninsula University of Technology

### Introduction

The palm oil plantation is one of the cash producing crops in the south western, south eastern and south southern states of Nigeria supplying palm oil and palm kernel products for local farmers, chemical and allied industries. Palm oil contains a good amount of vitamin A and E known to cure various forms of cancer and heart disease. The assessment of accumulation of radionuclides in pressed palm oil is essential because the palm oil can be contaminated from other sources other than the soil. Plants accumulate radionuclides and their progenies through unwholesome agronomical practices. More of the effects of radiation are manifested in pulmonary and kidney cancer, leukaemia and anaemia. Naturally occurring radioactive materials (NORM) (40-K, 238-U and 232-Th) are generally persistent in the environment because they have long half-life and it takes days and years to completely decay depending on the energy of the emitted radiation and half-life. It is pertinent to assess these naturally occurring radionuclides as a baseline or monitoring evaluation to ascertain they do not exceed the permissible levels in the environment. The analysis of radionuclides using the Hyper Pure Germanium Detector (HPGe) provided analysed values of radionuclides and other required data for the calculations of these radionuclides which were compared with standard and permissible values.

### Materials and Methods

Palm oil samples were collected in 1Liter plastic bottles and the containers were labelled PO1-PO15 (Abak-Umuabi as seen in Fig 2 and Table 1) with respect to the fifteen sampling points then transferred to previously cleaned Marinelli beakers. This was properly sealed with paraffin film to prevent any escape of radon gas. Palm oil samples were kept for a month for the radon gas and its progeny to attain secular equilibrium after which, gamma spectrometry measurements of the samples were carried out to determine the activity concentration of the naturally occurring radionuclide materials in the palm oil samples. The gamma-counting equipment was a Canberra vertical high-purity coaxial germanium (HPGe) crystal detector. The photo-peaks observed with regularity in the samples were identified to belong to the natural radioactive decay series headed by 238-U and 232-Th, and a third non-series natural radionuclide, 40-K, for a counting time of 36000 seconds. The risk assessment indices such as Radium Equivalent (Ra), Absorbed Dose Rate (D), and Annual Effective Dose Equivalent (E) were also measured for the palm oil samples.

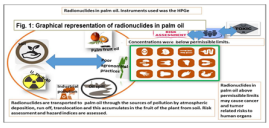



Table 1: Activity for palm oil (Bq/L)

| Code | | Activity of $^{40}K$ (Bq/L) | Activity of $^{238}U$ (Bq/L) | Activity of $^{232}Th$ (Bq/L) |
|---|---|---|---|---|
| Palm Oil | | | | |
| PO1 | Abak | 236.1±9.02 | 2.677±0.96 | 6.881±0.01 |
| PO2 | Acharu | 214.3±5.01 | 4.790±0.34 | 5.432±0.02 |
| PO3 | Agbarho | 156.4±5.54 | 4.790±0.11 | 2.764±0.03 |
| PO4 | Ago-Emokpae | 197.5±5.02 | 1.715±0.12 | 4.243±0.01 |
| PO5 | Apoje | 367.8±9.03 | 3.757±0.45 | 3.461±0.24 |
| PO6 | Badagry | 122.3±3.01 | 2.690±0.01 | 3.443±0.33 |
| PO7 | Benin City | 347.2±9.02 | 3.924±0.39 | 4.315±0.01 |
| PO8 | Igede Ekiti | 327.8±9.01 | 2.963±0.11 | 6.378±0.21 |
| PO9 | Ikire | 266.7±6.02 | 3.190±0.16 | 4.109±0.17 |
| PO10 | Iresa Apa | 212.5±5.15 | 2.661±0.41 | 1.199±0.03 |
| PO11 | Nsukka | ND | 2.475±0.06 | 5.249±0.02 |
| PO12 | Okitipupa | 179.4±0.09 | 1.240±0.01 | 8.061±0.01 |
| PO13 | Onishere | 360.5±9.02 | 6.610±0.02 | 5.209±0.01 |
| PO14 | Ubeja | 229.8±5.02 | 1.996±0.01 | 5.042±0.02 |
| PO15 | Umuahi | 238.6±5.01 | 6.651±0.03 | 1.109±0.01 |

Table 2: Ra, D, and E in palm oil

| Palm Oil Sample Code | $Ra_{eq}$ (Bq/L) | D (nGy/h) | E (mSv/y) $\times 10^{-2}$ |
|---|---|---|---|
| PO1 | 30.70 | 15.24 | 1.87 |
| PO2 | 29.06 | 14.45 | 1.77 |
| PO3 | 19.45 | 9.787 | 1.20 |
| PO4 | 22.22 | 11.17 | 1.44 |
| PO5 | 36.87 | 18.16 | 2.23 |
| PO6 | 17.23 | 8.514 | 1.05 |
| PO7 | 36.62 | 18.05 | 2.23 |
| PO8 | 37.32 | 18.60 | 2.23 |
| PO9 | 28.61 | 15.08 | 1.86 |
| PO10 | 22.74 | 10.91 | 1.33 |
| PO11 | 9.961 | 4.315 | 0.53 |
| PO12 | 25.59 | 12.62 | 1.60 |
| PO13 | 88.00 | 45.29 | 56.9 |
| PO14 | 26.60 | 13.55 | 1.67 |
| PO15 | 27.18 | 13.60 | 1.71 |

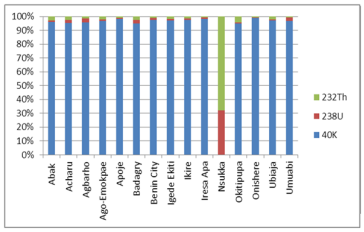



**Fig 2: Concentrations of NORM in palm oil**

### Results and Discussions

The activity concentrations in the palm oil ranged from 122.3 to 968.0, 1.240 to 6.651, and 1.199 to 8.061 Bq/L for 40-K, 238-U, and 232-Th. The Radium Equivalent, Gamma Absorbed Dose Rate, and the Annual Effective Dose Rate in the palm oil samples ranges from 9.981 to 88.00 Bq/L, 4.315 to 46.29 nGy/h, and 0.53 × 10-2 to 56.90 x 10-2 mSv/y, respectively. These are represented in Tables 1 and 2 and Figure 2. The activity concentration of 40-K and 238-U were highest in Onishere (PO13) plantation. The activity of 232-Th was highest in (PO12 ) plantation. The activity concentrations reported for palm oil samples were lower than the recommended world average values given by UNSCEAR. Risk assessment indices were also below permissible limits. Figure 2 represents a graphical representation of

### Conclusion

Concentrations were below permissible limits and hence NORM in the palm oil caused no risk to humans when consumed

### Acknowledgement

The authors wish to thank the Cape Peninsula University of Technology for Funding the Research and Bowen University Iwo for the staff development award for Olafisoye Oladunni Bola.