

**ASSESSMENT OF RADIOLOGICAL AND HEAVY METAL POLLUTION DUE TO
CEMENT INDUSTRY IN OBAJANA AND ITS ENVIRONS, NIGERIA**

BY

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**ASSESSMENT OF RADIOLOGICAL AND HEAVY METAL POLLUTION DUE TO
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BY

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**A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES,
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OCTOBER, 2018

DECLARATION

I declare that this Thesis entitled Assessment of Radiological and Heavy Metal pollution in Obajana Cement Factory and Environs, Kogi State, North Central Nigeria, has been carried out by me in the Department of Physics. The information derived from the literature has been acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other institution.

Ibrahim Ayodeji Bello
Name of Student

.....
Signature

.....
Date

CERTIFICATION

This thesis entitled ASSESSMENT OF RADIOLOGICAL AND HEAVY METAL POLLUTION AROUND OBAJANA CEMENT FACTORY AND ENVIRONS, NIGERIA by Ibrahim Ayodeji BELLO meets the regulation governing the award of the degree of Doctor of Philosophy (PhD Radiation Biophysics) of Ahmadu Bello University Zaria and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This research work is dedicated to Late **Prof. Y.I. Zakari**. He was part of the supervisory team before his late exist, may God grant him eternal rest.

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ABSTRACT

The Radiological and heavy metal concentration due to cement production activities in Obajana cement factory and environs were investigated. A total of twelve (12) Soil samples, six (6) Cement finished product, ten (10) water samples, six (6) rock samples, six (6) and plant crop (Cassava) were collected and analyzed. The radiation dose level of all sampling point were measured with a portable survey meter (Rados model RDS 120). Gamma spectrometry using NaI(Tl) detector was used in determining the activity concentration of primordial radionuclides in solid samples, water samples were analyzed using MPC 2000 gross Alpha/Beta counter for gross Beta and Alpha radioactivity, Atomic Absorption Spectrometry (AAS) was used for the analysis of some selected heavy metals in Water and Rock samples, while Neutron Activation Analysis (NAA) was used for elemental concentrations in soil samples. The mean activity concentration of primordial radionuclides (^{226}Ra , ^{232}Th and ^{40}K) in soil, mining site, Cement finished product and Cassava were found to be: (47.2956, 77.5699, 601.8127) Bqkg^{-1} , (26.84435, 59.98768, 362.3639) Bqkg^{-1} , (36.0011, 49.2077, 146.6098) Bqkg^{-1} , and (20.3514, 37.4710, 164.4322) Bqkg^{-1} respectively, which were slightly below world standard. Transfer Factor (TF) of natural radionuclide (0.428, 0.531, 0.398) for (^{226}Ra , ^{232}Th and ^{40}K) respectively, from soil to the selected cultivated crops around the farms closed to the factory were below the World standard of unity and varied in order of $^{232}\text{Th} > ^{226}\text{Ra} > ^{40}\text{K}$. There exists strong positive correlation ($p < 0.05$) between $^{226}\text{Ra}_{\text{soil}}$ and $^{226}\text{Ra}_{\text{food}}$ ($R = 0.9699$), which suggest that these radionuclides originated from the same source for individual environmental matrix. The alpha and beta geometric mean of the whole samples were found to be 0.0156 ± 0.01487 Bq/l and 10.9 ± 13.8373 Bq/l respectively. All the samples were below the regulation for gross alpha activity in portable water. Also, about 20% of the samples were below regulation for gross beta activity and 80% of the samples have above regulation for gross beta activity in portable water. The highest heavy metals concentration in Water and Rock samples corresponds to Zn. The increasing trend was in the order of $\text{Zn} > \text{Cu} > \text{Cd} > \text{Pb} > \text{Cr}$. The heavy metals were detected at varying concentrations in the samples except for Cr and Pb, which were not detected in some samples due to the detection limit of the machine used. The soil around the factory had high concentration of common low toxic metals Na (15169.333 mg/kg), K (80493.333 mg/kg), Ba (1039.3 mg/kg) and Fe (8977.83 mg/kg), high concentration of two toxic metals Cr (10.188 mg/kg) and Co (3.501 mg/kg) were detected. The average concentration of most heavy metals around the study area compared favorably with other related published studies for soil around Cement Factory.

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ABBREVIATIONS AND SYMBOLS

AAS	Atomic Absorption Spectrometry
ANOVA	Analysis of Variance
BDL	Below Detection Limit
BH	Borehole
CERT	Center for Energy Research and Training
DCF	Dose Conversion Factor
DCP	Dangote Cement Plc.
EOI	Element of Interest
EPA	Environmental Protection Agency
FAO	Food and Agricultural Organization
FP	Finished Product (Cement)
FS	Food Sample
GPS	Global Positioning System
HPGe	High Pure Germanium detector
IAEA	International Atomic Energy Agency
ICRP	International Commission for Radiological Protection

INAA	Instrumental Neutron Activation Analysis
MCA	Multi-Channel Analyzer
MNSR	Miniature Neutron Source Reactor
MPL	Maximum Permissible Limit
MS	Mining Soil
NaI(Tl)	Sodium Iodide Thallium-drifted detector
NESREA	National Environmental Standard and Regulation Enforcement Agency
NiRR-1	Nigeria Research Reactor-1
NORM	Natural Occurring Radioactive Material
NSDWQ	Nigerian Standard for Drinking Water Quality
ppm	parts per million
RS	Rock Sample
STRM	Stream Water
SS	Soil Sample
TENORM	Technically Enhanced Natural Occurring Radioactive Material
TLD	Thermo-Luminescence Dosimeter
UNSCEAR	United Nations Scientific Committee on Effects of Atomic Radiation

USEPA United State Environmental Protection Agency

WHO World Health Organization

WW Well Water

CHAPTER ONE

INTRODUCTION

1.1 Background

Cement industry is one of the most important industries in the world and is considered strategic and economical Industry. Furthermore, for period of time the national development was measured by production and measuring of cement. Therefore, cement remains the key material to modern infrastructure industry and criterion for advancement of urbanization in Nigeria. It is the basic material for building and civil engineering construction (Alsop, 2007).

Cement is produced mainly from limestone and some small quantities of other materials such as clay, gypsum, laterite, shale and iron oxide (White, 1981). There is no two cement plants that will have exactly the same raw mix design formula because of the vast range of raw materials and their different composition (Alsop, 2007). In Dangote cement factory, cement production undergoes different processes such as quarrying and handling of raw materials, grinding the clinker, blending, packing and shipping of the finished products. A crucial process in cement production is the quarry process. Research has shown that this process increases the activity concentration of possible natural radionuclide in the production environment (Gbadebo, 2011).

Limestone and shale constitute the major raw materials for cement production are of geological origin and known to contain natural radioactive elements such as ^{238}U , ^{232}Th and ^{40}K . It is postulated that the by-products of cement production may find their ways into the soil and the underground water systems, hence representing a direct and indirect exposure pathways to man in his environment, through soil, to plant, to man pathway (soil \rightarrow plant \rightarrow man) and water to man (Olowoyo et. al., 2015). Furthermore, it has been established from other countries that

dust containing elevated amount of trace metals emanating from the vicinity of cement factories may adversely affect human, plants and soil composition within the vicinity. Most cement factories have been noted as potential sources of metals such as Hg, Zn, Pb, Cr and Cd (Abimbola et. al 2007). The effects and concentrations of the trace element as pollutant vary and depend largely on technology employed from the cement to ameliorate environmental degradation (Olowoyo et. al., 2015).

1.2 Statement of Research Problem

Over the years, there has been a tremendous increase of industrial establishment for socio-economic purposes, which has led to huge releases of various types of materials into the environment contributing to environmental pollution. Environmental pollution has remained a threat and recent challenge.

Cement industry is one of the most basic industries involved in the development of a country. Cement is the most widely used building material throughout the world. With increase in demand for cement in Nigeria, the number of factories are increasing each year, both consumption and production of cement has increased greatly in recent years. The cement industry has been recognized to be playing a vital role in the imbalances of the environment and producing pollution hazards(Alsop, 2007).

Dangote cement factory is the largest cement factory in Sub-Saharan Africa. Obajana and its environs are endowed with large deposits of limestone (CaCO_3) and shale which are the major raw materials in cement production (Musa *et al.*, 2013). Limestone which is the main constituent in cement contains primordial radionuclides, which is a potential source of indoor/external exposure materials for the earth's crust that are used for building.

A crucial process in cement production is the quarry process. Research has shown this process increases the activity concentration of the radionuclide in the production environment (Gbadebo, 2011). Cement mill workers and environment are exposed to dust at various manufacturing and production processes, such as quarry and handling of raw materials, during grinding the Clinker, blending, packing and shipping of the finished product. Furthermore, within the vicinity of the cement factory, it has been observed that there is a noticeable whitish solid particles settling on agricultural plants due to accumulation of dust resulting from cement production processes. This dust has resulted in anxiety among the area population(Alsop, 2007).

The main raw materials used in Obajana for cement production includes limestones (CaCO_3), clay, sandstone (SiO_2), Bauxite (BaCO_3) and gypsum ($\text{Ca}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$) and involves the release of various particulates, dust, gases and heavy metals. Most cement factories have been noted as potential sources of heavy metal such as Hg, Zn, Pb, Cr and Cd. High concentration of heavy metal deposits can pollute the ground water and the environment(Gbadebo, 2011).

Finally, it is due to these reasons, stated above that this research work is to assess the radiological and chemical effects of cement production around Obajana cement factory and its environs. The effect of cement production due to radiological and heavy metals in soil, plant and water is the major case of study.

1.3 Justification of the Study

Cement is one of the important materials used by the building industry in the world. Many analysts have pointed out that after petroleum industry, cement industry is next in the country because cement constitutes over 95 percent inputs of basic infrastructural developments in Nigeria (Okojie, 2014). Cement used as a building material can cause significant gamma dose exposure, due to their natural radionuclide content depending on the naturally occurring

radioactivity of its raw materials (Muhanned, 2013). Natural radioactivity under certain conditions can reach radiologically hazardous levels, it becomes necessary to study the natural radioactivity levels in cement production processes and its risk.

Deposition of trace metals from dust emanating during cement production (especially at mine and manufacturing sites) occur at various distances around the cement factory. From previous studies, it has been established that dust containing elevated amount of trace metals emanating from the vicinity of cement factories may adversely affect humans, plant and soil composition within the vicinity (Olowoyo *et al.*, 2015).

Generally, groundwater account for about 98% of the world's fresh water resources and it is well distributed throughout the world (Bouwer, 2002). Therefore, with construction of Obajana Cement factory, which is exploiting the Obajana marble deposit through mining, there is a need to asses from time to time environmental impact of mining and extent to which it affected the quality of ground water for domestic use.

Relevant information necessary for remedial solution cannot be obtained without the assessment of the Radiological and chemical effect on the study area. The investigation is therefore important to create awareness and establish baseline pollution level of Obajana environment. It will also contribute to literature for further studies.

1.4 Aim and Objectives of the Study

The aim is to determine the Radiological and Heavy metal pollution of cement production around Dangote cement factory at Obajana. This is hoped to be achieved through the following specific objectives.

1. To determine the activity concentrations of the natural radionuclides (^{226}Ra , ^{232}Th and ^{40}K) in Soil and Crop samples around the factory.
2. To evaluate the level of Transfer Factors (TF) of natural radiation from soil to plant, in crop sample around the area.
3. To determine the alpha and beta radioactivity in water around the factory.
4. Compute the effective equivalent dose due to alpha and beta emitting radionuclides in drinking water around the factory.
5. Determine and assess the heavy metals concentration in water and rocks around the study area using Atomic Absorbtion Spectrometry (AAS).
6. Determine the levels of heavy metals in Soil particles around the factory using Neutron Activation Analysis.

1.5 Scope of the research

This study sought to investigate level of possible pollution that occur as a result of cement production processes (quarry, grinding the clinker, blending, packing and shipping) of the Dangote cement factory at Obajana.

Obajana Village is located within the vicinity of the cement factory, was also used for the study. Soil and plant samples from farmland, stream and well water (sources of water for domestic use) within the sampling area were used as environmental matrices for the investigation. Dust and soil particles within the industrial complex were taken for analysis.

A random sampling technique was adopted. The study is restricted to measure the Radiological and heavy metal pollution of soil, water, dust and air in the study area, using the following analytical techniques: gamma spectrometry, atomic absorption spectrometry and Neutron Activation Analysis (NAA).

CHAPTER TWO

LITERATURE REVIEW

2.1 The Concept of Nuclear Radiation

2.1.1 The Atoms

Atoms are the basic building blocks of ordinary matter. Atoms can join together to form molecules, which in turn form most of the objects around us. Atoms are composed of particles called protons, electrons and neutrons.

The nucleus is composed of protons and neutrons. The protons carry positive charge and are equal in number to the extra nuclear electrons. This number is called the atomic number of the atom and it is usually denoted by the letter Z . When elements are arranged in order of increasing atomic number, a regular repetition or periodicity in their chemical properties is observed. The table so derived is called the periodic table. Atoms that occupy the same position in the periodic table are called isotopes. For example, ^{189}Ir , ^{190}Ir , ^{191}Ir , ^{192}Ir , ^{193}Ir and ^{194}Ir are isotopes of the same element Iridium ($Z = 77$) with ^{192}Ir being very useful in industrial radiography.

2.1.2 Radioactivity

Radioactivity is the spontaneous emission of particles (alpha, beta, neutron) or radiation (gamma, K capture), or both at the same time, from the decay of certain nuclides that these particles are due to an adjustment of their internal structure.

The nucleons (i.e. neutrons and protons), are held together in the nucleus by a very strong nuclear force, the mathematical form of which is still not exactly known. They are at the same time being destabilized by the repulsive force between the positively charged protons that are packed together in a small volume. A stable nucleus is that for which the nuclear force overcomes the repulsive force and there is enough binding energy. If the number of protons in

relation to the neutrons is such that the balance cannot be maintained, the nucleus becomes unstable because the binding energy is not enough to keep the nucleons in equilibrium. It is a natural tendency for any physical system to attain stability (Momoh, 2013).

The unstable nucleus therefore seeks stability by undergoing an intra-nuclear spontaneous transformation that shifts the N/Z ratio to a more stable configuration. Below are some examples:

- i. A proton may be converted to a neutron by β^+ emission or electron capture.
- ii. A neutron may be converted to a proton by β^- emission.
- iii. A combination of proton/neutron may be emitted as α - particle.

These transitions and others, each of which produces the nucleus of another element, are known as radioactivity or radioactive decay. That is, radioactivity is a tendency towards stability. The transmission of the emitted particles and/or the accompanying energy through space is called nuclear radiation.

2.2 Sources of Radiation

Ionizing radiation could be found naturally also known as natural background radiation and it could be manmade as well.

2.2.1 Naturally Occurring Radioactive Materials (NORMs)

Apart from exposure due to nature of work, there is exposure to radiation due to the nature of the environment with or without a radiation facility. Five components of natural background have been identified and these are: cosmic radiation, radioactivity within the earth, in air, water and human body. Their respective contributions vary from one location to another. It is important to highlight the origin of each one:

- i. Cosmic Radiation:** Cosmic rays are high-energy extraterrestrial radiation, which interact with the earth's atmosphere on reaching the earth's surface. They consist of 87% protons,

12 % α - particles and 1% heavier nuclei with energies ranging between 109 eV to 1017 eV. When these high energy particles react with the particles of the atmosphere, many products are emitted: mesons, electrons (β -particle), photons, protons and neutrons all of which in turn produce other secondary particles as they travel down to the earth's surface.

- ii. Radioactivity of the Earth:** The earth is made of the different elements, about 100 in all. Among these are the primordial elements ^{238}U , ^{232}Th and ^{40}K which are radioactive with half-lives comparable with the age of the earth. They therefore still exist in small amounts in the earth, soil and rocks. Both ^{238}U and ^{232}Th have long decay series with members (^{226}Ra , ^{222}Rn , ^{214}Bi etc.), all of which are radioactive. Natural potassium, an ubiquitous element in the soil, contains 0.0119% radioactive ^{40}K . Radiations emitted by these three elements and members of the decay chains present within 15 - 30cm topsoil reach the earth surface.
- iii. Radioactivity in Air:** The background, which is found in air, is due mainly to the presence of radon (^{222}Rn) and thoron (^{220}Rn) gases formed as daughter products in the ^{238}U and ^{232}Th series, respectively. They emanate readily from the soil to build up in air concentrations that depend on meteorological conditions.
- iv. Radioactivity in water:** This depends on the type of water one is talking about. For example, seawater contains a large amount of ^{40}K while many natural spring sand boreholes contain substantial amounts of U, Th and hence, their daughter products. ^{222}Rn in aquifers have been shown to be readily soluble in underground water.
- v. Radioactivity in the Human body:** Since small amounts of radioactive substances are found in soil and water, some activity is expectedly transferred to the human body system

by way of food-chain cycle. Radioactivity in the human body includes ^{40}K , ^{226}Ra , ^{222}Rn , ^{228}Ra and ^{14}C . Of these, ^{40}K is the most abundant.

2.3 Artificial (man-made) Radionuclides

In addition to the inevitable natural background radiation sources described above, man is exposed to various man-made radiations sources, or natural sources that are enhanced by human activities such as mining. Many of the chemical elements have a number of isotopes. The isotopes of an element have the same number of protons in their atoms (atomic number) but different masses due to different numbers of neutrons. There are 82 stable elements and about 275 stable isotopes of these elements. When a combination of neutrons and protons, which does not already exist in nature, is produced artificially, the atom will be unstable and is called a radioactive isotope or radioisotope. For example, Cobalt-60 is produced by bombarding a sample of Cobalt-59 with an excess of neutrons in a nuclear reactor (Momoh, 2013). The Cobalt-59 atoms absorb some of the neutrons and increase their atomic weight by one to produce the radioisotope Cobalt-60. The same is true of Iridium-192 production. This process is known as activation:



There are also a number of unstable natural isotopes arising from the decay of primordial uranium and thorium. Overall there are some 1,800 radioisotopes. At present there are up to 200 radioisotopes used on a regular basis, and most of them are produced artificially. Radioisotopes can be manufactured in several ways. The most common is by neutron activation in a nuclear reactor. This involves the capture of a neutron by the nucleus of an atom resulting in an excess of neutrons (neutron rich).

2.4 The Detection of Ionizing Radiation

Various instruments and devices are used for the detection of radiations. The best known device is the Geiger-Muller counter. This device consists of two parts, a detecting tube and a counter. The heart of the system is the detecting tube, which consists of a pair of electrodes surrounded by an ionizable gas. As radiation enters the tube, it ionizes the gas. The ions produced travel toward the electrodes, between which there is a high voltage. The ions cause pulses of current at the electrodes, which are picked up and recorded on the counter.

The Geiger tube is most sensitive to beta radiation. Gamma radiation can pass right through the tube without being counted, and some alpha radiation can't make it through the window of the tube. The Geiger-Muller counter indicates the counts per minute of radiation entering the tube, but it doesn't tell you the energy of the radiation (Oladipo, 2012).

A scintillation counter is a device that not only counts radioactivity, but also enables the operator to determine the energy of the radiation. The principle of operation involves the radiation reacting with a crystal containing sodium iodide and thallium iodide, which produces a series of flashes of varying intensity. The intensity of the flashes is proportional to the energy of the radiation.

Film badges are small portable devices that are worn by people such as x-ray technicians and nurses, who may be exposed to radiation. The badge contains a piece of photographic film that is removed monthly and developed. The darker the film badge, the greater the degree of exposure.

Another device called a dosimeter is quickly replacing the film badge. One type of dosimeter works on the property of thermo-luminescence, and is called a TLD for short. The TLD consists of a pen-like device and a reading unit. The pen-like device, which is worn by the individual, contains a crystal such as lithium fluoride, which absorbs radiation. When the lithium

fluoride crystal absorbs the radiation, its structure changes slightly. To determine the amount of radiation that the crystal has absorbed, the pen-like device is placed in its reading unit, where it is heated quickly. This causes the lithium fluoride crystal to return to its original state. As it does, it gives off visible light. The visible light is proportional to the radiation absorbed by the lithium fluoride crystal.

2.5 Gamma Spectrometer

Gamma spectroscopy is the analysis of gamma radiation sources or radioisotopes by measuring the energy distribution of the sources. In gamma spectroscopy, output pulses are separated from a detector to provide detailed information that is useful in identifying unknown radionuclides and in counting one radionuclide in the presence of others, thus making it a technique for determining the elements of uranium, thorium, and potassium in bulk samples (Cember, 1996; Mu'azu, 2001; Jonah, 2005).

A gamma ray photon is uncharged which creates no direct ionization or excitation of the material through which it passes. The detection of gamma rays is therefore achieved by causing the gamma-ray photon to undergo an interaction that transfers all or part of the photon energy to an electron in the absorbing medium of the detector (Knoll, 2000). The interaction processes, classified into photoelectric absorption, Compton scattering and pair production all release fast electrons in the active volume of the detector (Davisson, 1974; Jenkin, 1979). The electrons created have a maximum energy equal to the energy of the incident gamma-ray photon at the point of creation, thus providing the only clue to the nature of the incident gamma rays. The electrons undergo loss of energy through ionization and excitation of atoms within the absorber material and through bremsstrahlung emission.

Any detector used in gamma ray spectroscopy is required to have a complete absorption of the created fast electrons; this therefore rules-out gas filled detectors for the spectroscopy of gamma ray unless the gas is at a very high pressure or if the incident photon has very low energy (Knoll, 2000). Two classes of detectors of major importance suitable for the detection of gamma ray energies above several hundred keV are inorganic scintillators (of which NaI(Tl) detector is the most popular) and germanium semiconductor detectors. For weak sources of gamma radiation, NaI(Tl) detector has two great advantages as a detector of gamma radiation:

- (i) high intrinsic efficiency,
 - a. photomultiplier tube output signals are of different amplitudes proportional to the released gamma photon energy during interaction with the crystal thus making discrimination between gamma photons of different energies possible in pulse analyzers (Neiler and Bell., 1974).

2.5.1 Sodium Iodide (Thallium Drifted) Detector (NaI(Tl))

NaI(Tl) detector is type of scintillation detectors which provides a much more efficient method of measuring gamma photons. In this detector, a sufficiently large transparent block of NaI activated with traces of thallium to enhance the emission of visible photons traps gamma photons with a degree of efficiency that depends on the photon energy and on the size of the crystal. The presence of iodine of moderately high atomic number makes photoelectric absorption process appreciable. The crystal is sufficiently large, therefore, gamma photons which experience energy loss by Compton Effect have a high probability of a subsequent complete capture by the photoelectric absorption (or by a succession of compton processes) before they escape from the crystal.

A fast electron, arising, say from the photoelectric absorption of a 1MeV gamma photon by an iodine atom in crystal, produces several thousand quanta of visible light at a fixed wavelength characteristic of a particular phosphor. This light is reflected from the walls of the crystal (surrounded by zinc oxide powder) and made to leave the crystal at its bottom face that is arranged to be in good optical contact with the window of a photomultiplier tube (PM).

At a cathode made of an alkali metal such as caesium, the PM re-converts the light quanta to photoelectrons at the rate of about one photoelectron per ten quanta, thus acting as an electron multiplier to amplify the photoelectric 'pulse' by a factor of 10^6 or more. Each gamma photon which produces one (or more) fast electrons in the crystal releases an amplified signal from the PM which can be further amplified and analyzed by 'pulse analyzer' which sorts the signals simultaneously into different channels according to their exact amplitudes (Van Lieshout, *et al*, 1974 and Jenkin, 1979).

2.6 Interaction of Radiation with Matter

When radiation passes through matter, it interacts with the atoms of the material. The characteristic processes of interaction are different for each radiation type and energy. The results of these interactions (excitation and ionization) are the basis for radiation detection and measurement and radiation bio-effects.

Any radiation type which by virtue of its energy is capable of causing ionization in matter as it passes through is referred to as ionizing radiation. This is to distinguish it from other types of radiation like visible light, infrared or radio waves which do not have the same ability. Ionizing radiations include all particulate radiations (α , β , etc.) and x-and γ - rays.

1. Alpha (α) particles: these are fast moving helium atoms. They have high energy, typically in the MeV range, but due to their large mass, they are stopped by just a few inches of air, or a piece of paper.

2. Beta (β^\pm) particles: these are fast moving electrons. They typically have energies in the range of a few hundred keV to several MeV. Since electrons are much lighter than helium atoms, they are able to penetrate further, through several feet of air, or several millimeters of plastic or less of very light metals.

2.6.1 Gamma Rays and X-Rays

Gamma rays (γ -rays) are electromagnetic radiation (photons). Gamma rays are electromagnetic rays similar to x-rays in every respect except in their modes of production. Gamma rays are emitted during energy level transitions in the nucleus of the daughter products following radioactive decays like α and β^- decays. Its emission can therefore not be controlled and the intensity of its emission decreases with time according to the decay law. X-rays are produced when the x-ray machine is switched on and the intensity is determined by the operating voltage. Both γ -rays and x-rays are used in different scanning operations but x-rays are used almost exclusively in baggage and cargo scanning operations. It is important to know the basic physics and their characteristics.

At a high accelerating voltage, some electrons give their energy to and subsequently eject bound electrons from the target atoms from inner (K or L) shells. Electrons from higher energy states promptly fill the resulting vacancy. The energy difference is released as an electromagnetic radiation in x-ray region (Bohr's theory). This type of x-rays is called characteristic x-rays because they are characteristic of the target material. The radiation found most suitable for mammography is 18 eV characteristic x-rays from a molybdenum target (Momoh, 2013).

2.6.2 Gamma and X-Ray Interaction with matter

Gamma and X-ray photons interact with matter through three major mechanisms: Photoelectric Effect, Compton Effect and Pair production.

2.6.2.1 Photoelectric Effect

In the photoelectric absorption process, a photon undergoes an interaction with an absorber atom in which the photon completely disappears. In its place, an energetic photoelectron is ejected from one of the bound shells of the atom. For gamma rays of sufficient energy, the most probable origin of the photoelectron is the most tightly bound or *K* shell of the atom. The photoelectron appears with an energy given by:

$$E_{e^-} = h\nu - E_b \text{-----} (2.1)$$

(E_b represents the binding energy of the photoelectron in its original shell)

Thus for gamma-ray energies of more than a few hundred keV, the photoelectron carries off the majority of the original photon energy. Filling of the inner shell vacancy can produce fluorescence radiation, or x ray photon(s).

2.6.2.2 Compton Effect

Compton scattering takes place between the incident gamma-ray photon and an electron in the absorbing material. It is most often the predominant interaction mechanism for gamma-ray energies typical of radioisotope sources. It is the most dominant interaction mechanism in tissue. In Compton scattering, the incoming gamma-ray photon is deflected through an angle θ with respect to its original direction. The photon transfers a portion of its energy to the electron (assumed to be initially at rest), which is then known as a *recoil electron*, or a *Compton electron*.

The Compton process is most important for energy absorption for soft tissues in the range from 100 keV to 10MeV.

2.6.2.3 Pair production

If a photon enters matter with energy in excess of 1.022 MeV, it may interact by a process called pair production. The photon, passing near the nucleus of an atom, is subjected to strong field effects from the nucleus and may disappear as a photon and reappear as a positive and negative electron pair. The two electrons produced e^- and e^+ , are not scattered orbital electrons, but are created, de novo, in the energy/mass conversion of the disappearing photon.

2.6.3 Properties of Gamma and X-Ray Beams

Gamma and X-rays are highly penetrating and this property accounts for their wide use in medical diagnosis and therapy as well as in many industrial applications as their absorption in a medium is due mainly to the afore mentioned three processes: Compton scattering, Photoelectric absorption and Pair production.

2.7 Activity of a Radioactive Material

The quantity which expresses the degree of radioactivity or the radiation producing potential of a given amount of radioactive material is activity. The curie was originally defined as that amount of any radioactive material that disintegrates at the same rate as one gram of pure radium. The curie has since been defined more precisely as a quantity of radioactive material in which 3.7×10^{10} atoms disintegrate per second. The International System (SI) unit for activity is the Becquerel (Bq), which is that quantity of radioactive material in which one atom is transformed per second. The radioactivity of a given amount of radioactive material does not depend upon the mass of material present. For example, two one-curie sources of ^{137}Cs might have very different masses depending upon the relative proportion of non-radioactive atoms

present in each source. Radioactivity is expressed as the number of curies or Becquerel per unit mass or volume.

The concentration of radioactivity, or the relationship between the mass of radioactive material and the activity, is called "specific activity." Specific activity is expressed as the number of curies or Becquerel per unit mass or volume. Each gram of cobalt-60 will contain approximately 50 curies. Iridium-192 will contain 350 curies for every gram of material. The shorter half-life, the less amount of material that will be required to produce a given activity or curies. The higher specific activity of iridium results in physically smaller sources.

2.8 Modes of Radioactive Decay

- a. Alpha decay is the emission of an alpha particle (2 protons and 2 neutrons) from an unstable nucleus. The daughter nuclide has an atomic number 2 less than the parent nuclide and a mass number 4 less than the parent nuclide. The daughter nucleus commonly releases its excitation energy by gamma emission.
- b. Beta-minus decay effectively converts a neutron to a proton and an electron, which is immediately ejected from the nucleus. The daughter nuclide has its atomic number increased by 1 and the same mass number compared to the parent.
- c. Beta-plus decay effectively converts a proton to a neutron and a positron, which is immediately ejected from the nucleus. The daughter nuclide has its atomic number decreased by 1 and the same mass number compared to the parent.
- d. In electron capture, the nucleus absorbs an electron from the innermost orbit. This electron combines with a proton to form a neutron.

- e. Internal conversion occurs when a gamma ray, emitted by the nucleus as it goes from the excited state to the ground state, interacts with one of the innermost electrons of the same atom. The electron is ejected from the atom.
- f. An isomeric transition is the decay of an excited nucleus to a lower-energy level by the emission of a gamma ray.

2.8.1 Gamma Emission

Gamma radiation is a high-energy electromagnetic radiation that originates in the nucleus. It is emitted in the form of photons, discrete bundles of energy that have both wave and particle properties. Often a daughter nuclide is left in an excited state after a radioactive parent nucleus undergoes a transformation by alpha decay, beta decay, or electron capture. The nucleus will drop to the ground state by the emission of gamma radiation.

2.8.2 Decay Chains

When an unstable nucleus decays, the resulting daughter nucleus is not necessarily stable. The nucleus resulting from the decay of a parent is often itself unstable, and will undergo an additional decay. This is especially common among the larger nuclides. It is possible to trace the steps of an unstable atom as it goes through multiple decays trying to achieve stability. The list of the original unstable nuclide, the nuclides that are involved as intermediate steps in the decay, and the final stable nuclide is known as the decay chain (Omeje, 2009).

2.9 Biological Effects of Ionizing Radiation

When an organism is exposed to radiation, the amount of damage it suffers will depend on the energy carried by the radiation. Ionizing radiation carries sufficient energy to be dangerous to living cells. Several things can happen when ionizing radiation hits a living cell:

- the cell may not be damaged as the radiation passes through it

- the cell could be damaged, but is able to repair itself
- the cell could be killed
- The cell's DNA may be damaged but remains able to reproduce itself, in its modified form. This cell could become malignant and turn into a cancer. If the cell is a sex cell, the radiation may cause a mutation in a gene. What actually happens to a cell will depend on the absorbed dose of radiation, the type of radiation and the cell type.

However, massive cell death can sometimes be beneficial. In a radiotherapy treatment, for example, a tumour may be eradicated by submitting it to intense X-rays. Lower energy radiation such as UV light can still cause painful sunburn and has been linked to skin cancer.

2.10 Radioactivity in Water (Alpha and Beta Gross Activities)

Radioactivity in water can be natural or anthropogenic. The natural radioactivity emanate from the primordial nuclides in the earth's crust from cosmic ray bombardment which occur in the atmosphere. Anthropogenic radioactivity on the other hand is linked to human activities. The energy accompanying transformation of unstable atom is primarily released in form of one three primary particles: alpha, beta or gamma. These three particles have different health effect on humans. An alpha particle is massive and has a short range in air and if ingested could be very damaging to the cells of the body. Beta particles are less massive and less damaging. A gamma radiation is massless and has a high penetrating power but less lethal at the usually lower doses encountered in drinking water (WHO and GoP, 2005).

In order to estimate radioactivity in water index called gross alpha and beta activity is used. This quantity is not nuclide-specific; rather it is the sum of the activities of all radioactive elements within the water. A gross alpha test is the preliminary test towards determining the

level of radioactivity in drinking water. The gross beta activity is usually measured so as to extend the safety margin (Onoja, 2015).

Generally, the gross activity can be expressed as

$$Activity (\alpha,\beta) = \frac{Rate (\alpha,\beta) - Bgd (\alpha,\beta)}{Sample\ efficiency \times Channel\ Efficiency \times Sample\ Volume} \dots\dots\dots (2.2)$$

2.11 Radioactivity in Air

Radioactivity in air can be natural or artificial. The natural radioactivity emanate from the primordial nuclides in the earth’s crust due to cosmic ray bombardment which occur in the atmosphere. Anthropogenic radioactivity is linked to human activities burning of coals, dust from quarry site, gas (carbon monoxide) from vehicle exhaust and dust from cement production. The cement manufacturing industry has been identified as one with great potential of causing atmospheric particle pollution. The main airborne pollutants of cement production to the environment are the emission of dust and gases. Dust is significantly emitted during all these processes of exposing workers and the environment to particulate pollution. In cement facility 1kg of cement manufacture generates about 0.07kg of dust, which is lost to the atmosphere. (Addo et. al., 2014).

Materials used to manufacture cement (limestone, shells and chalk), are derived from rock and soil. These ingredients contain mainly natural radionuclide (²³⁸U, ²³²Th and ⁴⁰K) can be a source of external radiation exposure through gamma-ray emission whereas internal exposure occurs through the inhalation of radon gas. For instance, having identified that cement contain naturally occurring radionuclide, there is no difficulty in the understanding that the dust may also have these same radionuclide constituents. Airborne pollutants can therefore be regarded as an important environmental issue since it has direct effect on human health. Considering the fact that humans breathe in and out approximately every 4s which equates to over 8 million in a year,

the airborne uranium can be inhaled and may enter the human system. Uranium, in its soluble form, is chemo-toxic and can primarily affect the kidney (Addo et. al, 2014).

Atmospheric pollutants like natural radionuclide in a dusty environment may affect public health, particularly of young children, because they are more sensitive than adults (i.e their organs are developing),also they have greater probability of contact with the suspended dust. Therefore, it is necessary to conduct air quality survey, in order to determine levels of Total Suspended Particulates (TSP) and levels of ^{238}U , ^{232}Th and ^{40}K contamination in the ambient air at various direction and radii distances from the factory.

2.12 Measurement of Chemical Effect

The measurement of trace elements will be undertaken using neutron activation analysis (NAA) analytical technique. The basis and theory of this analytical technique are discussed fully in the following subsections.

2.12.1 The Theory of Neutron Activation Analysis (NAA)

Neutron Activation Analysis (NAA) is a nuclear process used for determining the concentrations of elements in a vast amount of materials. NAA relies on excitation by neutrons so that the irradiated sample emits gamma-rays. It allows the precise identification and quantification of the elements, above all of the trace elements in the sample. NAA has applications in chemistry but also in other research fields, such as geology, archaeology, medicine, environmental monitoring and even in the forensic science.

To carry out NAA analysis, the specimen is placed into a suitable irradiation facility and bombarded with neutrons, this creates artificial radioisotopes of the element presents. Following

irradiation, the artificial radioisotopes decay through the emission of particles or more importantly gamma-rays, which are characteristics of the element of which they were emitted.

It is also a nuclear process (i.e. not based on electronic transitions) used for determining certain concentrations of elements as it disregards the chemical form of a sample and focuses solely on its nucleus. The method is based on neutron activation and therefore requires a source of neutrons. In this work, NIRR-1 nuclear reactor at CERT, Ahmadu Bello University, Zaria was used for the analysis.

2.12.2 Instrumental Neutron Activation Analysis (INAA)

INAA is a nuclear analytical technique for measuring the concentrations of large number of elements (trace and major) in a single sample. This technique can be applied to the analysis of a wide variety of matrices and involves exposing the sample along with prepared standards to a field of neutrons. This exposure causes most of the elements within the sample to become radioactive. As these radioactive nuclides decay, they emit gamma rays whose energies are characteristic for each nuclide. Comparison of the intensity of these gamma rays with those emitted by a standard permit a quantitative measure of concentrations of the various nuclides.

2.12.3 Radiochemical Neutron Activation Analysis (RNAA)

RNAA technique involves exposing the samples to a neutron field to create radioactive emitters. However, it involves chemical separation of the sample to isolate one or more elements from the sample matrix. Isolation of the elements is performed to eliminate any spectral interferences and to lower the background. Using this technique, it is possible to achieve lower detection limits than are obtained using conventional INAA. RNAA has been used to analyze a wide variety of sample types.

2.12.4 Principles of Neutron Activation Analysis

In the technique, a stable isotope is made radioactive by bombarding the isotope called the target nucleus with a neutron. The radioactive nucleus subsequently emits delayed gamma corresponding to different energy peaks which are characteristic of specific elemental compositions. These are then measured using gamma ray spectrometric analysis. Each element emits gamma radiation of discrete energy values. Energy peaks in gamma spectrum are then used to identify which elements are present in a sample.

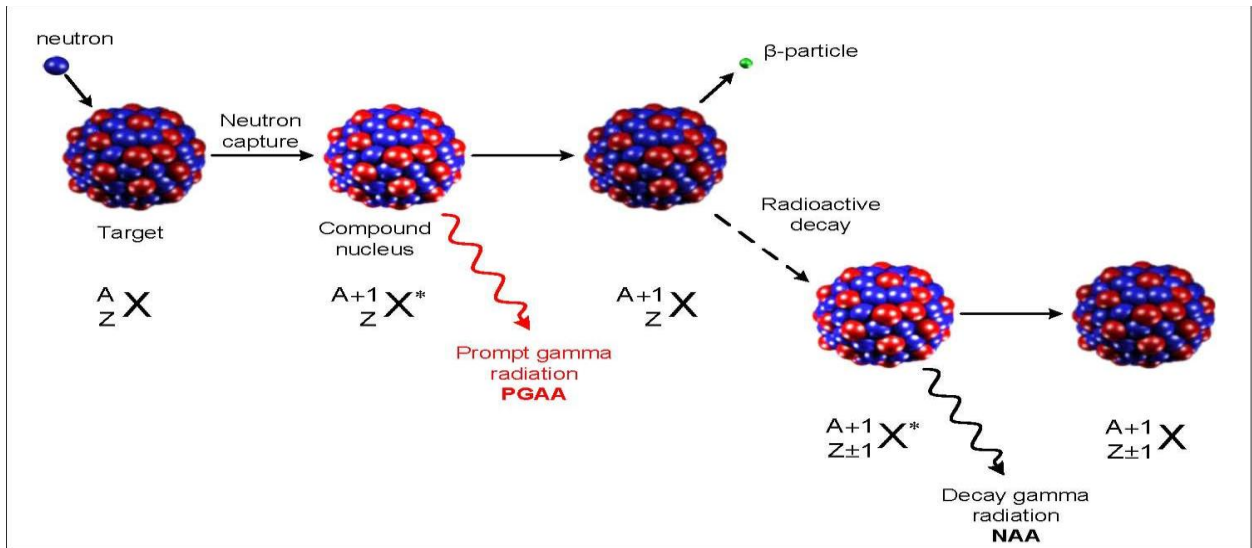


Figure 2.1: Illustration of the Activation process

2.12.5 Interaction of Neutrons with Matter

Neutrons are uncharged particles like protons and interact only through collision with the nucleus. No coulombic interaction exists with the electrons or the nucleus. Neutrons interaction is real and occurs only when the nucleus come within 10^{-13} cm of the nucleus. Neutron interactions undergo different nuclear processes, it depends on the energy of the incoming neutron. Neutrons are classified according to their energies in the following ways.

2.12.5.1 Fast Neutrons

These are neutrons in the energy range of 100eV to 100MeV. The probability of neutron-induced reactions those are useful in detectors decreases with increasing photon energy.

Here, the importance of thermalization becomes greater. In event of the neutron energy being sufficiently high, inelastic collision can take place in which the recoil nucleus goes into one of its excited states. The nucleus quickly de-excites through emission of a gamma ray and the neutron loses greater fraction of energy than it would in an equivalent elastic collision.

2.12.5.2 Epithermal Neutrons

A fission neutron that has slowed down but not yet reached thermal energies is called epithermal neutron. Epithermal neutrons consist of neutrons within energy range 0.5eV to 0.5MeV. Cross sections for both capture and fission reactions often have multiple resonance peaks at specific energies in the epithermal energy range.

The necessity for neutron activation analysis came as a result of the fact that some elements have isotopes with resonance in the epithermal neutron region. The isotopes have high resonance integrals which are the epithermal equivalent of thermal neutron cross section.

2.12.5.3 Slow Neutrons

It is also known as Thermal neutrons. It has a low kinetic energy and their significant mode of interaction include elastic scattering with absorber nuclei and other forms of neutron-induced nuclear reactions. Elastic collision tends to bring the slow neutrons to thermal equilibrium with the absorber medium before a different type of interaction takes place. Most of the low-energy neutrons which are found among the thermal neutrons have an average energy of about 0.025eV at room temperature (Knoll, 2000).

The slow neutron interactions that are of interest are the neutron-induced reactions that can produce secondary radiations which energies are sufficient to be directly detected. The relative capture or (n,γ) reaction is the most probable reaction and plays a crucial role in the attenuation of shielding of neutrons.

2.12.6 Classification of Neutron Activation Analysis

The method of Neutron activation analysis are classified into the absolute, k_0 method and the relative method.

2.12.6.1 The Absolute Method

In the absolute method of activation analysis, it is necessary to determine the absolute activity of the sample, A_{tc} (dps) corresponding to the decay of radionuclide formed at time t_1 , when the irradiation process was completed.

From the absolute activity.

$$A_{tc} = \frac{N_A \phi \sigma \theta m [1 - \exp(-\lambda t)] \exp(-\lambda_c t_c)}{M} \text{----- (2.3)}$$

where: m = weight of element to be determined, N_A = Avogadro Constant, θ = relative natural isotopic abundance of the activated isotope and M = atomic weight of the element to be determined.

2.12.6.2 k_0 - Method

Using the k_0 standardization method, the concentration of any analyte “a” is obtained from its measured isotope/gamma ray from the expression below.

$$Q_a = \frac{(N_p / W t_m SDC)_a}{(N_p / W t_m SDC)_{Au}} \times \frac{1}{K_{o,Au}(a)} \times \frac{f + Q_{o,Au}(a)}{f + Q_{o,a}(a)} \times \frac{\epsilon_{p,Au}}{\epsilon_{p,a}} \text{----- (2.4)}$$

where: Au = co-irradiated gold monitor of energy 411.8 keV, N_p = net number of counts in full energy peak, W = weight of sample, w = weight of gold monitor, t_m = measuring time,

$S = 1 - \exp(-\lambda t_{irr})$, λ = decay constant, t_{irr} = irradiation time.

$D = \exp(-\lambda t_d)$, t_d = decay time, $C = [1 - \exp(-\lambda t_m)/\lambda t_m]$, f = thermal-to-epithermal neutron flux ratio. $Q_a = I_o/\sigma_o$, α = measure for the epithermal flux distribution, ϵ_p = full-energy peak detection efficiency.

2.12.6.3 *Relative Method*

The relative method of activation analysis is based on comparison of activities of the sample (A_x) and the standard (A_s). This method, though sample often times encounter difficulties with respect to its reproducibility. The sample and standard are activated under as nearly identical conditions as possible. Measurement must be carried out under practically identical conditions (such as cross sections, decay constants, atomic weights, geometry and isotopic abundances) as any variation can affect the precision remarkably.

The procedure commonly used to determine the concentration (in ppm) of elements in the unknown sample relative to the standard can be determined using the expression.

$$\frac{A_x}{A_s} = \frac{m_x}{m_s} \cdot \frac{(e^{-\lambda T_d})_x}{(e^{-\lambda T_d})_s} \quad \text{-----} \quad (2.5)$$

where m = mass of the element, λ = decay constant for the isotope and T_d = decay time

When short irradiations are performed, the counting times for all samples and standards are fixed. Hence, the time-dependent term in the above equation vanishes and the equation reduces to

$$C_x = C_s \frac{W_s}{W_x} * \frac{A_x}{A_s} \quad \text{-----} \quad (2.6)$$

where: C_x and C_s are the concentrations of sample and standard respectively.

The relative method has the following disadvantages:

- (i) The preparation, irradiation and measurement of large number of standards is time consuming and is prone to errors.

- (ii) Handling of a large number of standards causes a great difficulty in Computer-coupled automated activation analysis.
- (iii) Quantitative analysis is impossible for unexpected elements since no standards are provided.
- (iv) The calculation of detection limit is impossible without standard.
- (v) It is sometimes difficult to ensure identical irradiation conditions for standards and samples.

These difficulties can however be reduced by using synthetic multielement standards, standard reference material and so on.

2.12.7 Multi-Element Comparator Method

This method is based on comparison of the activities of the sample (A_{sample}) and a standard (A_{standard}) of which contains Element Of Interest (EOI) to be determined in known amounts. The sample and standard are activated under as nearly identical conditions as possible: simulations activation being the best standard should be placed as close as possible to the sample to eliminate errors due to inhomogeneity in the neutron flux. If the standard contains a known amount (W_{standard}) of the element to be determined the amount of the element in sample (W_{sample}) is given by:

$$W_{\text{sample}} = W_{\text{standard}} \frac{A_{\text{sample}}}{A_{\text{standard}}} \text{ --- (2.7)}$$

2.12.8 Advantages of NAA

NAA analytical techniques was chosen for the measurement of chemical effect in this work because of the following advantages:

1. It is used for the determination of the concentrations of elements in a sample very accurately.
2. It non destructive and can been used for analysis of works of art and historical artifacts.
3. In its instrumental form (INAA), it is advantageous because of its rapidity, reproducibility of results, complementarily to other methods, freedom from analytical blank and independence of chemical state of elements (Jonah et al., 2006).
4. It is also used to find activity of a sample.
5. The analysis time is reduced, which is advantageous when treating large numbers of samples.

2.13 Theory of Atomic Absorption Spectrometry(AAS)

This technique is applicable to most gas phase elements over a wide range of concentrations and involves detecting, measuring and analyzing radiation that is either absorbed or emitted from the atoms or ions of the element of interest (McMahon, 2007). It involves three techniques: Absorption, emission and fluorescence. In all the above, the sample is decomposed by intense heat into hot gases consisting of free atoms and ions of the element of interest (McMahon, 2007). As atoms are the simplest and purest form of matter and cannot rotate or vibrate as a molecule does when subjected to high energy radiation, electrons within the atom undergo transitions. The high energy radiation is commonly produced by Flame in Flame Atomic Absorption Spectroscopy (FAAS).

2.13.1 Principle of AAS

An atom is made up of positively charged nucleus surrounded by a number of negatively charged particles necessary to provide neutrality. These atoms occupy discrete energy levels but it is

possible for an electron to be moved from one level to another by introduction of energy. Such transitions will only occur if the available energy is equal to the difference between the two levels. Energy levels and the energies associated with electron transitions are unique for each element. When light (energy) of a characteristic wavelength enters an analytical system, outer shell electrons of corresponding atoms within the light path will be excited as energy is absorbed. The amount of light transmitted through the system from a source to the detector will be less. The loss of light is proportional to the number of atoms. The measurement of the radiation transmitted (using Beer-Lambert's law) in such a transition form the basis of AAS. The AAS involves the measurement of the drop in light intensity of initial radiation I_0 to final radiation I depending on the concentration of the metal. Modern instruments automatically convert logarithmic values into absorbance (Nollet, 2011).

2.13.2 Instrumentation of AAS

Any atomic absorption spectrometer consists basically of a light source which emits the sharp line spectrum of elements to be determined, a method to produce atomic vapour of the sample to be analyzed, a monochromator for the spectral dispersion of the source radiation, a detector connected to an amplified read out system and a computer

2.13.3 Light source

A continuous source of radiation is required. A series of sources which can give sharp emission lines for a specific element are used. A hollow cathode glow discharge lamp is used. A hollow cathode lamp has two electrodes; one is cup shaped and made of a specific element. The metal used for the cathode is the same as the metal to be analyzed. The lamp is filled with noble gas at low pressure. It will produce a glow discharge from the hollow cathode. Metal atoms are

evaporated by sputtering. The atoms accept energy of excitation and emit radiation with the lines of the metal. Hollow cathode lamps made out of several elements are available (Khopkar, 1998)

2.13.4 Flame Atomization

Several types of atomizers are used for atomization. These include flame, electro thermal, cold vapour technique for mercury and hydride generation. The flame atomizers consist of a nebulizer and a burner. The nebulizer is designed to convert the solution into a fine mist or aerosol. In flame atomization, atomization is carried out by flame. Heat energy is utilized to convert the metallic element to atomic dissociated vapour. The temperature should be controlled very carefully to convert it to atomic vapour. At too high or too low temperatures, atoms will be ionized and they will not be absorbed. In atomization, fuel and oxidant gases are fed into a mixing chamber which passes through baffles to the burner head. A flame is produced and the sample is aspirated through the air into the mixing chamber. Only droplets of a small size pass through the baffles to the burner head. A narrow burner is therefore preferred and careful readjustment of the gas (Khopkar, 1998).

2.13.5 A monochromator

A monochromator produces monochromatic light by removing unwanted wavelengths from the source light beam. It isolates a single atomic resonance line from the spectrum of lines emitted by hollow cathode lamp. Essentially it is an adjustable filter that selects a specific, narrow region of spectrum for transmission to the detector and excludes all wavelengths outside this region. A monochromator comprises an entrance slit, a dispersion device and an exit slit.

- (i). the entrance slit selects a defined beam of light from the source
- (ii). the dispersion device causes the different wavelength of light in the source beam to be dispersed at different angles

(iii). the exit slit enables selection of a particular wavelength to produce the required monochromatic light

2.13.6The detector

Two detectors are used in atomic absorption spectrometers; photomultiplier tubes and solid state Detectors (Nielsen, 2010). Detectors convert the radiant energy reaching it into an electrical Signal. The signal is processed to produce either an analogue or digital read out. Modern Instruments are interfaced with computers for data collection, manipulation and storage.

2.14 Review of Previous Related Works

In recent past few years, attention has been devoted to matter relating environmental contamination in our environment, due to natural radioactivity and trace element. As a result, a lot of research work has been undertaken in this study area.

Ajayi et al, (2012) investigated the absorbed doses in raw materials and end product from Dangote cement factory using gamma ray spectrometer. The study revealed, that the calculated absorbed doses in the cement (342.22nGy/h or 2.998mSv/y) have higher activity of the isotopes than the permissible level suggested by ICRP (80nGy/h or 0.7mSv/y).

Abdulahman et al, (2013) analyzed the concentrations of ^{40}K , ^{226}Ra and ^{232}Th in the cement samples manufactured in Tlemcen (Algeria) using a high-efficiency gamma ray spectrometer. Measurements of radioactivity in the environment are of great importance to monitor and control the levels of radiation to which man is exposed directly or indirectly. He concluded that, the average values of activities concentrations obtained for the natural radionuclide in different samples of cement are lower than the corresponding global values reported in UNSCEAR publications.

A similar work was also reported by Jibiril and Agomuo, (2007) where they analyzed some crops of important nutritional value and soil samples collected from farmlands located in Bitsichi an old tin mining town in north central of Nigeria using NAA in order to determine the trace element concentration level. These workers also determined the activity concentration due to natural radionuclide in the food and soil samples collected within the root zone of the crops using the gamma-ray spectrometry. The NAA results showed higher concentrations of potassium among the essential elements in all crops. Calcium concentration in both maize and guinea corn was below detection limit, also Zn was determined in green beans, sweet potato and cassava.

They concluded that mining activities in that area influenced the concentration of the trace elements and radionuclides in the food crops, but are seen not to pose any serious internal health burden due to ingestion by individual in the study area.

Olowoyo et al, (2015) measured the concentration of trace metals in soil and plants around a cement factory in Pretoria, South Africa. Thirty soil and plant samples were collected in different directions of the sites. Their result showed that soil pH was in acidic medium and ranged from 5.12 ± 0.23 – 5.67 ± 0.23 . The pollution index (PI) revealed that the soil has been moderately polluted with element such as Pb, Ni, Cr, Zn, Cd and Cu. Strong positive correlations were recorded for most of these elements, suggesting a common source for them. They observed that the levels of trace metals from the plants exceed the acceptable limits for human and livestock consumption. The study revealed that the source of the trace metals as pollutants cannot be attributed to the cement factory only, but also to vehicular emissions.

The health hazards of Cement dust from cement Industry were also studied by Sultan (2006). He reviewed the potential toxic effect of cement dust and to minimize the health risk in cement mill workers by providing them with information about the hazards of cement dust, such as lung function impairment, chronic obstructive lung disease, pneumoconiosis and carcinoma of the lungs, stomach and colon.

Ibeanu, (2002) measured the dose rates and activity concentration of natural radionuclides in environmental samples of a Nigerian tin mine and its tailing sites and found that the measured concentration levels of U and Th in tailing samples. The measured dose rate was found to be elevated with values up to approximately 100 times above background levels of the control soils. The author advised that for the purpose of protection of workers and the public, the

sites should be properly monitored, controlled and potential remediation strategies is considered in order to avoid any radiological impact to the population.

In another, Bello et al, (2014) determined the external and internal hazard indices from natural occurring radionuclide in rock, sediment and building samples collected from Sikiti, Oyo State Nigeria, via gamma spectrometry using NaI(Tl) detector. The author discovered that the external and internal hazard indices for rock samples were above permissible limit (i.e. >1). Therefore, the samples may be used by farmers, miners and resident of the area with a lot of caution, to prevent radiation exposure which may result from long term cumulative effect.

Musa et al, (2013) analyzed the heavy metal concentration in groundwater around Obajana and its environs, following reported cases of the occurrence of heavy metals in groundwater within the area which by nature are injurious to human health. The laboratory analysis he used, involved the use of instruments such as water spectrophotometer, pH meter and addition of some test reagents to the collected water samples. The concentration values of the water sample collected fall below the limits specified by World Health Organization (WHO). The worker also recommended that periodic and systematic study of the heavy metals concentrations in ground water sources in the study area should be carried out regularly.

However, there are limitations to the above reviewed works because most of them were done outside the study area whereas, those done within the study area were in a small region not as extensive as the one proposed. The proposed work would cover the areas that have not been undertaken by other researchers using some of the analytical techniques available at Centre for Energy Research and Training (CERT), Ahmadu Bello University (ABU) Zaria.

CHAPTER THREE
MATERIALS AND METHODS

3.1 Materials

- Global Position System (GPS)
- Hand Auger
- Polyethene bags
- Masking Tape
- Hot plate
- Plastic container (2 l)
- Sensitive Weighing Balance
- Nitric acids(HNO_3)
- Hydrochloric acid (HCl)
- Planchette
- Portable Survey meter(Rados Model RDS 120)
- Hand glove
- Filter paper
- Recording Jotter
- Stop watch
- Hoe
- Cutlass

3.2 The Study Area

The study area lies within longitude 6°24'E to 6°27'E and latitude 7°54'N to 7°56'N. It can be accessed through Lokoja-Kabba road. The establishment of Dangote cement factory rapidly led to increased population of the community, from about 400 to 5000. The community is rich with large deposits of limestone and other minerals needed for production of cement. Dangote cement was incorporated as Obajana cement Plc on 4th November, 1992 by the Kogi State government to operate plant (s) for the preparation, manufacturing, control, research and contribution of cement and related products. It was acquired by Dangote Industries Limited (DIL) in 2002 and commenced the construction of the first cement production plant in 2004. In July 2010, the company's name was changed from Obajana Cement Plc to Dangote Cement Plc (DCP). The plant is completely integrated and fully automated for production of cement (Musa et al, 2012).

The major occupation in the community is agriculture. The agricultural system in the study area can be categorized into an intensive smallholder rain-fed agriculture. The only source of water in the study area, River Oinyi - dries up during the dry season, there is generally no irrigation farming in the study area. Over the years, groundwater has served as a potential source of water supply especially through springs, hand dug wells and boreholes.

Due to mining activity of cement raw materials, farm practices around the mining area and ground water that serve as major source of water. It becomes necessary to establish a baseline radioactivity level in the study area

3.3 The Geology of the Study Area

The study area lies within the Benin-Nigeria sheet, situated in the Pan-African mobile zone extending between the ancient Basements of West African and Congo Cratons in the region of Late Precambrian to Early Palaeozoic orogenies (Ekwueme, 2003). The Basement Complex rocks of Nigeria are composed predominantly of migmatite gneiss complex; slightly migmatised to unmigmatised parashists and metaigneous rocks; charnockitic, older granite suites and unmetamorphosed dolerite dykes (Rahaman, 1976). The Precambrian Basement rocks of Obajana area, comprise of schists and gneisses which have been subjected to major supracrustal tectonic events such as the Dahomeyan ($3000\pm 200\text{Ma}$), Eburnean ($1850\pm 250\text{Ma}$), Kibaran ($1000\pm 100\text{Ma}$), and Pan-African ($550\pm 100\text{Ma}$) (Ezepue and Odigi, 1993). The Obajana gneisses (Figure 2) comprise of three types of rocks designated as quartz-biotite gneiss; quartz-biotite-hornblende-pyroxene gneiss and quartzbiotite- garnet gneiss (Odigi and Ezepue, 1993). According to these authors, igneous rocks of this area occur as small, circular to oval outcrops and include members of the older granite suite mainly granites, granodiorites and syenites while associated schists in the area are: quartz-biotite schist, amphibolite schist, muscovite schist and quartzitic schist (Musa *et. al.*, 2013).

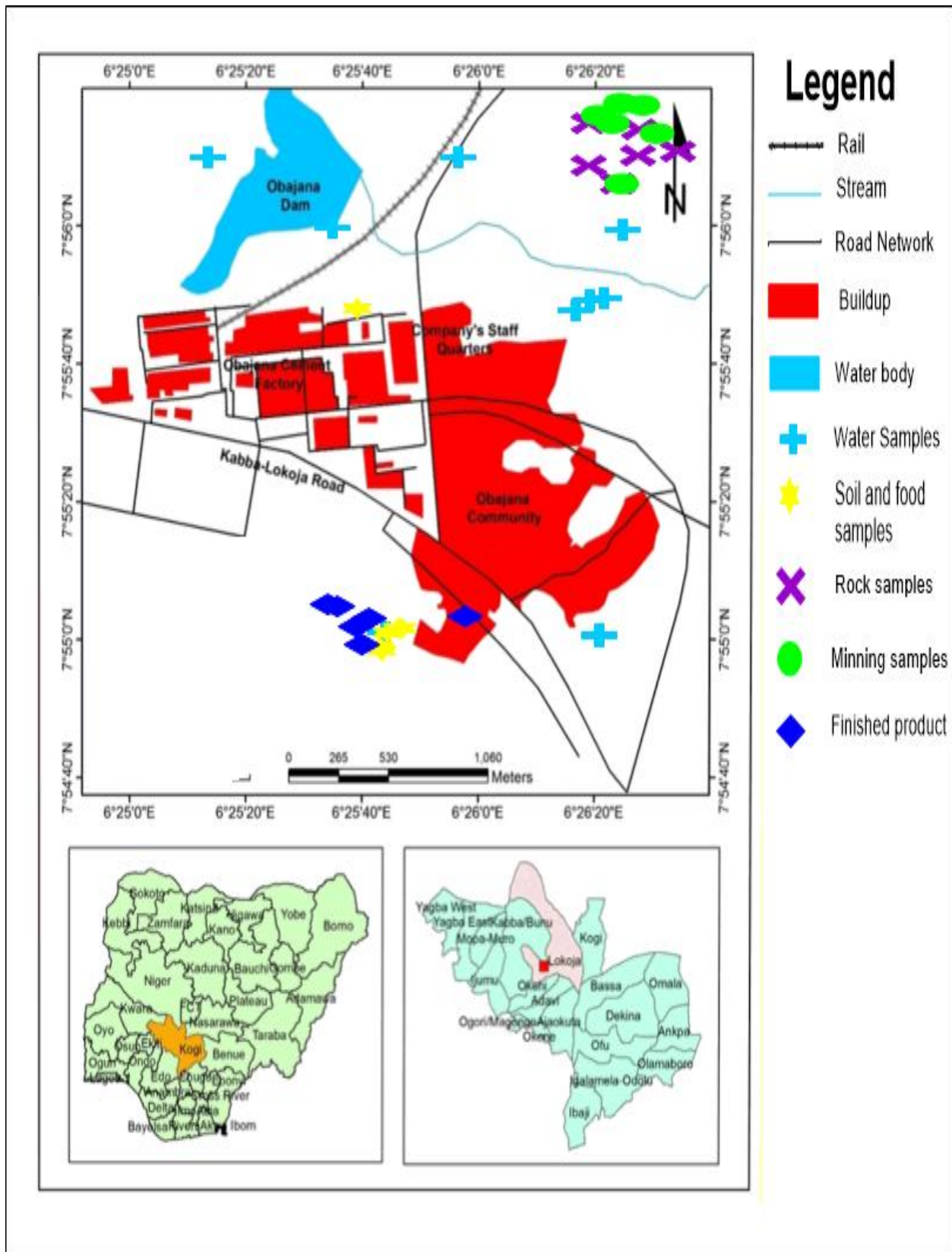


Figure 3.1: The Study Area



Plate 3.1: Quarry Site (Part of Mining area)



Plate 3.2: Part of the Quarry site



Plate 3.3: Part of Settlement around Obajana



Plate 3.4: Nomadic farmer in Obajana



Plate 3.5: A Farmer returning from farm (Stream used for Domestic purpose)



Plate 3.6: Road leading to the Quarry site

3.4 Calibration of Spectrometer

The accuracy of the quantitative measurements depends on the calibration of the spectrometer, adequate energy, and background measurement. Calibrating the detector system is important so as to identify and quantify the radionuclide present in a sample. The procedure for identifying the radionuclide in a sample is based on the proper channel-energy calibration. In this case, the gamma energy produced is directly proportional to the height of a specific pulse and its corresponding channel number (N). However, the correct quantification of radioactivity in a sample depends on proper detection efficiency calibration (Bello, 2012).

3.4.1 Efficiency and Resolution of NaI(Tl) Detector

Due to the large size and high density of NaI(Tl) crystal used as the active volume of the detector, they usually have higher efficiency compared to germanium detectors. However, the energy resolution of scintillators is poor which makes them unsuitable in situation where many closely spaced gamma ray energies must be separated or in the detection of weak sources of discrete energies when superimposed on a broad continuum (Knoll, 2000).

The efficiency can be calculated using the relationship below.

$$E_p = \frac{C}{A\gamma mt} \text{-----} (3.1)$$

where E_p is the detection efficiency, C is the net count above the background after counting a reference sample of known activity A ($\text{Bq}\cdot\text{kg}^{-1}$), m is the mass (kg) for a time, t (s) and γ is the gamma yield.

3.4.2 Radioactivity Counting

Each sample will be counted for 36,000 seconds and the background was subtracted from them to obtain the Net count for each sample. The Uranium content of the samples was determined from the intensity of the 1.760 MeV photo-peak of ^{214}Bi , the Thorium content from

the 2.614 MeV photopeak of ^{209}Th and Potassium content from the 1.460 MeV photopeak of ^{40}K decay.

3.4.3 Background Count

A sealed empty container of the same dimensions as those used for the samples will be put inside the Scintillation counter and the background count for each of the radionuclide will be obtained after 36,000 seconds.

3.5 Sample Counting

Radioactive decay is a random counting process that is described quantitatively in statistical terms. Therefore repeatedly counting radioactive transformations in a sample under identical conditions will not necessarily result in identical values. The result of counting sample radiation is as follows:

$$\text{Number of sample counts} = N_s \text{ (Net counts)} \text{-----} \quad (3.2)$$

The standard deviation of the sample counts, based on Poisson statistics, is:

$$\text{Standard deviation of sample counts} = \delta_s = \sqrt{N_s} \text{-----} \quad (3.3)$$

Noise originating in the background, also a random process, simultaneously generates counts that are indistinguishable from those originating in the sample, and therefore the total or gross counts observed from counting a sample including background counts.

$$\text{Gross sample counts} = N_g = N_s + N_b \text{-----} \quad (3.4)$$

where N_s = sample counts (Net counts), N_b = background counts.

It follows that the counts due to sample radioactivity are obtained by subtracting the background noise count from the sample gross counts (Bello, 2012).

$$N_s = N_g - N_b \text{-----} \quad (3.5)$$

The counting rate due to sample radioactivity is

$$R_s = N_s/t_s \text{-----} (3.6)$$

where t_s = sample counting interval.

The sample counting rate can also be expressed as:

$$R_s = R_g - R_b = (N_g/t_g) - (N_b/t_b) \text{-----} (3.7)$$

where R_g = gross sample count rate,

R_b =background counting rate.

t_g =gross sample count interval, and

t_b =background counting interval.

3.5.1 Standard Deviation and Confidence Levels

The standard deviation is a measure of the dispersion of values at a random variable about the mean value (Bello, 2012). It is a precise indicator of the degree of variability within a set of numbers. The standard deviation of the net counts δ_{N_s} is given by:

$$\delta_{N_s} = \sqrt{(\delta_{N_g}^2 + \delta_{N_b}^2)} \text{-----} (3.8)$$

Where δ_{N_g} = standard deviation of the gross sample counting rate, and δ_{N_b} = standard deviation of the background counting rate.

The net count sample plus or minus one standard deviation is reported as

$$N_s \pm \delta_{N_s} = N_s \pm \sqrt{(\delta_{N_g}^2 + \delta_{N_b}^2)} \text{-----} (3.9)$$

3.6 Activity Concentration

The activity concentrations of the samples will be determined using the net counts after correcting for background and Compton contribution. The activity concentrations of ^{232}Th , ^{226}Ra and ^{40}K were obtained using:

$$A_c = \frac{C_{net}}{I_\lambda \times E_{ff} (E_\lambda) \times m \times t} \text{-----} (3.10)$$

where C_{net} is the net peak counts, I_λ is absolute gamma decay intensity for the specific energy photopeak (including the decay branching ratio information). $E_{\text{ff}}(E_\lambda)$ is the absolute efficiency of the detector at this energy and m is the mass of the sample in kg.

3.7 Secular Equilibrium

Secular equilibrium can only occur in a radioactive decay chain if the half-life of the daughter radionuclide B is much shorter than the half-life of the parent radionuclide. In such a situation, the decay rate of parent radionuclide, and hence the production rate of daughter radionuclide, is approximately constant, because the half-life of parent radionuclide is very long compared to the timescales being considered. The quantity of radionuclide daughter radionuclide builds up until the number of daughter atoms decaying per unit time becomes equal to the number being produced per unit time; the quantity daughter of radionuclide then reaches a constant, equilibrium value. Assuming the initial concentration of daughter radionuclide is zero, full equilibrium usually takes several half-lives of daughter radionuclide to establish (Oladipo, 2012).

The quantity of daughter radionuclide when secular equilibrium is reached is determined by the quantity of its parent and the half-lives of the two radionuclide. This can be seen from the time rate of change of the number of atoms of radionuclide daughter:

$$\frac{dN_B}{dt} = \lambda_A N_A - \lambda_B N_B \text{ ----- (3.11)}$$

where λ_A and λ_B are the decay constants of radionuclide A and B, related to their half-lives $t_{1/2}$ by $\lambda = \ln(2) / t_{1/2}$ and N_A and N_B are the number of atoms of A and B at a given time.

Secular equilibrium occurs when

$$\frac{dN_B}{dt} = 0 \text{ Or } N_B = \frac{\lambda_A}{\lambda_B} N_A \text{ ----- (3.12)}$$

3.8 Determination of Radiation Hazard Indices

To get clearer information on radiation effects around the cement factory including the effects on the environment the following health hazard indices were estimated (Agbalaba et. al, 2012):

- a) Radium equivalent activity index (Ra_{eq});
- b) Representative level index (I_γ);
- c) Absorbed dose rate (D);
- d) Annual effective dose rate;
- e) External hazard index (H_{ex}); and
- f) Internal hazard index (H_{in}).

a. Radium equivalent activity index (Ra_{eq})

To represent the activity levels of ^{40}K , ^{226}Ra , and ^{232}Th by a single quantity, which takes into account the radiation hazards associated with them, a common radiological Index has been introduced (Diab et al., 2008). This Index is called Radium equivalent (Ra_{eq}) activity and is mathematically defined by (UNSCEAR, 2000):

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_k \text{ ----- (3.13)}$$

where C_k , C_{Ra} , and C_{Th} are the activity concentrations of ^{40}K , ^{226}Ra , and ^{232}Th respectively. In the above relation, it has been assumed that 10 Bqkg⁻¹ of ^{226}Ra , 7 Bqkg⁻¹ of ^{232}Th and 130 Bqkg⁻¹ of ^{40}K produce equal gamma dose. The maximum value of Ra_{eq} in soil must be less than 370 Bqkg⁻¹.

b. Representative level index (I_γ)

Another radiation hazard index used for the estimation of gamma radiation associated with the natural radionuclides in the soil called the representative level index (I_γ).

$$I_\gamma = \frac{C_{Ra}}{150} + \frac{C_{Th}}{100} + \frac{C_k}{150} \leq 1 \text{ ----- (3.14)}$$

The safety value for this index is ≤ 1

c. Absorbed Dose Rate (D)

The absorbed dose rates in outdoor and indoor (D) due to gamma radiations in air at 1 m above the ground surface for the uniform distribution of the naturally occurring radionuclides (^{40}K , ^{226}Ra , and ^{232}Th) were calculated based on guidelines provided by (UNSCEAR, 2000).

$$D(\text{nGy}^{-1}) = 0.462C_{Ra} + 0.621C_{Th} + 0.0417C_k \text{ ----- (3.15)}$$

$$D(\text{nGy}^{-1}) = 0.92C_{Ra} + 1.1C_{Th} + 0.08C_k \text{ ----- (3.16)}$$

d. Annual Effective Dose Rate

To estimate the annual effective dose rates outdoor and Indoor, one has to take into account the conversion coefficient from absorbed dose in air to effective dose (0.7 Sv Gy^{-1}) and outdoor occupancy factor (0.2) and 0.8 for outdoor and indoor respectively proposed by (UNSCEAR, 2000) are used. Therefore, the annual effective dose rate (mSv yr^{-1}) was calculated by the formula (UNSCEAR, 2000):

$$OAE(\text{mSvyr}^{-1}) = D_{out}(\text{nGyh}^{-1}) \times 8760\text{hr}^{-1} \times 0.7 \times 10^{-6} \times 0.2$$

$$OAE(\text{mSvyr}^{-1}) = D_{out} \times 1.2264 \times 10^{-3} \text{ -----(3.17)}$$

$$IAE(\text{mSvyr}^{-1}) = D_{in}(\text{nGyh}^{-1}) \times 8760\text{hr}^{-1} \times 0.7 \times 10^{-6} \times 0.8$$

$$IAE(\text{mSvyr}^{-1}) = D_{in} \times 4.9056 \times 10^{-3} \text{ ----- (3.18)}$$

$$TAE(mSvyr^{-1}) = OAE + IAE \quad \text{-----} \quad (3.19)$$

where TAE is the mean Total annual effective dose equivalent, OAE is Outdoor annual effective dose equivalent and IAE is Indoor annual effective dose equivalent.

The worldwide annual effective dose from the natural sources of radiation in areas of normal background is estimated to be 1 mSv⁻¹ by UNSCEAR (1993).

e. External Hazard Index (H_{ex})

A widely used hazard Index (reflecting the external exposure) called the External hazard index H_{ex} is defined as follows (UNSCEAR, 2000).

$$H_{ex} = \frac{C_{Ra}}{370} + \frac{C_{Th}}{259} + \frac{C_k}{4810} \quad \text{-----} \quad (3.20)$$

f. Internal Hazard Index (H_{in})

In addition to external hazard index, radon and its short- lived products are also hazardous to the respiratory organs. The internal exposure to radon and its daughter progenies is quantified by the internal hazard index H_{in}, which is given by the equation.

$$H_{in} = \frac{C_{Ra}}{185} + \frac{C_{Th}}{259} + \frac{C_k}{4810} \quad \text{-----} \quad (3.21)$$

The values of the indices (H_{ex}, H_{in}) must be less than unity for the radiation hazard to be negligible (Diab et al., 2008).

g. Transfer Factor (TF)

The soil-to-plant TF measured the transfer of radionuclides from soil to plant taken through the plant roots. From observed activity concentrations of the radionuclide in the plant and in the corresponding soil, the TF values were calculated according to the equation below (Shayamal et al., 2013).

$$Tf = \frac{\text{Activity concentration in plant}}{\text{Activity concentration in soil}} \quad \text{-----} \quad (3.22)$$

The values of the indices (Tf) must be less than unity for the radiation hazard to be negligible.

h. Excess Life time Cancer Risk (ELCR):

This is potential carcinogenic effects that are characterized by estimating the probability of cancer incidence in a population of individuals for a specific lifetime from projected intakes and exposures. This was calculated using mathematical expression of equation 2.14 (Taskin et al, 2009).

$$ELCR = TAE \times DL \times RF \text{-----} (3.23)$$

where AEDE is the Annual Effective Dose Equivalent, DL is the average Duration of Life (assumed to be 70years) and RF is the Risk Factor (fatal cancer risk factor which is 0.05 Sv^{-1}).

i. Annual Gonad Equivalent Dose (AGED):

This is a measure of threat to sensitive cells from exposure to a particular level of radiation. These sensitive cells include the gonads, surface cells and the bone marrow. Annual gonadal equivalent dose is calculated using the equation (Ajibode et al., 2013).

$$AGED (\text{mSvyr}^{-1}) = 3.09C_{Ra} + 4.18C_{Th} + 0.314C_K \text{-----} (3.24)$$

where C_{Ra} , C_{Th} , C_K are activity concentrations of ^{226}Ra , ^{232}Th , and ^{40}K respectively.

j. Aerial Dose rate Values (ADV)

The environmental reading at each sampling location was recorded with the aid of digital survey meter in ($\mu\text{Sv/hr}$). The dose was converted to (mSv/yr) with the given equation below, in order to obtain the annual dose rate value.

$$ADV = \text{Environmental reading } (\mu\text{Sv/h}) \times 24\text{h} \times 365 \text{-----} (3.25)$$

k. Ingestion dose to human

The annual effective ingestion dose to an adult member of the public due to the intake of natural radionuclides from consumption of food crops in the study area has been computed using the following relation (Jabbar et al. 2009)

$$E_{ingest} = \sum(A_i^r \times U^i) \times D_{cfr} \text{ ----- (3.26)}$$

where E_{ingest} is the annual effective dose per year (mSvyr^{-1}), A_i^r is the activity concentration of radionuclide r , U^i is the annual intake of food type i , D_{cfr} is the ingestion dose conversion factor for the radionuclides of interest, $2.8 \times 10^{-7} \text{ SvBq}^{-1}$ for ^{226}Ra , $2.3 \times 10^{-7} \text{ SvBq}^{-1}$ for ^{232}Th and $6.2 \times 10^{-9} \text{ SvBq}^{-1}$ for ^{40}K (IAEA 2011).

3.9 Heavy metal assessment Index (Statistical Technique)

In the statistical technique, indices were applied to assess the contamination load in soil. There are two types of indices i.e., single index and integrated index. Integrated indices are the geo-statistical techniques applied on aggregate elemental contaminants rather than single elements pollution, but each of integrated indices could be obtained from single pollution load index as suggested by Qingjie and Jun (2008).

3.9.1 Contamination factor

Contamination factor (CF) is also called single pollution index (PI). Contamination factor is the quotient obtained by dividing the concentration of metals related to the target area by reference area. Their results are mostly associated with single pollution load, while their n-root was used for integrated pollution load index. The contamination factor can be calculated through the following formula as suggested by Harikumar et al. (2009).

$$CF = C_n / B_n \text{ ----- (3.27)}$$

In the above equation, C_n is the concentration of metals in the target area, and B_n is the metals concentration of the reference area.

Table 3.1: Classification of contamination factor.

Contamination factor	Classification
$CF < 1$	Low
$1 \leq CF < 3$	Moderate
$3 \leq CF < 6$	Considerable
$CF \geq 6$	Very high

(Hakanson, 1980)

3.9.2 Geo-accumulation index

Geo-accumulation index is used to quantify the degree of anthropogenic or geogenic accumulated pollutant loads in soil and can be determined through the following formula:

$$I_{geo} = \log_2(C_n/1.5B_n) \text{ -----(3.28)}$$

where C_n and B_n are the determined concentration of metals in the target and reference areas respectively. The factor 1.5 is possible anthropogenic variations of contaminants in reference areas (Fagbote and Olanipekun, 2010). The classification of the index is tabulated below.

Table 3.2: Classification of geo-accumulation Index

Geo accumulation Index	Classification	Level of Contamination
$5 < I_{geo} \leq 10$	6	Extremely Serious
$4 < I_{geo} \leq 5$	5	Strong to Extremely Serious
$3 < I_{geo} \leq 4$	4	Strong
$2 < I_{geo} \leq 3$	3	Moderate to Strong
$1 < I_{geo} \leq 2$	2	Moderate
$0 < I_{geo} \leq 1$	1	Light to Moderate
$I_{geo} \leq 0$	0	Non Contamination

(Hakanson, 1980)

3.9.3 Ecological risk factor

Ecological risk index (ERI) is critical to measure both risk factor and metals concentrations in soil. The potential ecological risk index can be determined through the following formula:

$$ERI = CF * TRF \text{-----} (3.29)$$

where ERI is the potential ecological risk factor/index, TRF represents the toxic-response factor, and CF represents contamination factor. The toxic response values for some of the toxic and trace elements are As=10, Cr=2, Cd=30, Cu=5, Pb=5, Ni=5, and Zn=1 as suggested by Hakanson (1980).

Table 3.3: Classification of Ecological risk factor.

Potential Ecological Risk	Classification
PER<40	Low
40≤PER<80	Moderate
80≤PER≤160	Considerable
160≤PER≤320	High
PER≥320	Very high

(Hakanson, 1980)

3.9.4 Pollution load index

Pollution load index (PLI) is simple statistical technique used to determine elemental contents in soil beyond the reference concentration and provide comprehensive information about the metals toxicity in respective samples (Yang et al.2011). Pollution load index can be determined through the following formula:

$$PLI = \sqrt[n]{CF_1 * CF_2 * CF_3 * \dots * CF_n} \text{ ----- (2.30)}$$

where PLI represents the pollution load index, CF is the contamination factor, and n is the number of elements. The $PLI > 1$ indicates polluted, while $PLI < 1$ indicates no pollution

3.9.5 Hazard Quotient

The soil Hazard Quotient (HQ) is the ratio of the heavy metal concentration of surveyed soil samples to reference permissible limit and is computed using the relation;

$$HQ = C_c / C_p \text{ ----- (2.31)}$$

where C_p and C_c = reference maximum permissible limit of heavy metal concentration and the concentration obtained in the sampled area respectively. The maximum allowed limits were set by W.H.O and the Romanian guideline and weretabulated in table 3.4 and 3.5.

Table 3.4: Maximum Allowed concentration limits of some toxic metals in soil (mg/kg).

Toxic Metal	WHO Maximum Allowed limits(mg/kg)
Nickel(Ni)	80
Copper(Cu)	30
Cadmium(Cd)	3.0
Chromium(Cr)	100.0
Lead(Pb)	100.0
Zinc(Zn)	300

(WHO, 1996)

Table 3.5: Romanian guidelines on toxic metals level permitted in soil for pollution assessment.

Element	Literature Values		Romanian norms				
	European median in soil	World median	NV*	ALS*	ALLS*	ITS*	ITLS*
As	7.03	6	5	15	25	25	50
Cd	0.145	0.35	1	3	5	5	10
Cr	60	70	30	100	300	300	600
Cu	13	30	20	100	250	200	500
Ni	18	50	20	75	200	150	500
Pb	22.6	35	20	50	250	100	1000
Zn	52	90	100	300	700	600	1500

*NV=normal value; ALS and ITS=Alert level and Intervention threshold in the sensitive area; ALLS and ITLS=Alert level and Intervention threshold in the less sensitive area (Hakanson,1980).

3.10 Field Measurement and Sampling

3.10.1 Introduction

The field measurements and sampling were made at different locations of the Dangote Cement Company and environment, which are the marble mine site, the industrial processing site and the villages around the factory. Also dust particles emanating from the factory were trapped for analysis. Representative samples of soil and crop close to the factory were also collected. For the purpose of comparison with outside environment free from the cement production activities going on at the study area, field measurements and soil sampling were made at three other locations namely, Along Kabba-Road, Ebunu and Lokoja, to serve as controls.

3.10.2 In-situ Measurement

In-situ measurements of gamma radiation were made based on the assumption that there exists laterally uniform distribution of natural radionuclides in the environment and that the vertical contribution from soil is limited to the first horizon (Ibeanu, 1999). These measurements were made with a portable survey meter (Rados model RDS 120) having sensitivity range of $0.05\mu\text{Svh}^{-1}$ - 10Svh^{-1} .

3.10.3 Samples Collection

3.10.3.1 *Soil Samples*

The soil samples were collected randomly with the aid of hand steel geological auger at a depth of 100 cm. A global Position System (GPS) was used to measure longitude and latitude at each sampling location. The collected samples were packed in well-labelled polyethene bags and taken to the laboratory at Center for Energy Research and Training (CERT) for preparation.

3.10.3.2 *Water Samples*

At each sampling point, 2.0L plastic container was used for the collection of the water sample. Sample containers were rinsed with distilled water to minimize contamination. Hand dug shallow well water samples were collected directly from wells of varying depths (5.0 to 10.0m). For the borehole waters, before samples were collected the taps were first turned on at full capacity for a few minutes to purge the plumbing system (Tchokossa et al., 1999). The samples of river/stream waters were collected from the host community domestic water fetching spot using the grab sampling method as reported by Avwiri and Agbalagba (2007).

3.10.3.3 *Cassava Samples*

The Cassava samples were collected randomly with the aid of a hoe from the farms. A Global Positioning System (GPS) was used to measure longitude and latitude at each sampling location. The collected samples were packed in well-labelled polyethylene bags and taken to the laboratory at Center for Energy Research and Training (CERT) for preparation.

3.10.3.4 *Rock Samples*

The samples were collected randomly from rock located around the Obajana environment. A Global Positioning System (GPS) was used to measure longitude and latitude at each sampling location. The collected samples were packed in well-labelled polyethylene bags and taken to the laboratory at Center for Energy Research and Training (CERT) for preparation.

3.10.3.5 *Cement (Finished product) sample*

The samples were collected directly from the production plant of the Obajan cement factory. The collected samples were packed in well-labelled polyethylene bags (500g) and taken to the laboratory at Center for Energy Research and Training (CERT) for preparation.

Table 3.6 Summary of sample collected

Types of Samples	Numbers
Soil sample	12
Water (well, Stream and borehole water)	10
Rock sample	08
Cultivated Crop	06
Cement (Finished product)	06
Total	40

3.11 Sample Preparation and Analysis

Sample preparations were based on the sample type and the intended analytical technique used.

3.11.1 Soil Sample (NORMS Measurement)

The soil samples collected were air dried for 72hrs under laboratory temperature. The samples were then ground and packed to fill already weighed cylindrical plastic containers of dimension 7.2cm in diameter and 6.0cm high to satisfy the selected best sample container height that will adequately match the detector's dimensions, which allowed for the adequate covering of the detector shield (Ibeanu, 1999). Before sealing, the mass of each sample was determined and recorded.

The sealing of the sample containers were done in three stages, namely, vaseline wax sealing, candle wax sealing and the use adhesive masking tape, all done to prevent the escape of ^{222}Rn gas. The samples were then stored for a minimum period of four weeks to achieve an approximate secular equilibrium between Rn and Th, and their respective progeny before commencing their gamma spectrometry analysis.

In order to determine the activity concentrations of uranium, thorium, and potassium in the soil samples, NaI(Tl) detector gamma spectrometry described in chapter two was chosen as the analytical method. The choice was based on its efficiency, cheapness, speed of analysis, relative ease of sample preparations and the simplicity of the data reduction procedures.

In this gamma spectrometer, the characteristic photon energy is measured and used to quantify the different radionuclides. This is made possible by recording the count rate in distinct energy windows specific for the gamma radiation energy of a particular nuclide (Ibeanu, 1999).

3.11.2 Cassava Sample

The samples collected were air dried under laboratory temperature. The samples were then ground and packed to fill already weighed cylindrical plastic containers of dimension 7.2cm in diameter and 6.0cm high to satisfy the selected best sample container height that will adequately match the detector's dimensions, which allowed for the adequate covering of the detector shield (Ibeanu, 1999). Before sealing, the mass of each sample was determined and recorded.

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3.11.3 Water Sample

The samples were acidified immediately after collection with 2 ml of nitric acid solution (HNO_3) to the container in order to prevent the growth of micro-organism. Evaporation was done in the laboratory using hot plates, without stirring and at moderate heat in an open 600 ml beaker. It took an average of about 16 hrs to complete the evaporation of one liter of each sample. During evaporating process, the samples were transferred into petri dish, when level of samples in the beakers were about 50 ml. The sample were later placed under infrared source to completely dry the residue. The samples were allowed to cool before weighing was done.

The prepared samples were counted to determine alpha and beta activity concentration using the low background Gas-less Alpha/Beta counting system (Protean Instrument Corporation (PIC) MPC 2000DP), calibrated with alpha (^{239}Pu) and (^{90}Sr) standards. The system used a solid state

silicon (passivated implanted Planar Silicon, PIPS) detector for alpha and beta detection. The samples were counted for 200 min. The alpha and beta efficiency were determined to 87.95% and 42.06% respectively. The Detection limit of the alpha and beta activity concentration were 0.16 and 1.47 cpm respectively. The background reading of the alpha and beta activity concentration were 0.14 and 77.82 cpm. All the measurement was done at Low Background Laboratory, at Center for Energy Research and Training, Ahmadu Bello University Zaria, Nigeria.

3.11.4 Sample preparation and Analysis for AAS

The samples (100 ml) were transferred quantitatively into beakers, concentrated HNO₃ acid (10ml) and concentrated HCl (5 ml) in ratio (2:1) were added and heated on a hot plate making sure the sample did not boil, until the volume was reduced to about 15 ml. The samples were then allowed to cool, filtered and quantitatively transferred into a 100 ml standard volumetric flask and made up to mark with distilled water. Solution of samples were then taken and aspirated into Atomic Absorption Spectrophotometer (Unicam Solar A.A.S 969 model) for analyzing metals. A calibration graph was plotted for each element using measured absorbance and the corresponding concentration. The calibration curve was used to determine the concentration of the metal. The water sample and ground rock sample were analysed using ASS.

3.11.5 Sample Preparation and Analysis for NAA

3.11.5.1 Sample Size

There has been a strong emphasis on the small size of sample required to determine trace elements. Consequently, a weighing balance will be used to measure the quantity of sample to be irradiated. The quantity of sample varies according to category of matrix in Table 3.3.

Table 3.7: Sample size for Different Sample Categories

Sample Category	Sample size (g)
Biological	0.2500 – 0.3000
Liquid	0.2500 – 0.3000
Geological	0.1500 – 0.2000

(Jonal et al., 2006)

3.11.5.2 *Sample Preparation*

The weighted samples was transfered into pre-treated polyethylene bags and sealed with a hot soldering iron into 7cm³ rabbit capsules. Thereafter, the capsules were packaged into bigger vials in readiness for irradiation. Hand gloves, spatula and forceps were used in the process of the packaging. After preparation of each sample, the hand gloves were changed and spatula thoroughly cleaned to avoid cross-contamination.

3.11.5.3 *Sample Irradiation*

Neutron Irradiation is the exposure of a sample to neutron radiation in a reactor. The vials containing the rabbit capsules sent to the reactor irradiation sites using the channels (sites): B₁, B₂, B₃, and B₄. B₁, and B₃, are called the inner irradiation channels, while B₂ and B₄ are the outer irradiation channels with B₁ being dedicated solely to those nuclides with very short half-lives. Sample irradiations were done based on two protocols:- short irradiation for radionuclides with short half-lives elements and long irradiation for radionuclides with long-half lives elements.

Table 3.8: Irradiation and Counting Regimes for Geological Samples

Protocol	Irradiation Time	Counting Time	Sample Geometry
First (short)	1 minute	600 seconds	H2
Second (short)	600 seconds	600 seconds	H1
First (long)	6 hours	1800 seconds	H1
Second (long)	6 hours	3600 seconds	H1

(Jonal et al., 2006)

3.11.5.4 *Counting Regimes/Analytical procedures*

The process of using a very sensitive (high resolution) gamma spectrometer to register gamma rays is called counting. The NIRR-1 operates two Hyperpure Germanium (HeGe) detectors that operate at liquid nitrogen temperature. The computer-coupled multichannel analyzer sorts the delayed gamma according to their energies. The gamma ray acquisition system was used for the measurement of associated radioactivity (Onoja, 2015).

3.12 Statistical Analysis

There are many softwares used for statistical analysis in various disciplines but the most versatile and widely used is (Excel, 2016), which was used to analyze measured data in this studies. Descriptive statistics, Correlation and Analysis of variance (ANOVA) single factor were the statistical analysis performed in this study.

Correlation analysis

The correlation analysis was used to predict the model and access the strength of the relationship between the measured data in this studies of interest is whether one variable generally increases as the second increases, whether it decreases as the second increases, or whether their patterns of variation are totally unrelated.

Measures of correlation (here designated in general as ρ) have the characteristic of being dimensionless and scaled to lie in the range $-1 \leq \rho \leq 1$. When there is no correlation between two variables, $\rho = 0$. When one variable increases as the second increases, ρ is positive. When they vary in opposite directions, ρ is negative. The significance of the correlation is evaluated using a hypothesis test: $H_0: \rho = 0$ versus $H_1: \rho \neq 0$. When one variable is a measure of time or location, correlation becomes a test for temporal or spatial trend.

ANOVA (Single Factor)

The mean comparison test of one way ANOVA was used to test variance between two measured data. It compares the mean values of each group with overall mean of the entire data set. The ANOVA used the null hypothesis to test the variance associated with mean.

Measurement of ANOVA here designated as P-value (P-Probability) and F- ratio (the ratio of the Mean Sum of Squares (MS) between groups and within groups of measured Data).

If $P < 0.05(\alpha)$, $F > F_c$, i.e Reject null hypothesis. Therefore the data are Significant (it is effective).

If $P > 0.05(\alpha)$, $F < F_c$, i.e Reject null hypothesis. Therefore the data are Significant (not effective).

CHAPTER FOUR

RESULTS AND DISCUSSION

Table 4.1: Results obtained from field.

S/No.	Sample ID	Gamma Dose rate ($\mu\text{Sv/h}$)	Geographical Coordinate	
			Longitude	Latitude
Water Samples				
1	WW1	0.13	6 ⁰ 26'35.71"E	7 ⁰ 58'10.99"N
2	WW2	0.12	6 ⁰ 26'30.03"E	7 ⁰ 58'12.33"N
3	WW3	0.10	6 ⁰ 26'26.44"E	7 ⁰ 58'11.72"N
4	WW4	0.12	6 ⁰ 26'26.55"E	7 ⁰ 58'05.96"N
5	WW5	0.10	6 ⁰ 26'21.88"E	7 ⁰ 58'06.31"N
6	WW6	0.15	6 ⁰ 26'28.83"E	7 ⁰ 55'20.94"N
7	WW7	0.11	6 ⁰ 25'25.73"E	7 ⁰ 55'16.15"N
8	BH	0.10	6 ⁰ 26'28.71"E	7 ⁰ 55'20.42"N
9	STRM 1	0.11	6 ⁰ 26'35.66"E	7 ⁰ 58'11.02"N
10	STRM 2	0.12	6 ⁰ 25'27.16"E	7 ⁰ 55'21.77"N
Soil Samples				

11	SS1	0.12	6 ⁰ 25'18.81"E	7 ⁰ 58'07.13"N
12	SS2	0.15	6 ⁰ 25'31.62"E	7 ⁰ 55'24.30"N
13	SS3	0.10	6 ⁰ 25'30.81"E	7 ⁰ 55'24.20"N
14	SS4	0.15	6 ⁰ 25'27.77"E	7 ⁰ 55'21.75"N
15	SS5	0.12	6 ⁰ 25'25.48"E	7 ⁰ 55'14.93"N
16	SS6	0.49	6 ⁰ 25'25.90"E	7 ⁰ 55'13.17"N
Food Sample				
17	FS1	0.12	6 ⁰ 25'18.81"E	7 ⁰ 58'07.13"N
18	FS2	0.15	6 ⁰ 25'31.62"E	7 ⁰ 55'24.30"N
19	FS3	0.10	6 ⁰ 25'30.81"E	7 ⁰ 55'24.20"N
20	FS4	0.15	6 ⁰ 25'27.77"E	7 ⁰ 55'21.75"N
21	FS5	0.12	6 ⁰ 25'25.48"E	7 ⁰ 55'14.93"N
22	FS6	0.49	6 ⁰ 25'25.90"E	7 ⁰ 55'13.17"N
Rock Sample				
23	RS1	0.19	6 ⁰ 26'39.74"E	7 ⁰ 59'25.56"N
24	RS2	0.20	6 ⁰ 26'40.23"E	7 ⁰ 59'38.66"N
25	RS3	0.15	6 ⁰ 26'25.91"E	7 ⁰ 59'20.14"N
26	RS4	0.11	6 ⁰ 26'51.30"E	7 ⁰ 59'27.38"N
27	RS5	0.13	6 ⁰ 26'25.71"E	7 ⁰ 59'41.53"N
28	RS6	0.21	6 ⁰ 26'34.15"E	7 ⁰ 59'11.29"N
Mining Samples				
29	MS1	0.11	6 ⁰ 26'32.77"E	7 ⁰ 59'41.35"N
30	MS2	0.12	6 ⁰ 26'34.62"E	7 ⁰ 59'52.43"N
31	MS3	0.10	6 ⁰ 26'45.15"E	7 ⁰ 59'36.27"N
32	MS4	0.13	6 ⁰ 26'41.28"E	7 ⁰ 59'51.20"N
33	MS5	0.11	6 ⁰ 26'28.21"E	7 ⁰ 59'45.45"N
34	MS6	0.12	6 ⁰ 26'35.10"E	7 ⁰ 59'11.30"N
Finished Product				

35	FP1	0.14	6 ⁰ 25'10.41"E	7 ⁰ 55'36.15"N
36	FP2	0.15	6 ⁰ 25'22.35"E	7 ⁰ 55'28.50"N
37	FP3	0.12	6 ⁰ 25'18.47"E	7 ⁰ 55'24.42"N
38	FP4	0.11	6 ⁰ 25'20.39"E	7 ⁰ 55'15.30"N
39	FP5	0.10	6 ⁰ 25'50.31"E	7 ⁰ 55'30.28"N
40	FP6	0.11	6 ⁰ 25'13.24"E	7 ⁰ 55'34.50"N

Table 4.2: Activity concentration of ²²⁶Ra, ²³²Th and ⁴⁰K in Soil

S/No	Sample Location	Activity Concentration (BqKg ⁻¹)			
		²²⁶ Ra	²³² Th	⁴⁰ K	²³² Th: ²²⁶ Ra
1	SS1	35.3219±3.7559	81.5083±1.6907	460.0204±5.3628	2.3
2	SS2	26.9709±2.8369	53.7491±1.3368	259.2374±9.8139	2.0
3	SS3	40.1966±3.5961	44.1946±1.6514	226.0417±11.2619	1.1
4	SS4	79.1545±2.9168	74.4702±1.5728	282.8337±5.5237	0.9
5	SS5	49.5065±3.8758	88.1925±2.4378	1204.5910±12.2272	1.8
6	SS6	52.6232±4.9147	123.3044±3.0669	1178.1520±7.5079	2.3
	Average	47.2956±18.1941	77.56985±27.9676	601.8127±463.8799	1.7
	World Standard	32.0000	45.0000	420.0000	1.4

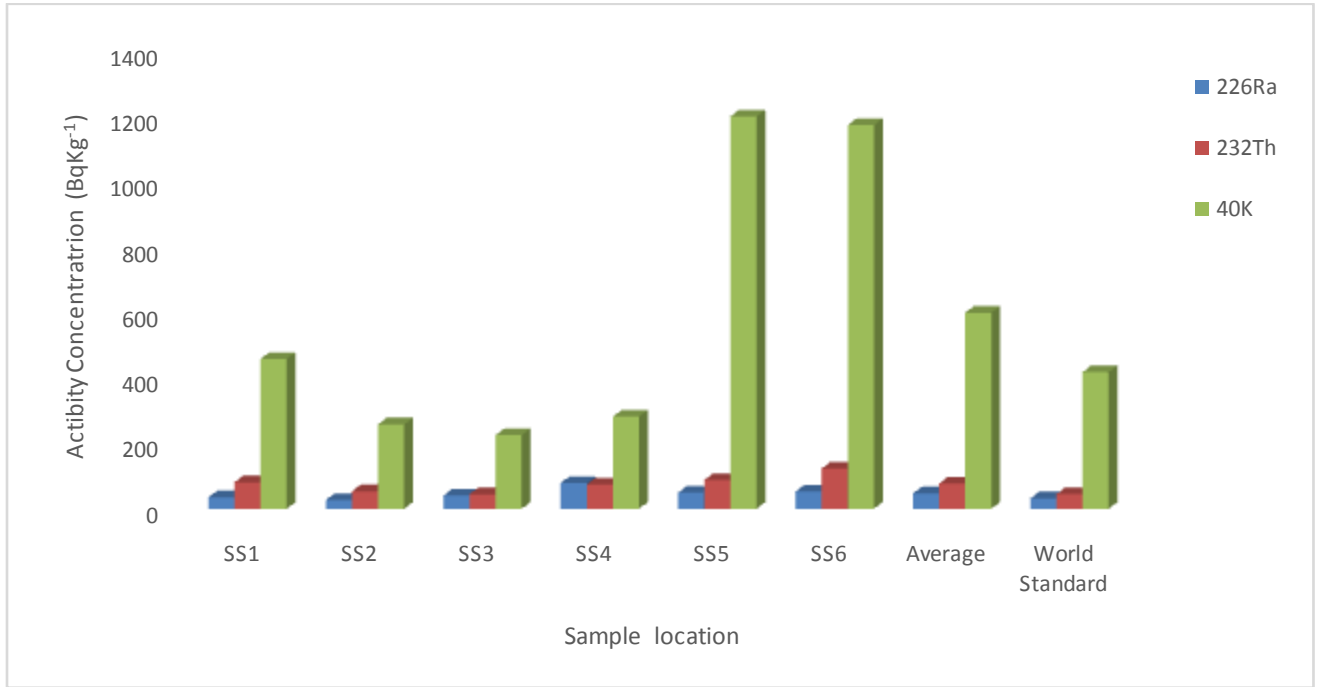


Figure 4.1: Activity concentration of ^{226}Ra , ^{232}Th and ^{40}K in Soil

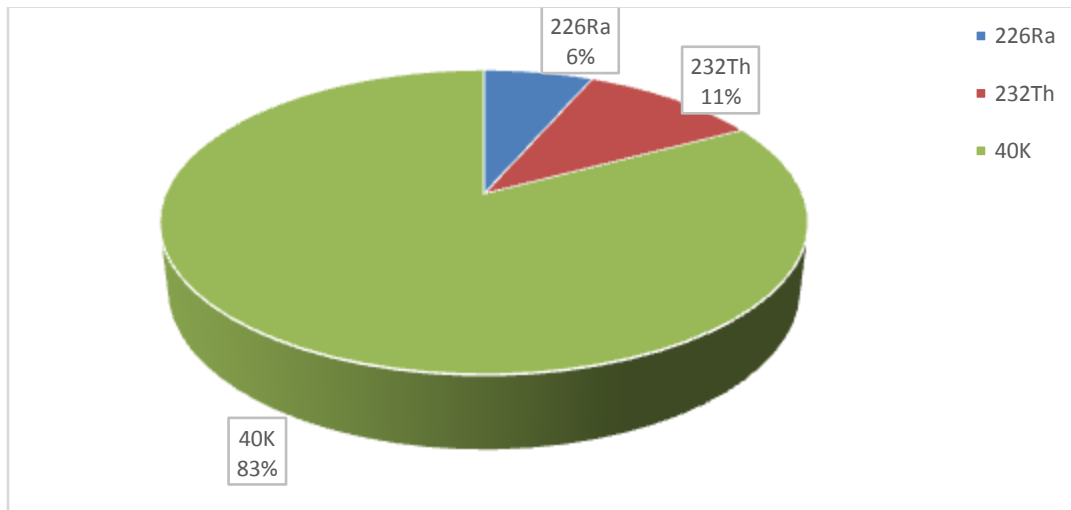


Figure 4.2: Average Percentage contribution of ^{226}Ra , ^{232}Th and ^{40}K in Soil

4.1 Activity concentration of NORM's

4.1.1 Activity concentration of ^{226}Ra , ^{232}Th and ^{40}K in Soil

Specific activity concentrations were determined for farm soil samples in different cultivated farm land of Obajana community. The measured activity concentrations of ^{226}Ra ranged from $(26.9709 \pm 2.8369 - 79.1545 \pm 2.9168)$ BqKg^{-1} , with mean activity concentration of $47.2956 \text{ Bqkg}^{-1}$. Also measured activity concentrations of ^{232}Th range from $(44.1946 \pm 1.6514 - 123.3044 \pm 3.0669)$ Bqkg^{-1} , with mean activity concentration of $77.5699 \text{ Bqkg}^{-1}$. The activity concentrations of ^{40}K range from $(226.0417 \pm 11.2619 - 1204.591 \pm 12.2272)$ Bqkg^{-1} , with mean activity concentration of $601.8127 \text{ Bqkg}^{-1}$. All the mean activity concentrations were above the corresponding world average concentration of 32 Bqkg^{-1} for ^{226}Ra , 45 Bqkg^{-1} for ^{232}Th and 420 Bqkg^{-1} for ^{40}K (UNSCEAR, 2000). The high concentration might be attributed to cement production activities and geological formation of the area, which could significantly increase the concentration of radionuclide in the farm soil particles.

The thorium to radium concentration ratio ($^{232}\text{Th} : ^{226}\text{Ra}$) was found to be 1.7 (Table 4.2), which is slightly higher than the world standard value of 1.4 given by UNSCEAR (UNSCEAR, 2000), this means that ^{232}Th activity concentration is higher than that of ^{226}Ra in the farm soil as shown in Figure 4.2.

Table 4.3:Radiological indices in soil

Location			Absorbed Dose(nGy ⁻¹)		Annual Effective Dose(mSvY ⁻¹)			Hazard Index		ELCR	AGED	ADV
	Ra _{eq} (Bqkg ⁻¹)	I _γ	D _{out}	D _{in}	OAE	IAE	TED	(H _{ex})	(H _{in})	(x 10 ⁻³)	(mSvY ⁻¹)	(mSvY ⁻¹)
SS1	187.300	1.357	86.118	158.957	0.106	0.780	0.885	0.506	0.601	3.099	594.296	1.051
SS2	123.793	0.890	56.649	104.676	0.069	0.513	0.583	0.334	0.407	2.040	389.412	1.314
SS3	120.800	0.861	55.442	103.678	0.068	0.509	0.577	0.326	0.435	2.018	379.918	0.876
SS4	207.425	1.461	94.610	177.366	0.116	0.870	0.986	0.560	0.774	3.451	644.683	1.314
SS5	268.375	2.015	127.871	238.925	0.157	1.172	1.329	0.725	0.859	4.651	899.861	1.051
SS6	319.666	2.369	150.013	278.300	0.184	1.365	1.549	0.863	1.005	5.422	1047.958	4.292
Average	204.560	1.493	95.117	176.984	0.117	0.868	0.985	0.552	0.680	3.447	659.355	1.650
World Standard	370.000	1	60.000		1	1		1	1	0.29	300	1

4.1.2 Assessment of radiological effects around the soil.

The Potential radiological effects due to external and internal radiation exposures can be assessed for the natural radionuclides ^{226}Ra , ^{232}Th and ^{40}K by deducting radium equivalent (Ra_{eq}), absorbed dose rates (D), annual effect dose (H), annual gonadal dose equivalent (AGDE) as well as external and internal radiation hazard index (Hex). The potential radiological effects of Obajana farm soil is as shown in Table 4.3.

(a) Radium equivalent (Ra_{eq})

The radium equivalent due to activity concentrations of Natural radionuclides in the farm soil was calculated using equation 3.13 (UNESCEAR, 2000). The Ra_{eq} ranged from 120.800 to 319.666 Bqkg^{-1} with mean value of 204.560 Bqkg^{-1} . All the farm soils around Obajana cement company were below the world standard of (370 Bqkg^{-1}). For exposure of NORMS. Therefore, the soil from the cultivated farm area around the company is safe for farming but a proper attention and soil monitoring could be given to the area due to cement production around the area.

(b) The Absorbed Dose Rate (D)

The absorbed dose rates outdoor and indoor (D) due to gamma radiations in air at 1m above the ground surface for the uniform distribution of the naturally occurring radionuclides (^{40}K , ^{226}Ra , and ^{232}Th) were calculated using equation (3.15) and (3.16) respectively. The absorbed dose rates outdoor (D_{out}) ranged from 55.442 to 150.013 nGy^{-1} with mean value of 95.117 nGy^{-1} . Also, absorbed dose rates indoor (D_{in}) ranged from 103.678 to 278.300 nGy^{-1} with mean value of 176.984 nGy^{-1} . The mean value of outdoor absorbed dose rate was greater than the world standard of 60 nGy^{-1} as shown in Table

4.3. This might be due to cement production activities and geological formation of the area.

(c) Annual effective dose (H)

The annual effective dose to the population due to activity concentration of NORM in obajana farm soil was calculated by summing up the outdoor and indoor annual effective dose using equation (3.17) and (3.18) respectively. The outdoor annual effective dose ranged from 0.069 to 0.184 mSv with mean value of 0.117 mSv and the indoor annual effective dose ranged from 0.509 to 1.365 mSv with mean value of 0.868 mSv. All the average value of the Annual effective dose around the farm were below the world standard of 1 (UNSCEAR, 2000).

(d) Representative level Index (I_γ)

The Representative Level Index was used to estimate gamma radiation associated with the natural radionuclides in the farm soil around Obajana. The values obtained ranged from 0.861 to 2.369 with mean value of 1.493. The mean value of representative level index is slightly above the world standard of Unity (ICRP, 2000). Therefore, It is of no cause for concern.

(e) External and Internal Hazard indices (H_{ex} and H_{in}).

The objective of hazard index is to keep value less than unity (ICRP, 2000). The mean H_{ex} and H_{in} values were found to be 0.552 and 0.680 using equation (3.20) and (3.21), respectively. The mean value of H_{ex} and H_{in} were below the world standard of unity (ICRP, 2000). It is of no cause for concern but subsequence monitoring should be done at regular interval.

(f) Annual Gonadal Dose Equivalent (AGDE)

The AGDE was computed using equation (3.24). The AGDE ranged from (379.918 to 1047.958) mSvy⁻¹ with mean value of 659.355 mSvy⁻¹. The mean value was twice above the world standard of 300 mSvy⁻¹ as shown in table 4.3.

(g) Excess life Time Cancer Risk (ELCR).

This is potential carcinogenic effects that are characterized by estimating the probability of cancer incidence in a population of individuals for a specific lifetime from projected intakes and exposures from the farm soil. This was calculated using mathematical expression of equation (3.23). The ELCR ranged from (2.018 to 5.442) x10⁻³ with mean value of 3.447x10⁻³. The mean value was above the world standard of 0.29 x10⁻³ as shown in table 4.3.

(h) Aerial Dose Rate Values

The aerial dose rate was calculated using equation (3.25). The ADV ranged from (0.876 – 4.292) mSv with mean value of 1.650 mSv. The mean value of ADV is slightly above the world standard of Unity (ICRP, 2000). It is of no cause for concern.

Table 4.4: Activity concentration of ²²⁶Ra, ²³²Th and ⁴⁰K in Marble Mining Site

S/No	Sample Location	Activity Concentration (BqKg ⁻¹)			
		²²⁶ Ra	²³² Th	⁴⁰ K	²³² Th: ²²⁶ Ra
1	MS1	24.5335±3.1566	61.9274±1.6514	542.7146±6.0600	2.5
2	MS2	34.2031±2.1976	49.0701±1.6514	193.9186±6.1672	1.4
3	MS3	36.9601±4.8348	55.8330±1.4155	287.2312±6.9716	1.5
4	MS4	31.0465±2.7970	74.5488±2.5951	392.1810±7.6152	2.4
5	MS5	21.2171±4.3153	30.9834±1.9266	484.5820±5.6309	1.5
6	MS6	13.1058±1.3186	87.5634±1.1796	273.5561±4.2366	6.7
	Average	26.84435±8.9431	59.98768±19.7682	362.3639±134.3564	2.7
	World Standard (UNSCEAR, 2000)	32.0000	45.0000	420.0000	1.4

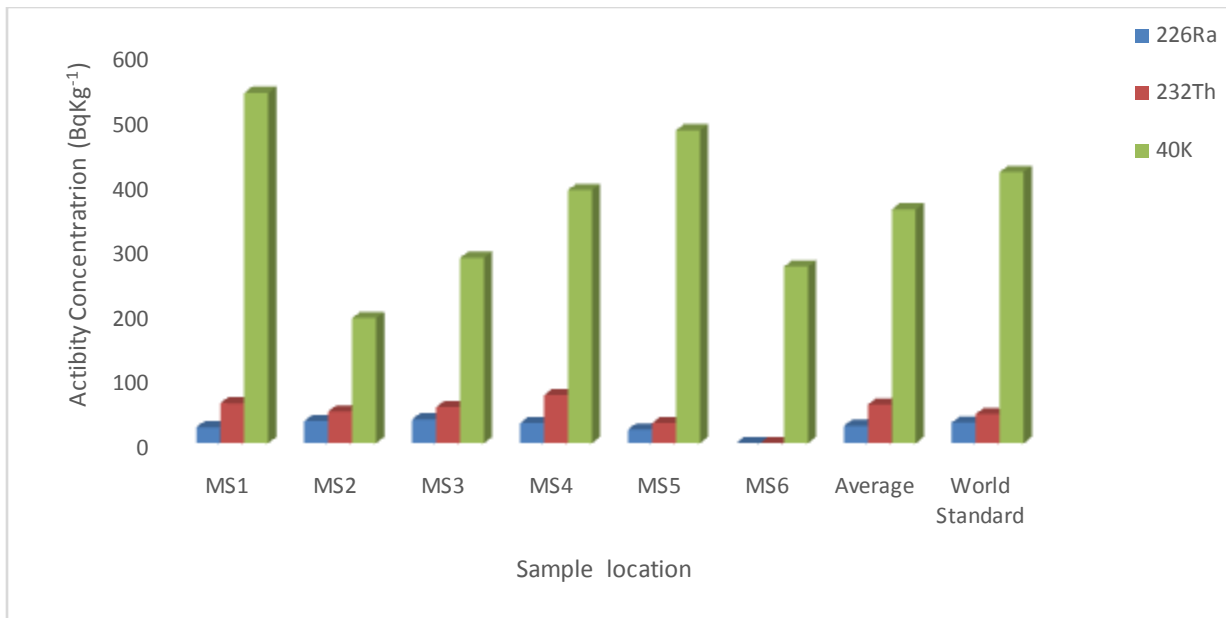


Figure 4.3:Activity concentration of ^{226}Ra , ^{232}Th and ^{40}K in Marble Mining site

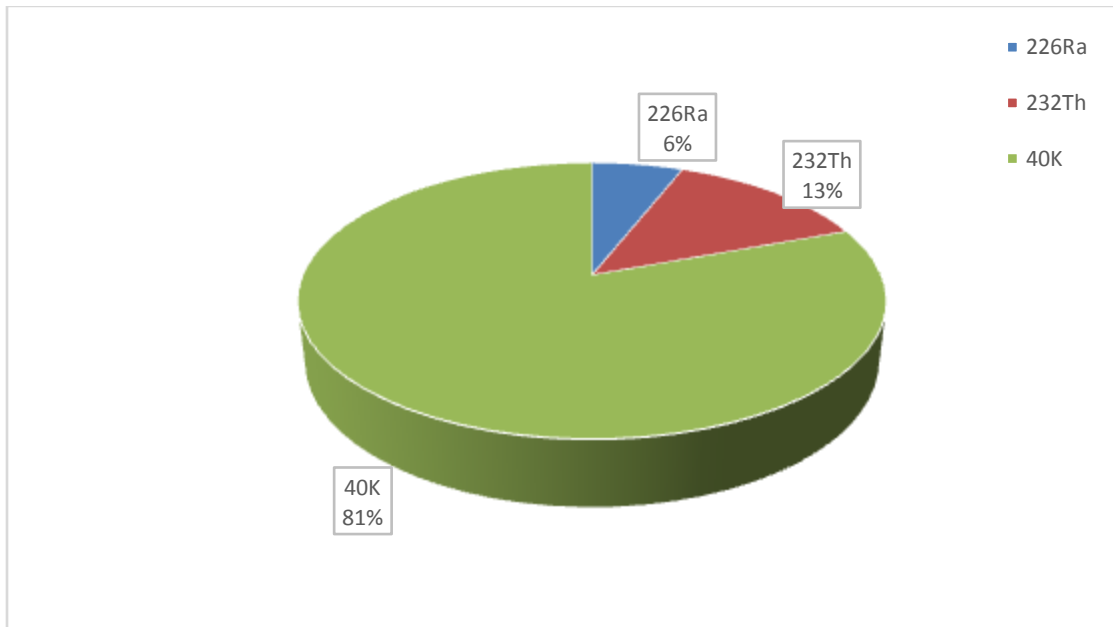


Figure 4.4: Percentage contribution of ^{226}Ra , ^{232}Th and ^{40}K in Marble Mining site

Table 4.5: Average activity concentrations of Soils and other related studies.

Location	Region	Activity Concentration (Bqkg ⁻¹)			References
		²²⁶ Ra	²³² Th	⁴⁰ K	
Obajana (Farmland)	North Central	47.29±18.19	77.57±27.97	601.81±463.88	Present Study
Obajana (Mining Site)	North Central	26.84±8.94	59.99±19.76	362.36±134.35	Present Study
Nasarawa	North Central	23.52	56.23	403.963	Ibrahim et al. (2013)
Kebbi	North west	23.85	18.80	425.96	Girigisu et al. (2014)
Sikiti	South west	15.6	195.3	304.20	Bello (2012)
Ekiti (Farmland)	South west	14.6	19.6	1023.3	Isinkaye (2012)
Abak	South South	24.826	5.172	98.709	Chad-Umoren and Umoh (2014)
Ghana	Volta	25.8±92.12	29.56±2.60	190.01±3.90	Addo et al. (2012)
Denmark		9 – 29	8 – 30	240 – 610	(UNSCEAR, 2000)
USA	Louisiana	64(34-95)	36(4-130)	472(43-719)	(UNSCEAR, 2000)
Egypt	Cairo	5.3 – 66.8	5 – 37.3	41.5 – 418	Nada et al. (2009)
Poland		5 – 120	4 – 77	110 – 970	(UNSCEAR, 2000)
Switzerland		10 – 900	4 – 70	40 – 1000	(UNSCEAR, 2000)

4.1.3 Activity concentration of ^{226}Ra , ^{232}Th and ^{40}K in Marble Mining site

The Natural radioactivity due to exposure of top surface associated with marble mining activities and mining waste, around the mining site in Obajana cement factory was determined as shown in Table 4.4. The activity concentration of mining samples collected from Obajana ranged between $(13.1058 \pm 1.3186 - 36.9601 \pm 4.8348) \text{ Bqkg}^{-1}$, $(30.9834 \pm 1.9266 - 87.5634 \pm 1.1796) \text{ Bqkg}^{-1}$ and $(193.9186 \pm 6.1672 - 542.7146 \pm 6.0600) \text{ Bqkg}^{-1}$ for ^{226}Ra , ^{232}Th and ^{40}K respectively with the average value $26.84435 \pm 8.9431 \text{ Bq.kg}^{-1}$, $59.98768 \pm 19.7682 \text{ Bq.kg}^{-1}$, and $362.3639 \pm 134.3564 \text{ Bq.kg}^{-1}$ for ^{40}K , ^{226}Ra and ^{232}Th respectively. The mean activity concentrations of ^{232}Th was above the corresponding world average concentration of 45 Bqkg^{-1} for ^{232}Th (UNSCEAR, 2000). The slight high concentration of ^{232}Th in the mining area might be due to exposure of the top soil around the mining site to mining activities.

The Thorium to Radium concentration ratio ($^{232}\text{Th} : ^{226}\text{Ra}$) was found to be 2.7 (Table 4.4), which is higher than the world average value of 1.4 given by UNSCEAR (UNSCEAR, 2000), this means that ^{232}Th activity concentration is higher than that of ^{226}Ra in the mining site soil samples as shown in Figure 4.4.

Table 4.5 compares the activity concentrations of ^{226}Ra , ^{232}Th , and ^{40}K in the mining soil samples observed in the present study was compared with related published studies in different part of the world. In comparison, it was found that the range of ^{226}Ra and ^{232}Th were higher compared to worldwide values. However, the values for ^{40}K is almost matching those of other studies. The high level of ^{226}Ra and ^{232}Th might attribute to cement production activities and geological formation of soil around the cement factory.

Table 4.6:Radiological indices in Mining Site

Location	$Ra_{eq}(Bqkg^{-1})$	I_{γ}	Absorbed Dose(nGy^{-1})		Annual Effective Dose($mSvY^{-1}$)			Hazard Index		ELCR	AGED	ADV
			D_{out}	D_{in}	OAE	IAE	TED	(H_{ex})	(H_{in})	$(\times 10^{-3})$	$(mSvY^{-1})$	$(mSvY^{-1})$
MS1	154.879	1.145	72.423	134.108	0.089	0.658	0.747	0.418	0.485	2.613	505.077	0.964
MS2	119.305	0.848	54.361	100.957	0.067	0.495	0.562	0.322	0.415	1.967	371.691	1.051
MS3	138.918	0.996	63.725	118.398	0.078	0.581	0.659	0.375	0.475	2.306	437.779	0.876
MS4	167.849	1.214	76.992	141.940	0.094	0.696	0.791	0.453	0.537	2.768	530.693	1.139
MS5	102.836	0.774	49.250	92.368	0.060	0.453	0.514	0.278	0.335	1.797	347.230	0.964
MS6	159.385	1.145	71.839	130.262	0.088	0.639	0.727	0.430	0.466	2.545	492.409	1.051
Average	140.529	1.020	64.765	119.672	0.079	0.587	0.667	0.379	0.452	2.233	447.480	1.007
World Standard	370.000	1	60.000		1	1		1	1	0.29	300	1

4.1.4 Assessment of radiological Indices around the marble Mining Site.

The potential radiological effects of natural radionuclides (^{226}Ra , ^{232}Th and ^{40}K) around the mining site was determined using the following radiological Hazard index.

(a) Radium equivalent (Ra_{eq})

The Radium equivalent around the mining site ranged from (102.835 - 167.894) with mean value of 140.529 using equation (3.13). All the recorded value of Ra_{eq} around the mining site were below the recommended value of (370 Bq kg^{-1}) for exposure of NORM. Indicating that the mining site is safe for mining exploration, but adequate monitoring should be taken at regular interval in order to prevent environmental contamination around the area.

(b) The Absorbed Dose (D)

The absorbed dose rates outdoor (D_{out}) ranged from 49.250 to 76.992 nGy^{-1} with mean value of 64.765 nGy^{-1} . Also, absorbed dose rates indoor (D_{in}) ranged from 92.368 to 141.940 nGy^{-1} with mean value of 119.672 nGy^{-1} . The mean value of outdoor absorbed dose rate was slightly greater than the world standard of 60 nGy^{-1} as shown in Table 4.6.

(c) The Annual Effective Dose (H)

The annual effective dose to the population was found using 3.17, 3.18 and 3.19. The outdoor annual effective dose ranged from 0.060 to 0.094 mSv with mean value of 0.079 mSv and the indoor annual effective dose ranged from 0.453 to 0.696 mSv with mean value of 0.587 mSv. The average value of the Annual total effective (TED) dose around the mining was below the world standard of 1 (UNSCEAR, 2000).

(d) Representative level Index (I_γ)

It ranged from 0.774 to 1.145 with mean value of 1.020. The mean value of representative level index around the mining area is slightly above the world standard of Unity (ICRP, 2000). It is of no cause for concern.

(e) External and Internal Hazard indices (H_{ex} and H_{in}).

The mean H_{ex} and H_{in} values around the mining site were found to be 0.552 and 0.680 using equation (3.20) and (3.21), respectively. The mean value of H_{ex} and H_{in} were below the world standard of unity (ICRP, 2000). It is of no cause for concern.

(f) Annual Gonadal Dose Equivalent (AGDE)

The AGDE was computed using equation (3.24). The AGDE ranged from (347.230 to 530.693) $mSv\,y^{-1}$ with mean value of 447.480 $mSv\,y^{-1}$. The mean value was slightly above the world standard of 300 $mSv\,y^{-1}$.

(g) Excess life Time Cancer Risk (ELCR).

The ELCR was calculated using mathematical expression of equation (3.23). It ranged from (1.797 - 2.768) $\times 10^{-3}$ with mean value of 2.233 $\times 10^{-3}$. The mean value was above the world standard of 0.29 $\times 10^{-3}$ as in table 4.8

(h) Aerial Dose Rate Values

The aerial dose rate was calculated using equation (3.25). The ADV ranged from (0.876 – 1.139) mSv with mean value of 1.007 mSv . The mean value of ADV is slightly above the world standard of Unity (ICRP, 2000). It is of no cause for concern.

Table 4.7: Activity concentration of ^{226}Ra , ^{232}Th and ^{40}K in Finished Product

S/No	Sample Location	Activity Concentration (BqKg^{-1})			
		^{226}Ra	^{232}Th	^{40}K	$^{232}\text{Th}: ^{226}\text{Ra}$
1	FP1	28.8488±1.1587	38.2967±1.1796	84.8930±3.8076	1.3
2	FP2	45.3910±3.9557	48.6769±0.9830	128.1171±5.2019	1.1
3	FP3	60.1351±8.5508	90.1191±6.2124	179.3318±11.4227	1.5
4	FP4	7.4719±1.9179	29.4892±1.1009	140.7197±3.9685	3.9
5	FP5	35.9612±2.7570	47.1435±1.0616	214.8871±8.4732	1.3
6	FP6	38.1987±3.0767	41.5209±0.7077	131.6029±6.2208	1.1
	Average	36.0011±17.5529	49.2077±21.1908	146.6098±45.0115	1.7
	World Standard (UNSCEAR, 2000)	32.0000	45.0000	420.0000	1.4

Table 4.8: Comparison of the mean values of ^{226}Ra , ^{232}Th , ^{40}K in the studied cement samples with other related studies.

Country	Cement brand	Activity Concentration (BqKg^{-1})			References
		^{226}Ra	^{232}Th	^{40}K	
Nigeria	Dangote (Obajana)	36.0 ± 17.6	49.2 ± 21.2	146.6 ± 45.0	Present Study
Nigeria	BUA	44.7 ± 12.5	32.5 ± 11.0	275.3 ± 27.7	Agbalagba et al. (2014)
Nigeria	Portland	43.80	21.50	71.7	Ademola (2008)
Brazil		61.70	58.50	564.00	Malanca et al. (1993)
Cameroon		16.62 ± 47.61	12.50 ± 32.46	ND	Ndontchueng et al. (2013)
Ghana	Diamond	35.94	25.44	251.00	Kpeglo et al. (2011)
Italy		38.00	22.00	218.00	Rizzo et al. (2001)

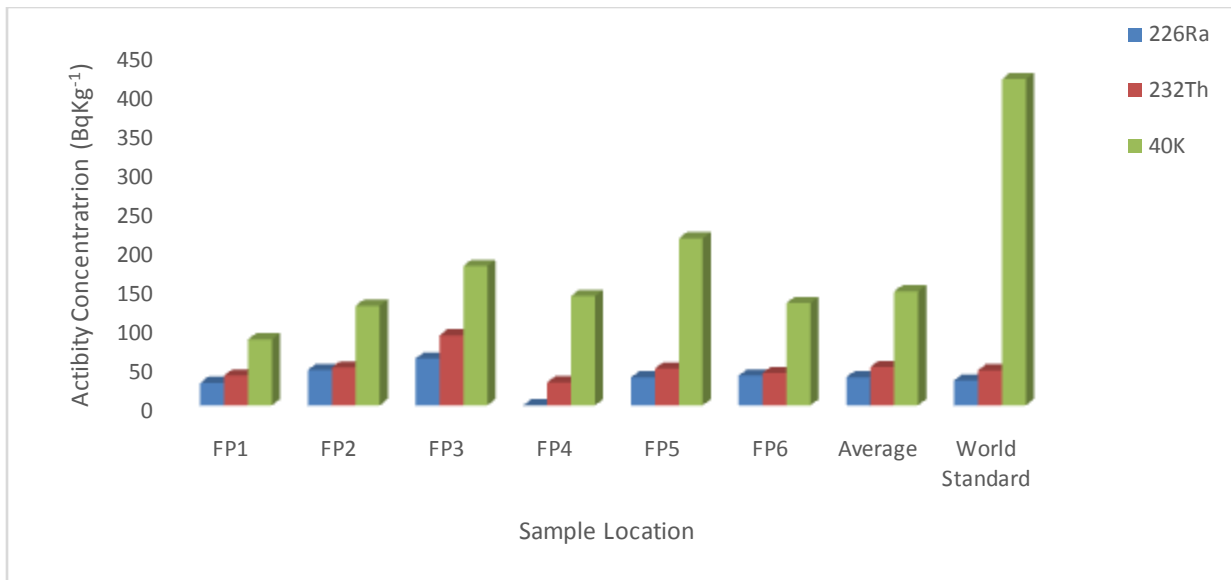


Figure 4.5: Activity concentration of ²²⁶Ra, ²³²Th and ⁴⁰K in Finished product

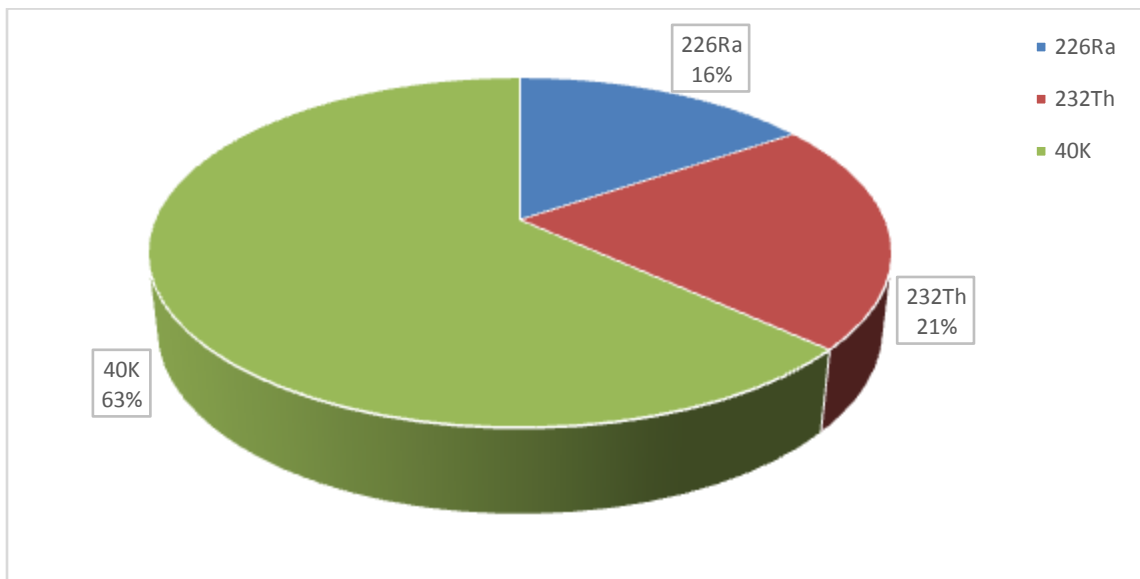


Figure 4.6: Percentage contribution of ²²⁶Ra, ²³²Th and ⁴⁰K in Finished Product

4.1.5 Activity concentration of ^{226}Ra , ^{232}Th and ^{40}K in Finished Product

Table 4.7 shows the activity concentration in different finished product of cement produce in Obajana Factory. The activity concentration of the finished product samples collected from Obajana ranged between $(7.4719 \pm 1.9179 - 60.1351 \pm 8.5508)$ Bqkg^{-1} , $(29.4892 \pm 1.1009 - 90.1191 \pm 6.2124)$ Bqkg^{-1} and $(84.8930 \pm 3.8076 - 179.3318 \pm 11.4227)$ Bqkg^{-1} for ^{226}Ra , ^{232}Th and ^{40}K respectively with the average value 36.0011 ± 17.5529 Bqkg^{-1} , 49.2077 ± 21.1908 Bqkg^{-1} , and 146.6098 ± 45.0115 Bqkg^{-1} for ^{40}K , ^{226}Ra and ^{232}Th respectively. The activity concentrations of ^{226}Ra and ^{232}Th were slightly above the corresponding world average concentration of 32 Bqkg^{-1} for ^{226}Ra and 45 Bqkg^{-1} for ^{232}Th (UNSCEAR, 2000). The high concentration might be attributed to material composition used for cement production in Obajana Cement Factory.

The thorium to radium concentration ratio ($^{232}\text{Th} : ^{226}\text{Ra}$) was found to be 1.7 (Table 4.6), which is slightly higher than the world average value of 1.4 given by UNSCEAR (UNSCEAR, 2000), this means that ^{232}Th activity concentration is higher than that of ^{226}Ra in the cement product of Obajana factory as shown in Figure 4.6.

Table 4.8 shows the comparison of average specific concentration of natural radionuclides of Obajana cement product with other cement brands observed within and outside Nigeria. It reveals that ^{232}Th was higher compares to other brands both ^{226}Ra and ^{40}K compares favorably with other cement brands. The high value of ^{232}Th , might be due to the Raw material formulation and Nature of the raw materials used for cement production in Obajana cement factory.

Table 4.9:Radiological indices in Finished Products (Cement)

Location			Absorbed Dose(nGy ⁻¹)		Annual Effective Dose(mSvY ⁻¹)			Hazard Index		ELCR	AGED	ADV
	Ra _{eq} (Bqkg ⁻¹)	I _γ	D _{out}	D _{in}	OAE	IAE	TED	(H _{ex})	(H _{in})	(x 10 ⁻³)	(mSvY ⁻¹)	(mSvY ⁻¹)
FP1	90.150	0.632	40.650	75.459	0.050	0.370	0.420	0.243	0.321	1.470	275.879	1.226
FP2	124.864	0.875	56.541	105.554	0.069	0.518	0.587	0.337	0.460	2.055	383.956	1.314
FP3	202.814	1.423	91.225	168.802	0.112	0.828	0.940	0.548	0.710	3.290	618.825	1.051
FP4	60.477	0.439	27.633	50.570	0.034	0.248	0.282	0.163	0.184	0.987	190.539	0.964
FP5	119.923	0.854	54.851	102.133	0.067	0.501	0.568	0.324	0.421	1.989	375.654	0.876
FP6	107.707	0.758	48.920	91.344	0.060	0.448	0.508	0.291	0.394	1.778	332.915	0.964
Average	117.656	0.830	53.303	98.977	0.065	0.486	0.551	0.318	0.415	1.928	362.961	1.066
World Standard	370.000	1	60.000		1	1		1	1	0.29	300	1

4.1.6 Assessment of radiological hazard indices from the Finished Product (Cement).

The potential radiological effects in some selected Finished Product (Cement) of Obajana Cement factory was determine using the follow radiological Hazard index.

(a) Radium equivalent (Ra_{eq})

The Radium equivalent of finished cement product ranged from (60.447 - 202.814) with mean value of 117.656 using equation (3.13). All the recorded value of Ra_{eq} were below the recommended value of (370 Bqkg^{-1}) for exposure of NORM. The low level of the radionuclide content is due to the nature of raw material use for cement production in Obajana cement factory. Indicating that the finished product is safe for building construction, but adequate monitoring of the finished product should be taken at regular interval in order to regulate the radionuclide contain of the raw material, used for cement production in Obajana Cement factory.

(b) The Absorbed Dose (D)

The absorbed dose rates outdoor (D_{out}) ranged from (27.633 – 91.225) nGy^{-1} with mean value of 53.303 nGy^{-1} . Also, absorbed dose rates indoor (D_{in}) ranged from (50.570 - 105.554) nGy^{-1} with mean value of 98.977 nGy^{-1} . The mean value of outdoor absorbed dose rate was slightly lower than the world standard of 60 nGy^{-1} .

(c) The Annual Effective Dose (H)

The outdoor annual effective dose ranged from 0.050 to 0.112 mSv with mean value of 0.065 mSv and the indoor annual effective dose ranged from 0.248 to 0.828 mSv with mean value of 0.486 mSv. The average value of the Annual total effective (TED) dose from the finished was below the world standard of 1 (UNSCEAR, 2000).

(d) Representative level Index (I_γ)

It ranged from 0.439 to 1.423 with mean value of 0.830. The mean value of representative level index from the finished product is slightly below the world standard of Unity (ICRP, 2000). Therefore, it is of no cause for concern.

(e) External and Internal Hazard indices (H_{ex} and H_{in}).

The mean H_{ex} and H_{in} values from finished product of Obajana cements were found to be 0.318 and 0.415 using equation (3.20) and (3.21), respectively. The mean value of H_{ex} and H_{in} were below the world standard of unity (ICRP, 2000). It is of no cause for concern.

(f) Annual gonadal dose equivalent (AGDE)

The AGDE from the finished product was computed using equation (3.24). The AGDE ranged from (190.539 to 618.825) $mSv\,y^{-1}$ with mean value of 363.961 $mSv\,y^{-1}$. The mean value was slightly above the world standard of 300 $mSv\,y^{-1}$.

(g) Excess Life Time Cancer Risk (ELCR).

The ELCR was calculated using mathematical expression of equation (3.23). It ranged from (0.987 - 3.290) $\times 10^{-3}$ with mean value of 1.928 $\times 10^{-3}$. The mean value was above the world standard of 0.29 $\times 10^{-3}$ as shown in table 4.9.

(h) Aerial Dose Rate Values

The aerial dose rate was calculated using equation (3.25). The ADV ranged from (0.876 – 1.314) mSv with mean value of 1.066 mSv . The mean value of ADV is slightly above the world standard of Unity (ICRP, 2000). It is of no cause for concern.

Table 4.10: Activity concentration of ^{226}Ra , ^{232}Th and ^{40}K in Cassava

	Sample Location	Activity Concentration (BqKg^{-1})			
		^{226}Ra	^{232}Th	^{40}K	$^{232}\text{Th}: ^{226}\text{Ra}$
1	FS1	17.2614±4.4752	32.9100±1.0616	157.1835±3.4858	1.9
2	FS2	11.0680±0.1998	29.0961±0.4718	203.4644±4.0757	2.6
3	FS3	16.9017±2.6372	36.0948±2.6737	84.6249±8.0978	2.1
4	FS4	36.8402±3.1566	42.8184±0.6291	160.2403±5.9527	1.2
5	FS5	17.6210±2.5173	51.6258±1.0616	130.4231±4.1830	2.9
6	FS6	22.4158±1.1587	32.2809±3.3421	250.6569±7.6152	1.4
	Average	20.3514±8.8456	37.4710±8.3514	164.4322±57.5398	2.0

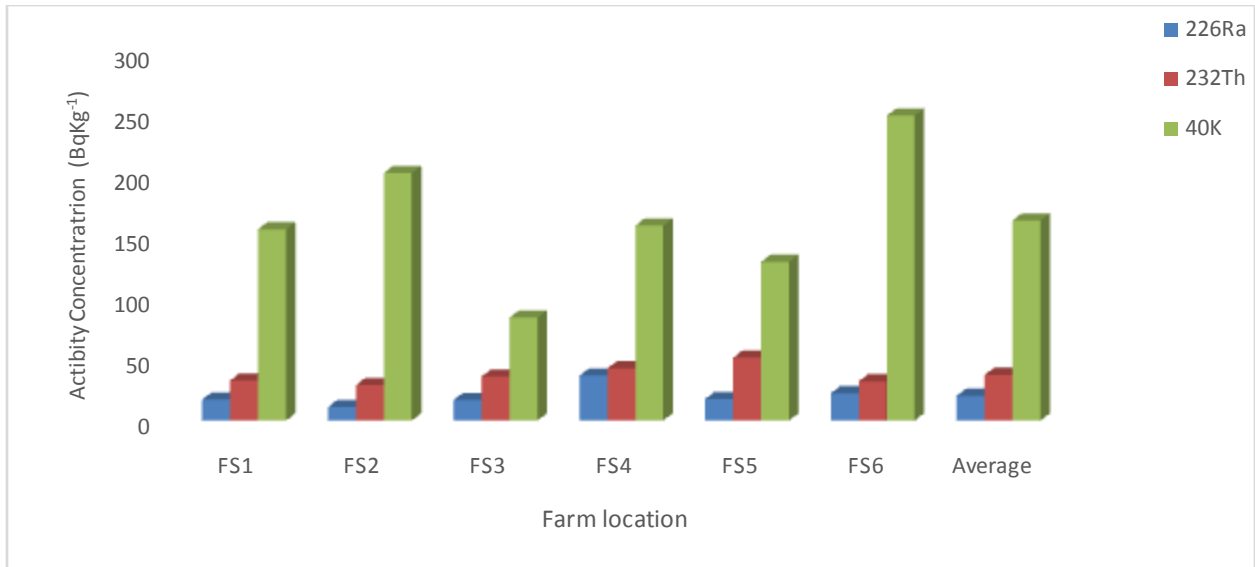


Figure 4.7:Activity concentration of ^{226}Ra , ^{232}Th and ^{40}K in Cassava sample

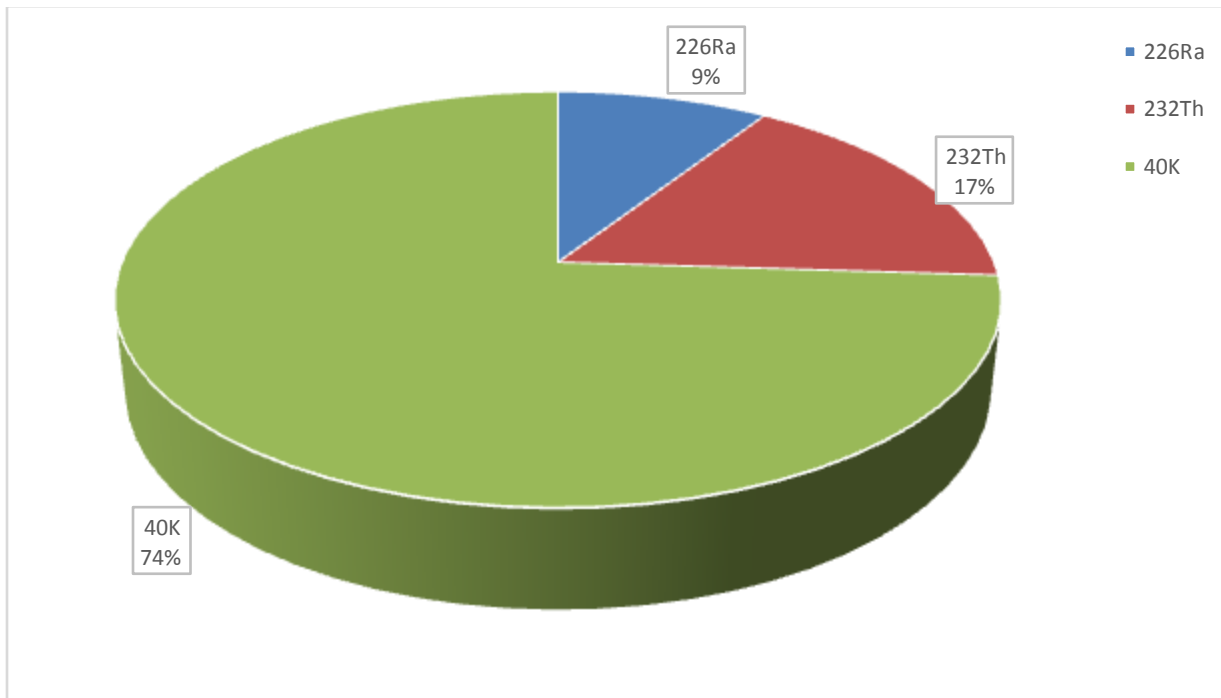


Figure 4.8:Percentage contribution of ^{226}Ra , ^{232}Th and ^{40}K in Cassava

Table 4.11: Comparison of Average radionuclide concentration in Cassavas (*Manihot esculenta*) around Obajana farms with related published studies.

Food type	Region	Activity Concentration (Bqkg ⁻¹)			References
		²²⁶ Ra	²³² Th	⁴⁰ K	
Cassava	Obajana Farm (North Central)	20.35±8.85	37.47±8.35	164.43±57.54	Present Study
Cassava	Ekiti (South west)	1.47±0.91	6.7±2.70	157.54±10.04	Arogunjo et al. 2005
Cassava	Jos (North Central)	27.4±9.4	22.2±5.2	539.6±21.2	Jibiri et al. (2007)
Cassava	Abeokuta (South west)	23.85	18.80	425.96	Jibiri and Abiodun (2012)
Cassava	Ghana (Volta Region)	15.54±1.01	27.97±1.64	447.10±7.47	Addo et al. (2012)
Cassava	Cameroon (south west)	----	17.9±2.0	527.29±46.56	Ele Abiama et al. 2012
Cassava	Brazil (North East)	64(34-95)	36(4-130)	826±27	Cardoso et al. 2013
Cassava	Ile-Ife (South west)	4.16±1.04	8.34±2.79	128.75±8.98	Arogunjo et al. 2005

4.1.7 Activity concentration of ^{226}Ra , ^{232}Th and ^{40}K in Cassava

The selected cultivated food sample used in this study is a tuber crop known as Cassavas (*Manihot esculenta*). The specific activity concentrations were determined in Cassavas (*Manihot esculenta*) around Obajana farms in 18 different cultivated farm land of Obajana. The measured activity concentrations of ^{226}Ra range from $(11.0680 \pm 0.1998 - 36.8402 \pm 3.1566)$ Bqkg^{-1} , with mean activity concentration of 20.3514Bqkg^{-1} . Also measured activity concentrations of ^{232}Th range from $(29.0961 \pm 0.4718 - 51.6258 \pm 1.0616)$ Bqkg^{-1} , with mean activity concentration of 37.4710Bqkg^{-1} . The activity concentrations of ^{40}K range from $(84.6249 \pm 8.0978 - 250.6569 \pm 7.6152)$ Bqkg^{-1} , with mean activity concentration of $164.4322 \text{Bqkg}^{-1}$.

The thorium to radium concentration ratio ($^{232}\text{Th} : ^{226}\text{Ra}$) was found to be 2.0 (Table 4.10), which is slightly higher than the world standard value of 1.4 given by UNSCEAR (UNSCEAR, 2000), this means that ^{232}Th activity concentration is higher than that of ^{226}Ra in the cultivated Cassavas (*Manihot esculenta*) around Obajana farms as shown in Figure 4.8.

The cassava samples were found higher in the radionuclide contents than that of high radiation areas of Abeokuta and Volta Region of Ghana, but was lower than that observed in high elevated radiation areas of Jos-plateau, Cameroon and Brazil (North east) as shown in Table 4.11. The high radionuclide levels in the cassava sample may be attributed to the cement dust infested soils, engineered as the result of activities from the cement factory

Table 4.12: Radiological hazard indices in Cassava Sample

Location	$Ra_{eq}(Bqkg^{-1})$	I_{γ}	Absorbed Dose(nGy^{-1})		Annual Effective Dose($mSvY^{-1}$)			Hazard Index		ELCR	AGED	ADV
			D_{out}	D_{in}	OAE	IAE	TED	(H_{ex})	(H_{in})	($\times 10^{-3}$)	($mSvY^{-1}$)	($mSvY^{-1}$)
FS1	76.426	0.549	34.966	64.656	0.043	0.317	0.360	0.206	0.253	1.260	240.257	1.051
FS2	68.342	0.500	31.666	58.465	0.039	0.287	0.326	0.185	0.214	1.140	219.710	1.314
FS3	75.033	0.530	33.752	62.024	0.041	0.304	0.346	0.203	0.248	1.210	229.675	0.876
FS4	110.409	0.781	50.292	93.812	0.062	0.460	0.522	0.298	0.398	1.827	343.133	1.314
FS5	101.488	0.721	45.639	83.434	0.056	0.409	0.465	0.274	0.322	1.628	311.198	1.051
FS6	87.878	0.639	40.855	76.184	0.050	0.374	0.424	0.237	0.298	1.483	282.905	4.292
Average	86.596	0.620	39.528	73.096	0.049	0.359	0.407	0.234	0.289	1.425	271.146	1.650
World Standard	370.000	1	60.000		1	1		1	1	0.29	300	1

4.1.8 Assessment of radiological hazard indices from Selected Cassavas (*Manihot esculenta*).

The potential radiological effects in Cassavas (*Manihot esculenta*) around Obajana farms were determine using the follow radiological Hazard index.

(a) Ingestion dose to human

The ingest does to human due to consumption of cassava was calculated using equation 3.26. The activity concentration of ^{40}K , ^{226}Ra , and ^{232}Th in the food crop samples collected from the obajana farm land was reported in Table 4.12, reported on a dried weight basis. The total ingested dose in the selected food crop around obajana farm was 4.806 Sv y^{-1} .

(b) Radium equivalent (Ra_{eq})

The Ra_{eq} of the cultivated crops (*Manihot esculenta*) ranged from (68.342 - 110.409) Bq kg^{-1} with mean value of $86.596 \text{ Bq kg}^{-1}$. All the cultivated Cassavas (*Manihot esculenta*) in the selected farms around Obajana cement company where below the world standard of (370 Bq kg^{-1}) for exposure of NORMS. This might be due to geology formation of the farm land area. Therefore, the Cassava tubers from the cultivated farm area around the company is safe for consumption but a proper attention and soil monitoring around cultivated farm vegetation area should be done due to cement production activities.

(c) The Absorbed Dose Rate (D)

The absorbed dose rates outdoor (D_{out}) ranged from 31.666 to 50.292 nGy^{-1} with mean value of 39.528 nGy^{-1} . Also, absorbed dose rates indoor (D_{in}) ranged from 58.465 to 93.812 nGy^{-1} with mean value of 73.069 nGy^{-1} . The mean value of outdoor absorbed

dose rate was lower than the world standard of 60 nGy^{-1} due to low level of radionuclide present in the farm soil and transfer intake from soil to the plant root.

(d) Annual effective dose (H)

The annual effective dose due to activity concentration of NORM was calculated by summing up the outdoor and indoor annual effective dose using equation (3.17) and (3.18) respectively. The outdoor annual effective dose ranged from 0.041 to 0.062 mSv with mean value of 0.049 mSv and the indoor annual effective dose ranged from 0.287 to 0.460 mSv with mean value of 0.359 mSv. All the average value of the Annual effective dose from the selected crops were below the world standard of 1 (UNSCEAR, 2000) table 4.11.

(e) Representative level Index (I_γ)

The Representative Level Index ranged from 0.549 to 0.781 with mean value of 0.620. The mean value of representative level index is below the world standard of Unity (ICRP, 2000) in table 4.12. It is of no cause for concern.

(f) External and Internal Hazard indices (H_{ex} and H_{in})

The mean H_{ex} and H_{in} values were found to be 0.234 and 0.289 using equation (3.20) and (3.21), respectively. The mean value of H_{ex} and H_{in} were below the world standard of unity (ICRP, 2000). It is of no cause for concern but subsequence monitoring to check the cultivated food sample should be done at regular interval.

(g) Annual gonadal dose equivalent (AGDE)

The AGDE was computed using equation (3.24). The AGDE ranged from (219.710 to 311.198) mSvy^{-1} with mean value of 271.146 mSvy^{-1} . The mean value was below the world standard of 300 mSvy^{-1} in table 4.12.

(h) Excess life Time Cancer Risk (ELCR).

This was calculated using mathematical expression of equation (3.23). The ELCR ranged from (1.140 to 1.827) $\times 10^{-3}$ with mean value of 1.425 $\times 10^{-3}$. The mean value was above the world standard of 0.29 $\times 10^{-3}$ in table 4.12.

Table 4.13: Transfer Factor from Soil to Plant (Cassava)

Sample Location		Transfer Factor from Soil to Plant (Cassava)			
		²²⁶ Ra	²³² Th	⁴⁰ K	Total
1	SP1	0.489	0.404	0.342	1.234
2	SP2	0.410	0.541	0.785	1.737
3	SP3	0.420	0.817	0.374	1.612
4	SP4	0.465	0.575	0.567	1.607
5	SP5	0.356	0.585	0.108	1.050
6	SP6	0.426	0.262	0.213	0.901
Average		0.428	0.531	0.398	1.357
World Standard		1	1	1	

Table 4.14: The Pearson's correlation matrix between the Soil and Plant radionuclide

	²²⁶ Ra _{soil}	²³² Th _{soil}	⁴⁰ K _{soil}	²²⁶ Ra _{food}	²³² Th _{food}	⁴⁰ K _{food}
²²⁶ Ra _{soil}	1					
²³² Th _{soil}	0.331068	1				
⁴⁰ K _{soil}	0.131969	0.830822	1			

$^{226}\text{Ra}_{\text{food}}$	0.969871	0.273577	-0.03904	1		
$^{232}\text{Th}_{\text{food}}$	0.537833	0.106079	0.406199	0.366569	1	
$^{40}\text{K}_{\text{food}}$	0.021141	0.658745	0.360994	0.053873	-0.47252	1

4.1.9 Transfer Factor from Soil to plant

The Soil to Plant Transfer Factor (TF) was determined to access the level of migration Natural Radionuclide from farm soil to cultivated crops around Obajana cement factory was determined as shown in Table 4.13. The TF for ^{226}Ra range from (0.410–0.489), with average of 0.428. Also Transfer factor for ^{232}Th range from (0.817–0.262), with average of 0.531. The TF of ^{40}K range from (0.108– 0.785), with average of 0.398. The TF varies in order of $^{232}\text{Th} > ^{226}\text{Ra} > ^{40}\text{K}$ and all the Transfer Factor were below the world standard of Unity.

The Pearson's correlation matrix, showing the interaction among the three radionuclides in the various environmental samples, is presented in Table 4.14. There exists strong positive correlation relationship between $^{226}\text{Ra}_{\text{soil}}$ and $^{226}\text{Ra}_{\text{food}}$ ($r = 0.9699$), there exist weak positive correlation between $^{40}\text{K}_{\text{soil}}$ and $^{40}\text{K}_{\text{food}}$ ($r = 0.3610$) and $^{232}\text{Th}_{\text{soil}}$ and $^{232}\text{Th}_{\text{food}}$ ($r = 0.1061$). The positive correlation found in the ^{226}Ra radionuclides in the soil and food samples suggest that these radionuclides originated from the same source for individual environmental matrix. This might be due to Cement Production activities around Obajana farm.

Table 4.15: Alpha and Beta Radioactivity concentration (Bq/l) of water samples around the Factory.

Sample Location	Sample Gross Radioactivity Measurement (Bq/l)	
	Alpha Activity	Beta Activity
WW1	$2.220\text{E-}02 \pm 1.97\text{E-}02$	$3.555\text{E+}00 \pm 6.94\text{E-}01$
WW2	$1.784\text{E-}02 \pm 1.34\text{E-}02$	$3.223\text{E+}01 \pm 7.30\text{E-}01$
WW3	$7.896\text{E-}02 \pm 7.01\text{E-}03$	$6.856\text{E+}00 \pm 3.36\text{E-}01$
WW4	$7.400\text{E-}03 \pm 2.17\text{E-}03$	$8.188\text{E-}01 \pm 2.28\text{E-}01$
WW5	$7.900\text{E-}03 \pm 2.49\text{E-}03$	$6.070\text{E+}00 \pm 2.78\text{E-}01$
WW6	$9.796\text{E-}03 \pm 4.64\text{E-}03$	$5.058\text{E+}00 \pm 1.94\text{E-}01$
WW7	$5.335\text{E-}02 \pm 2.53\text{E-}02$	$3.996\text{E+}01 \pm 1.13\text{E+}00$
BH (Bore hole)	$2.124\text{E-}02 \pm 8.12\text{E-}03$	$1.233\text{E+}01 \pm 3.38\text{E-}01$
STM1 (Stream1)	$2.871\text{E-}03 \pm 9.57\text{E-}03$	$2.937\text{E-}01 \pm 5.88\text{E-}02$

STM2 (Stream2)

$5.400\text{E-}03 \pm 1.19\text{E-}03$

$1.964 \text{ E+}00 \pm 4.44\text{E-}01$

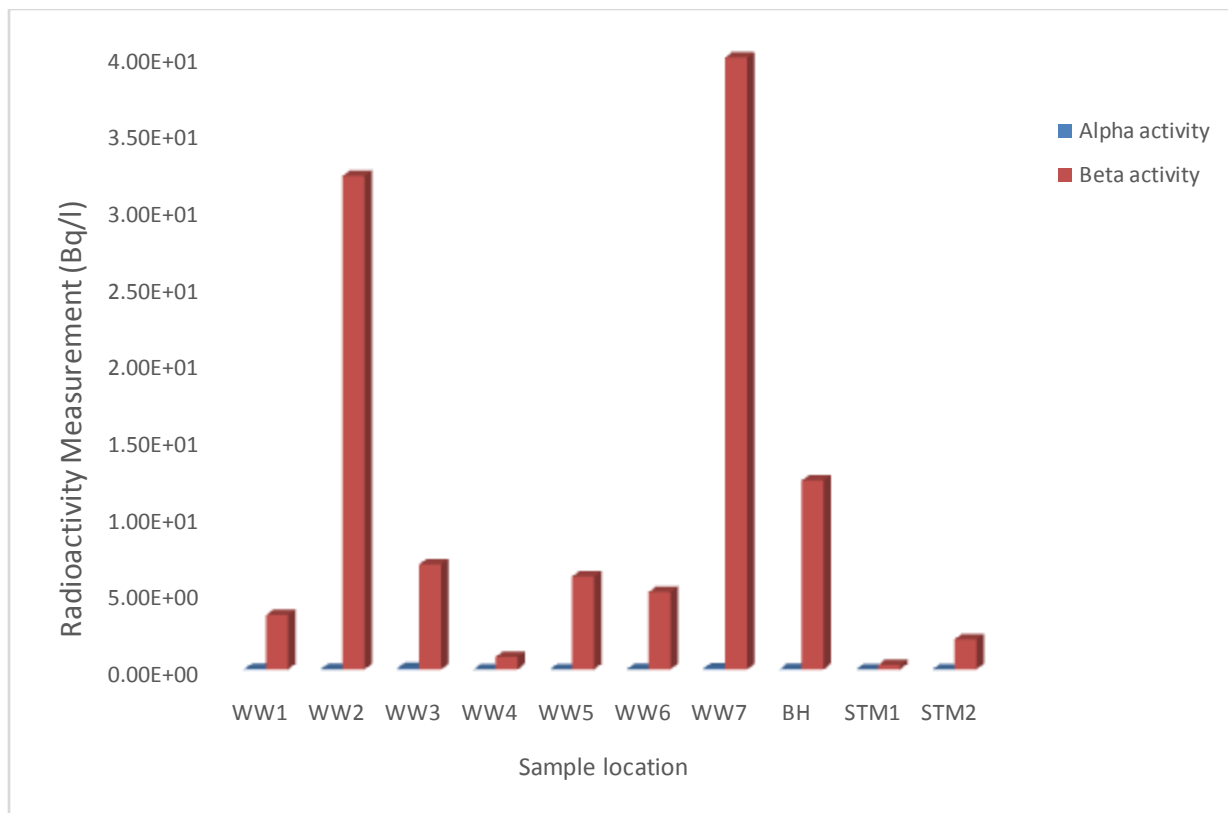


Figure 4.9: Alpha and Beta Radioactivity concentration (Bq/l) of water samples around the Factory.

4.2 Gross Alpha and Beta Radioactivity Analysis in Water Samples from different locations.

Samples collected from the sampling locations were screened using gas field proportional counter of the type Eurysis Measures for gross alpha and beta radioactivity concentration. Table 4.15 shows the sample gross alpha and beta radioactivity concentrations. The alpha activity measured ranged from 0.002871 ± 0.00957 to 0.05335 ± 0.0253 Bq/l, while the beta activity is in the range of 0.2937 ± 0.0588 to 39.96 ± 11.3000 Bq/l. The alpha and beta geometric mean of the whole samples were found to be 0.0156 ± 0.01487 Bq/l and 10.9 ± 13.8373 Bq/l respectively. The error quoted in the table represents the standard deviation from repetition measurements.

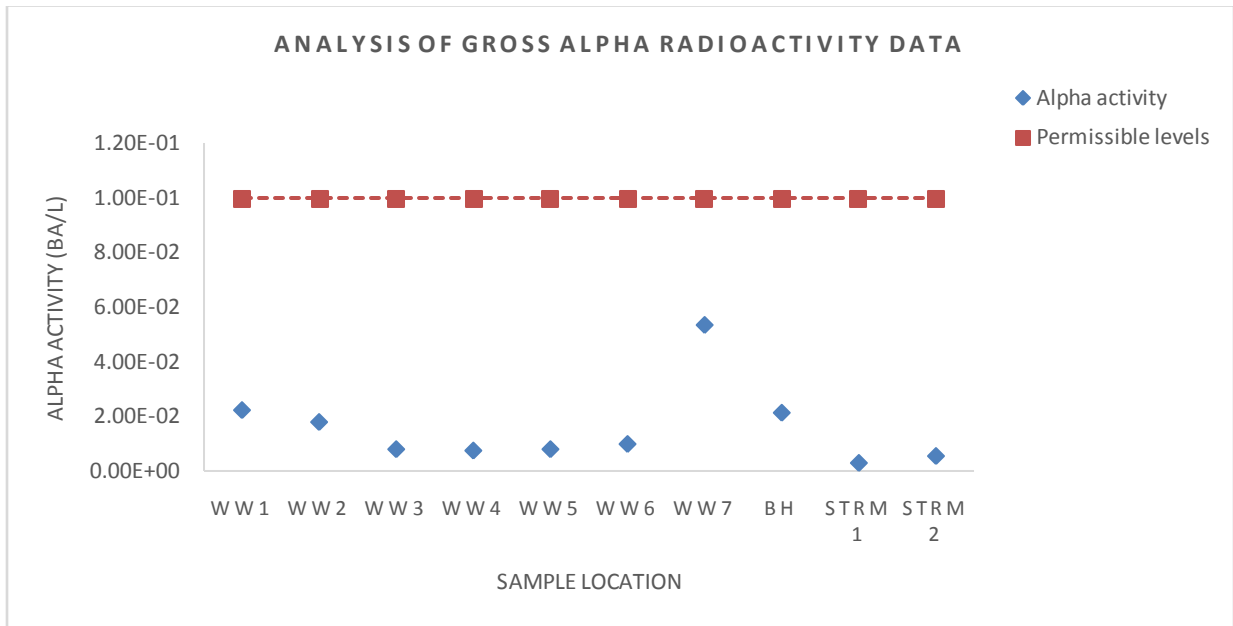


Figure 4.10: Gross Alpha Radioactivity Data with reference dose level (RDL)

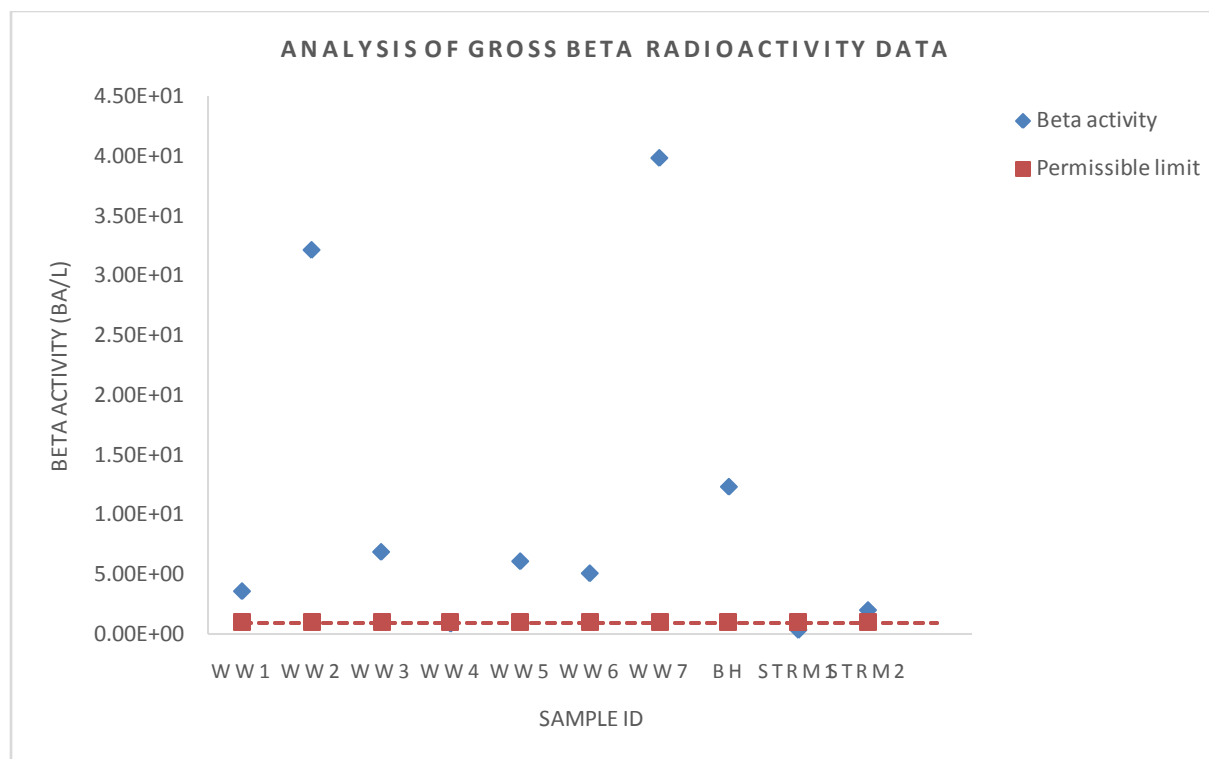


Figure 4.11:Gross Beta Radioactivity Data with reference dose level (RDL)

In comparison with the national primary drinking water regulation stated by the United States Environmental Protection Agency (USEPA), the results in Fig. 4.10, shows that all the samples were below the regulation for gross alpha activity in portable water. Also, in Fig. 4.11, about 20% of the samples were below and 80% of the samples have violated regulation for gross beta activity in portable water as recommended by (ICRP, 1997).

The results of the gross alpha and beta analysis of the ground water shows that the activities of alpha-emitters in all the samples were lower than the recommended limits of 0.1Bq/L (ICRP,1991). Also most of the Beta-emitters were above the recommended level of 1.0Bq/L with exception of Sample Identified as WW4 and Stream 1. The higher activity varies with location and could be the due to geological characteristics of the soil in the area. The high level of Beta activities around the area might be as a result of percolation of beta-emitting radionuclides (e.g. ^{210}Pb and ^{228}Ra) through the soil into the ground water (EPA, 2009). Sample identified as WW7

has the highest concentration of both alpha and beta emitters, it might be due to the location of the well which is the closest to the company and present of natural radionuclide. Stream 1 has the lowest concentration because the stream is situated at a far distance from the company and has a steady follow of water.

The mean alpha activity in Obajana envirom (1.56×10^{-2} Bq/l) is below the contaminant limit of 0.1 Bq/l and the mean beta activity (10.9 Bq/l) is above the contaminant limit of 1 Bq/l recommended by (ICRP, 1997). The result obtained is lower in comparison with some published result reported from other countries.

Table 4.16: Comparison of measured Gross- Alpha/Beta Activities in Obajana with national and international studies

Location	Measured Activity in Potable Water (Bq/l)								Source
	Alpha			Beta					
	Min	Max	μ	N	Min	Max	μ	N	
Obajana (Kogi State)	5.4×10^{-3}	5.34×10^{-2}	1.56×10^{-2}	10	1.96	40	10.9	10	Present Study
Germany	4.0×10^{-5}	8.0×10^{-4}	8.0×10^{-3}	371	1.0×10^{-5}	1.4×10^{-3}	8.8×10^{-5}	1307	1982
Netherland	28.0	64.0		5	35.0	129.0	76.0	5	
UK	30.0	150.0			300.0	330.0			
Venezuela	70.0	540.0	23.0	35					Sajo et al., 1996
Zaria	2.3×10^{-6}	5.8×10^{-3}	1.1×10^{-4}	50	3.7×10^{-5}	5.3×10^{-3}	3.1×10^{-4}	50	Onoja R.A., 2011
Warri (Delta State)	6.4×10^{-3}	1.82×10^{-2}	1.35×10^{-2}	4	4.60×10^{-2}	1.26×10^{-1}	9.23×10^{-2}	4	Adekoya et al.,

Belgium	5.6	27.8	13.6	30	56.0	722.0	175.0	30	CEC
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From Table 4.15, all the finding in this work compare favorably with those obtained from other places within Nigeria and around the world.

4.2.1 Effective dose

The annual alpha and beta effective dose due to intake of water were determined by averaging the individual annual committed effective doses contributed by the major alpha and beta emitters in the ^{238}U and ^{232}Th series of the natural occurring radionuclides as shown in equation (4.1).

$$E_{avg}(\alpha/\beta)(\text{mSv/yr}) = \sum_i^{R(\alpha/\beta)} A_{i(\alpha/\beta)} (\text{Bq/l}) \times DCF_{i(\alpha/\beta)} (\text{mSv/Bq}) \times 730 (\text{l/yr}) \text{-----(4.1)}$$

Where $E_{avg}(\alpha/\beta)$ is the average gross annual alpha or beta committed effective dose in the drinkable water, $A_{i(\alpha/\beta)}$ is gross alpha or beta concentration activity of individual radionuclide present in water sample and $DCF_{i(\alpha/\beta)}$ is dose conversion factor for ingestion of the individual natural radionuclides taken for an adult from UNSCEAR (2000) report. A daily water intake of 2 l/day is assumed by (EPA, 2000-05) thus resulting in annual consumption rate of 730 l/year.

The major contributors of gross β activities in drinking water are ^{210}Pb and ^{228}Ra (Gorur *et. al.*, 2011). Also it was considered that ^{226}Ra contribute more than 50% of annual dose from intake of water (Damla, 2006). DCF of $2.80 \times 10^{-4} \text{ mSvBq}^{-1}$ and $6.90 \times 10^{-4} \text{ mSvBq}^{-1}$ for both ^{210}Pb and ^{228}Ra were used for the effective dose calculation (WHO, 2004). The radionuclides in the gross alpha and beta activities in the sample water could not be determined due to limited functions of the machined.

Table 4.17: Total Effective equivalent dose due to both alpha and beta-emitting radionuclides in water

S/No.	Sample ID	Effective equivalent dose due to alpha radionuclides (mSv/yr)	Effective equivalent dose due to Beta radionuclides (mSv/yr)	Total Effective equivalent dose (mSv/yr)
1	WW1	4.54E-03	1.79E+00	1.80E+00
2	WW2	3.65E-03	1.62E+01	1.62E+01
3	WW3	1.61E-03	3.45E+00	3.45E+00
4	WW4	1.51E-03	4.12E-01	4.14E-01
5	WW5	1.61E-03	3.06E+00	3.06E+00
6	WW6	2.00E-03	2.55E+00	2.55E+00
7	WW7	1.09E-02	2.01E+01	2.01E+01
8	BH	4.34E-03	6.21E+00	6.21E+00
9	STREAM 1	5.87E-04	1.48E-01	1.49E-01

10	STREAM 2	1.10E-03	9.87E-01	9.88E-01
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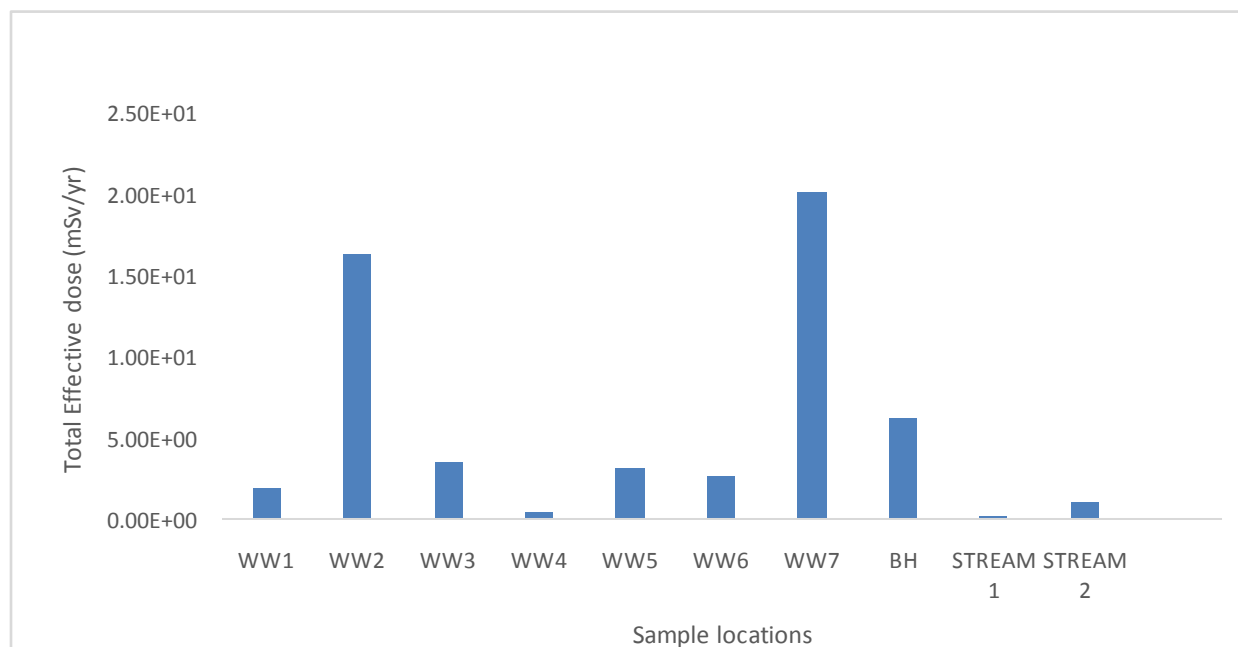


Figure 4.12: Total Effective equivalent dose due to both alpha and beta-e-mitting radionuclides in water

The total effective equivalent dose was greatest at WW7 (2.01E+01 mSv) and least at STRM1(1.49E-01 mSv). It was observed that all the sampling area exceed the Recommended Reference Dose Level (RDL) of 0.1 mSv from 1 year consumption of drinking water. Which might be due to high present of beta activity concentration in the sampled water

4.2.2: Correlation analysis between Gross Alpha and Beta activity.

A correlation studies was used to predict the model and access the strength of the relationship between the measured Beta and Alpha activity concentration in water sample around the Obajana environment.

The resulted of the correlation relationship were presented in Table 4.18 and Figure 4.13. The correlation coefficient (R), was found to be $R = 0.8181$, which shows there is a good relationship between the measured gross Alpha and Beta (activity). Therefore, there exist a strong linear correlation between the increase in gross alpha and beta activity contamination in the water around the cement factory (alpha activity increased with respect to beta activity) in table 4.18. Thus imply that increased in the two radionuclides might be responsible for the water contamination around the environment.

Table 4.18: Correlation analysis between Gross Alpha and Beta activity.

	<i>Alpha Activity (Ba/l)</i>	<i>Beta Activity (Ba/l)</i>
Alpha Activity (Ba/l)	1	
Beta Activity (Ba/l)	0.818138792	1

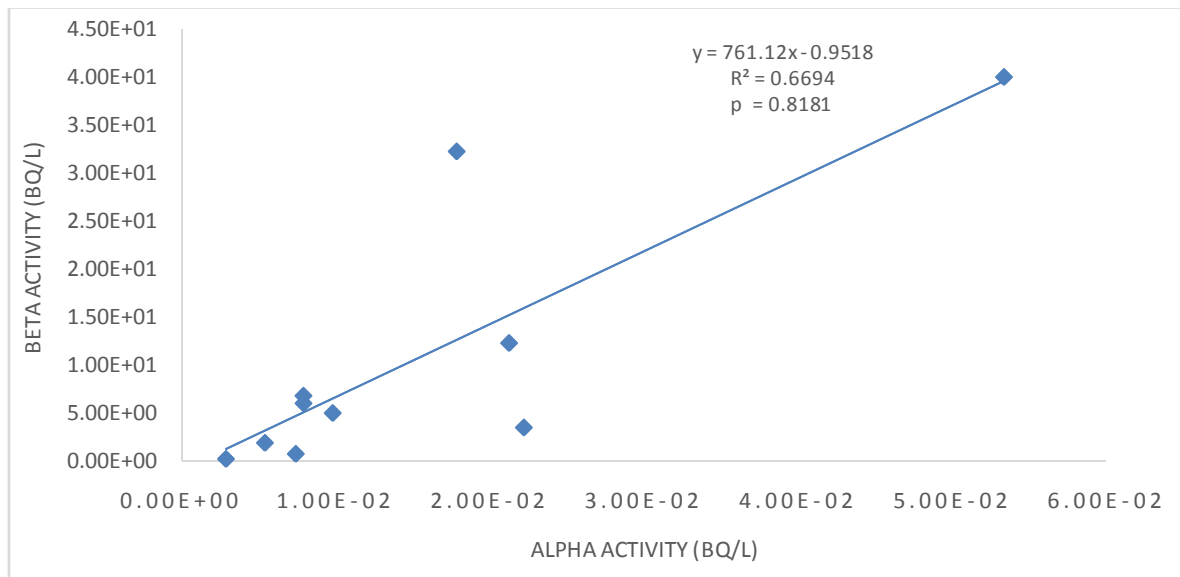


Figure 4.13: Scattered plot between Gross Alpha and beta Activity in Water Sample

4.2.3 Anova: Single Factor between Gross Alpha and Beta activity.

One-way analysis of Variance (ANOVA) was used to examine the measured Alpha and Beta activity concentration in water sample. It is a good method for testing the Significances difference between the groups of measured Alpha activity and Beta activity concentration.

Tabel 4.19, shows the ANOVA results of the Alpha and Beta activity concentration. The F-ratio is the ratio of the Mean Sum of Squares (MS) between groups and within groups of (gross Alpha and Beta activity). It tests whether the measured gross Alpha activity and Beta activity are normally distributed and statically significant. Therefore from the table above $P = 0.02$ (i.e. $p < 0.05(\alpha)$) and $F = 6.20$ (i.e. $F > F_C(4.41)$), thus reject null hypothesis. This implies there is a strong significant between the alpha and beta activity. Therefore, the alpha activity concentration increase as the beta concentration increase in water sample around the factory.

Table 4.19: Anova: Single Factor between Gross Alpha and Beta activity.

SUMMARY

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>
Alpha Activity (Ba/l)	10	0.155893	0.015589	0.000221
Beta Activity (Ba/l)	10	109.1355	10.91355	191.4703

ANOVA

<i>Source of Variation</i>	<i>SS</i>	<i>Df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	593.8277371	1	593.8277	6.202811	0.022751	4.413873
Within Groups	1723.234669	18	95.73526			
Total	2317.062406	19				

Table 4.20: Concentration level of heavy metals in Ground water samples using (AAS)

S/no.	Sample ID	Cd(mg/l)	Zn(mg/l)	Cu(mg/l)	Pb(mg/l)	Cr(mg/l)
1	WW1	5.90	7.95	10.3	BDL	BDL
2	WW2	6.00	9.75	8.55	BDL	BDL
3	WW3	6.50	13.20	8.85	BDL	BDL
4	WW4	6.30	22.10	9.95	BDL	BDL
5	WW5	6.15	11.35	12.40	BDL	BDL
	Average	6.17	12.87	10.01	0	0
	Control	3.05	6.15	6.15	0	0
	WHO Standard	0.03	3.0	2.0		

BDL: Below Detection Limit

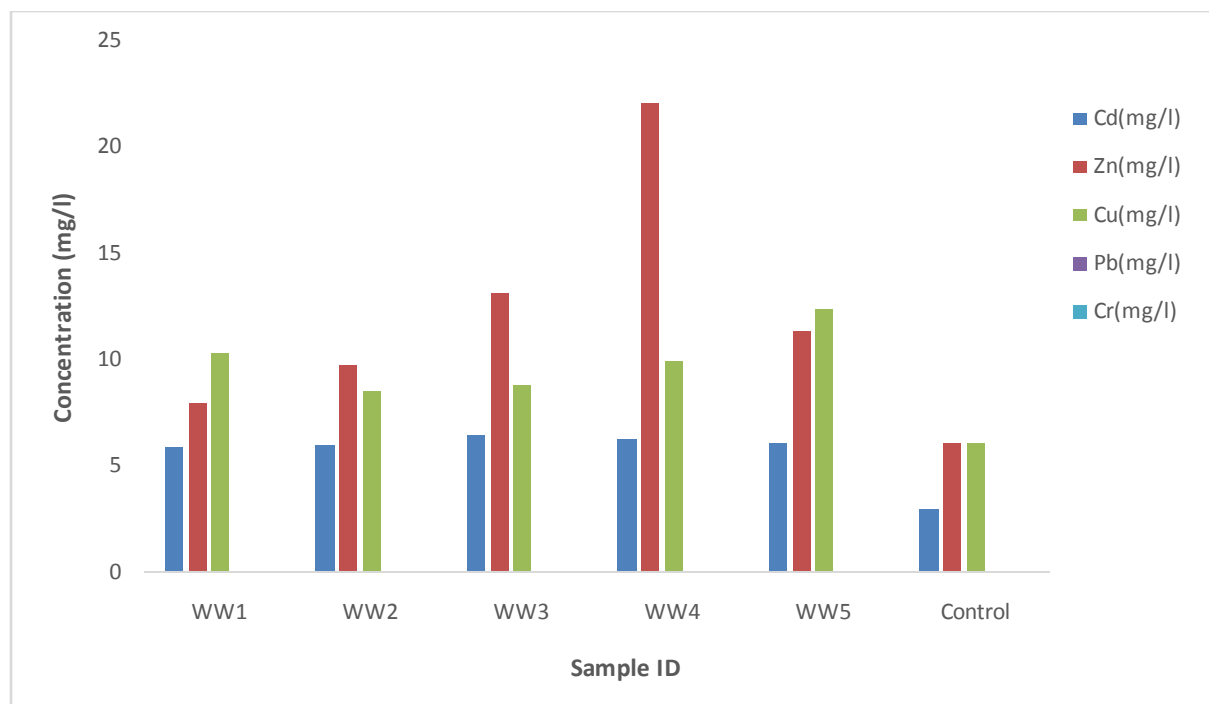


Figure 4.14: Concentration level of heavy metals in Ground water samples

Table 4.21: Average heavy metal concentration in groundwater with other International Standard

Metals	Present Study (mg/l)	WHO (mg/l)	NESREA (mg/l)	NSDWQ (mg/l)	USEPA (mg/l)
Cr	BDL	0.05	0.05	0.05	0.05
Zn	12.87	1.0	-	-	-
Cu	10.01	2.0	-	1.0	1.3
Cd	6.17	0.003	0.01	0.01	0.005
Pb	BDL	0.01	0.01	0.01	0.01

BDL: Below Detection Limit

WHO: World Health Organization

NESREA: National Environmental Standard and Regulation Enforcement Agency.

NSDWQ: Nigerian Standard for Drinking Water Quality

USEPA: United States Environmental Protection Agency

4.3 Concentration of Heavy metals using (AAS)

Using the AAS Techniques the following heavy metals were analyzed Zn, Cu, Cd, Cr, Pb for Water and Rock samples. Heavy metals were detected at varying concentrations in the samples except for Cr and Pb, were not detected due to the detection limit of the machine used.

The concentration of Zn, Cu, Cd, Cr, Pb, for water samples were analyzed in Table 4.20 and Figure 4.13. The highest average concentration in water samples corresponds to Zn (12.87 mg/l). The increasing trend was in the order of Zn>Cu>Cd>Pb>Cr. The concentration of all the element in the samples was found to be higher than that obtained in the control samples. This could be due to the steady flow of water in the stream that serve as control sample in the liquid samples. The average concentration of the samples in the area were compared with other international

standards for drinking water as shown in Table 4.21. The observed metals in the sampling were found to have concentration above other international standards. This may be due to cement production activities and geological formation of the area.

Table 4.22: Heavy Metal indices in Water sample

Metal	Concentration Factor (CF)			Geochemical accumulation Indices (I)			Ecological Risk Index (ERI)			Hazard Quotient (HQ)		
	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.
Cr	-	-	-	-	-	-	-	-	-	-	-	-
Zn	1.612	2.146	1.000	-0.690	-0.445	-1.537	55.574	69.934	30.000	0.188	0.217	0.102
Cu	1.523	2.016	1.000	-0.310	0.147	-0.955	1.612	2.146	1.000	9.917	13.200	6.150
Cd	1.825	2.131	1.000	-0.380	0.056	-0.955	7.615	10.081	3.000	1.873	2.480	1.230
Pb	-	-	-	-	-	-	-	-	-	-	-	-

4.3.1 Heavy Metal indices in water samples.

The heavy metal indices in water sources around the Cement factory were determined using the following parameters.

(a) Contamination Factor (CF)

The Contamination factor was determined from equation (3.27), the CF for Zn ranged from (1.000 – 2.146) with mean value of 1.612, CF for Cu ranged from (1.000 – 2.016) with mean value of 1.523, and CF for Cd ranged from (1.000 – 2.131) with mean value of 1.852. The mean value of the contamination factor for all the analyzed heavy metals in the groundwater falls within the moderate level as shown in Table 3.1.

(b) Geochemical Accumulation Indices (I)

The Geochemical Accumulation Indices (I) was determined from equation (3.28). The Geochemical Accumulation Indices (I) ranged from (-1.537 – -0.445), (-0.955 – 0.147), (-0.955 – 0.056) with mean value of -0.690, -0.310, and -0.380, for Zn, Cu and Cd respectively. The Geochemical Accumulation Indices of all the analyzed heavy metals falls within the Non – Contamination level as shown in Table 3.2.

(c) Ecological Risk Index (ERI)

The Ecological Risk Index (ERI) was determined from equation (3.29). The Ecological Risk Index (ERI) ranged from (30.000 – 63.934), (1.000 – 2.146), (5.000 – 10.081) with mean value of 55.574, 1.612, and 7.615, for Zn, Cu and Cd respectively. All the analyzed heavy metals were below the toxic response value except Zn. This may be due to geological formation of the area.

(d) Hazard Quotient (HQ)

The Hazard Quotient was determined from equation (3.31), the HQ for Zn ranged from (0.102 – 0.217) with mean value of 0.188, CF for Cu ranged from (6.150 – 13.200) with mean value of 9.917, and CF for Cd ranged from (1.230 – 2.480) with mean value of 1.873. The mean value for all the analyzed heavy metals except Cu in the groundwater were closed to the world standard of unity. Indicating that the concentration values of heavy metals were closed to maximum allowed limits set by the WHO.

Table 4.23: Comparison of heavy metals indices concentrations in water Samples.

Metals	Contamination Factor (CF)	Geo-accumulation index (I)	Ecological Risk index (ERI)	Hazard Quotient (HQ)
Zn	Moderately Contaminated	Non-Contaminated	Above Toxic Response value	Normal
Cu	Moderately Contaminated	Non-Contaminated	Below Toxic Response value	Normal
Cd	Moderately Contaminated	Non-Contaminated	Below Toxic Response value	Normal
Pb	N/A	N/A	N/A	N/A
Cr	N/A	N/A	N/A	N/A

N/A means not available

Table 4.24: The concentration level of heavy metals in Rock samples

S/no.	Type of Rocks	Cd(mg/kg)	Zn(mg/kg)	Cu(mg/kg)	Pb(mg/kg)	Cr(mg/kg)
1	Quartzite	12.7	28.4	27.3	BDL	BDL
2	Schist	14.3	105.8	39.1	BDL	BDL
3	Marble	17.3	64.5	37.6	29.6	BDL
4	Marble	13.3	25.9	23.9	BDL	BDL
5	Quartz robtz.	18.3	44.8	27.2	9.6	BDL
6	Quartzite	15.2	33	28.1	BDL	BDL

BDL: Below Detection Limit

Rock Type: Metamorphic rock

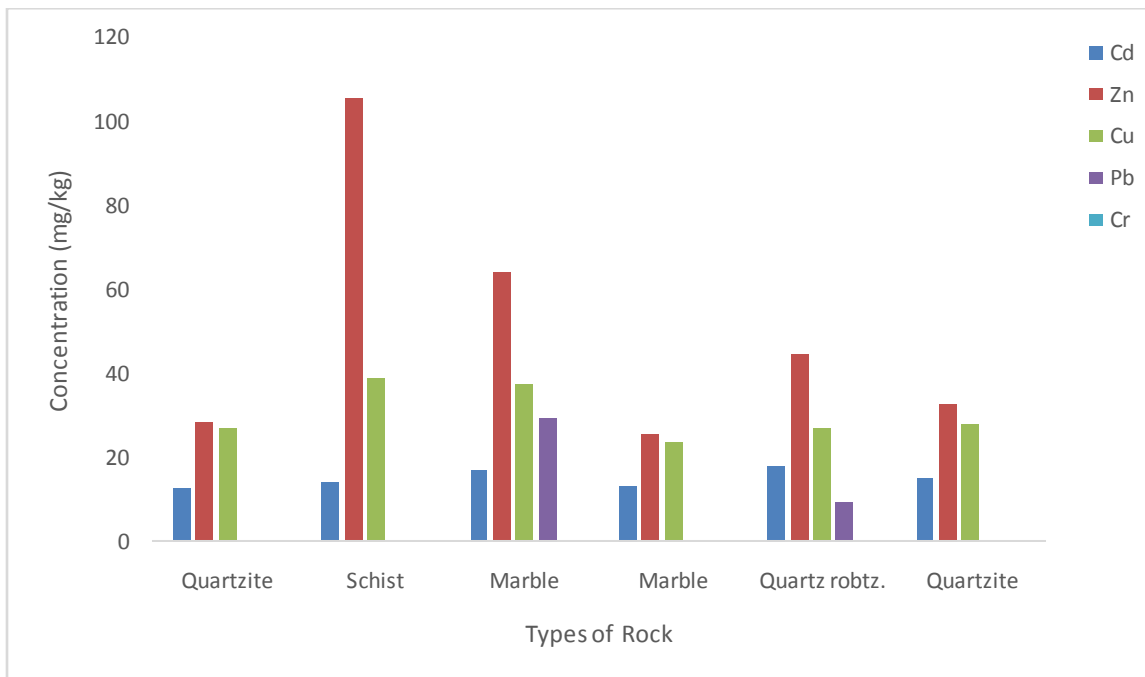


Figure 4.15: Concentration levels in rocks

Table 4.25: The average concentration of the heavy metals in Rock samples (mg/kg).

Toxic metal	Mean	Minimum	Maximum	Standard deviation
Cd	15.01	12.70	18.30	2.08
Zn	48.26	25.90	105.80	28.52
Cu	29.96	23.90	39.10	5.90
Pb	5.60	9.60	29.60	11.17
Cr	BDL	BDL	BDL	BDL

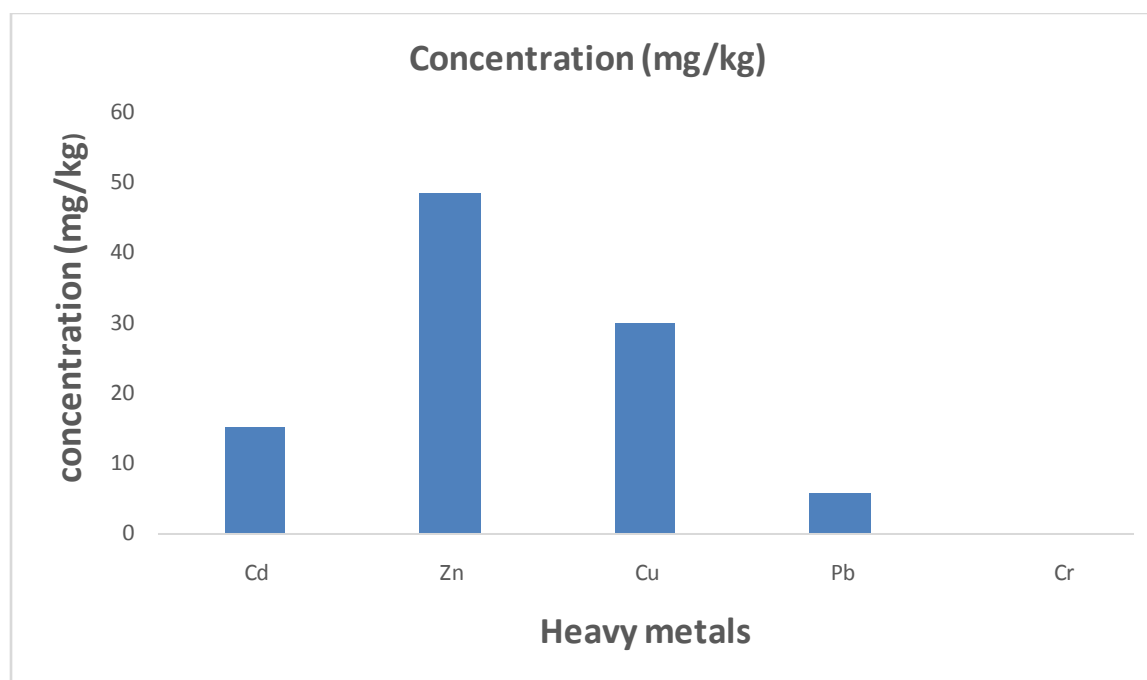


Figure 4.16: Average Concentrations levels in Rock samples

Table 4.26: Average Concentration of Rock samples with WHO Limit for Heavy metal concentrations (mg/kg).

Parameter	Zn	Cu	Cd	Cr	Pb
Average Control Concentration	24.50	20.60	12.30	BDL	BDL
Average Concentration of Sample points	48.26	29.96	15.01	BDL	5.60
Toxic Response Factor	1	5	30	2	5
WHO recommended level	200	30	3.00	100	100

Table 4.27: Comparison of present Study with concentrations (mg/kg) of other related Studies.

Cr	Cd	Pb	Cu	Zn	References
BDL	15.014	5.600	29.957	48.257	Present Work
BDL	12.300	BDL	20.600	24.500	Control Sample
1674	-	1387	-	-	Olayiwola, 2013
1475.5	1.0	205	185.7	555	Ahmad et. al, 2014
301.6	8.8	152	144.8	359.4	Rahib et, al, 2015
9.57	3.47	127.83	226.80	173.60	Boadu, 2014

N/d means not detected, BDL Below Detection Limit

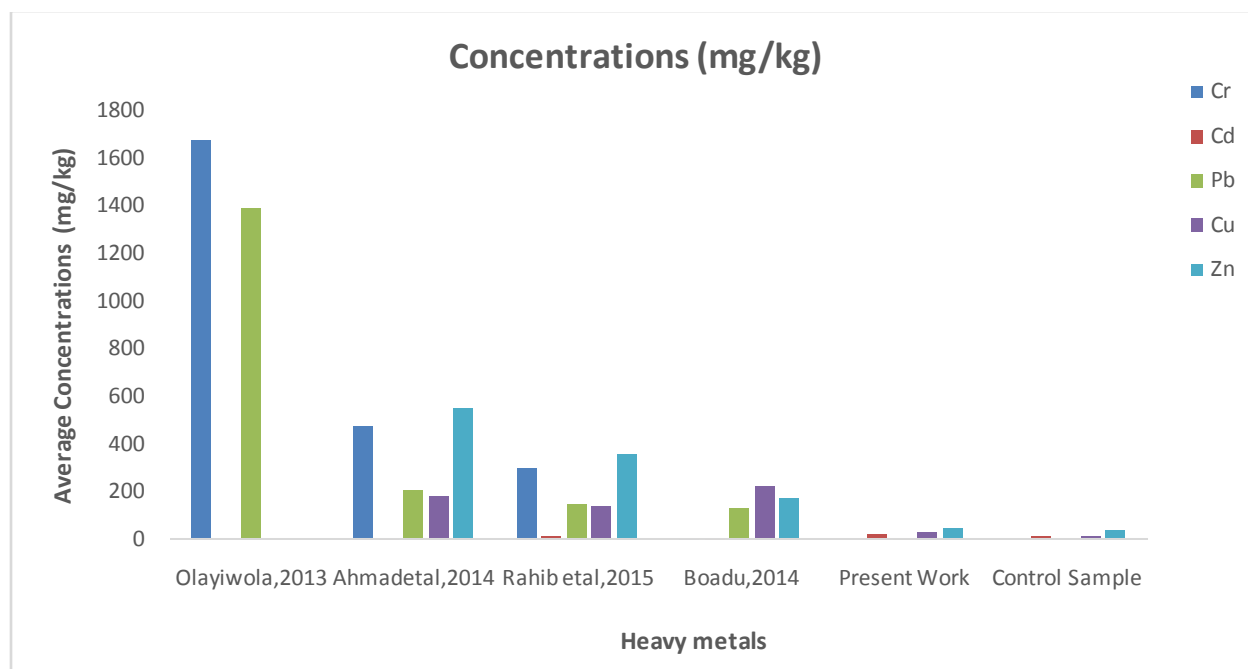


Figure 4.17: Comparison of present Study with concentrations (mg/kg) with other related studies

4.3.2 The concentration levels of heavy metals in Rock samples

The concentration of Zn, Cu, Cd, Cr and Pb for rock samples were analyzed in Table 4.24. The highest average concentration in the samples corresponds to Zn (48.26 mg/kg). The increasing trend was in the order of Zn>Cu>Cd>Pb>Cr. The concentration of all the element in the samples were found to be higher than that obtained in the control samples. This could be due the natural and anthropogenic factors for the rock samples.

The average concentration of the sample in the area were compared with the World Health Organization guidelines on the maximum limits of toxic metals (WHO, 1997) as provided in Table 4.26. The observed heavy metals in the sampling are were found to have concentration above WHO limits except Zn. This may be due to geological formation of the area.

The obtained Average concentrations around the Obajana environs were compared with other published results. Ahmad et. al, 2014 Analyzed heavy metals concentration in spinach grown, around waste water agricultural soil of Sargodha Pakistan. Rahib *et. al.*, (2015) access heavy metal contents in soils of gadoon Amazai industrial Estate, Pakistan. Olayiwola determined heavy metal contents in steel rolling industrial Area of Ikirun, Osun State Nigeria and Boadu *et.al.*, 2014 studied heavy metals contaminations of soil and water at scrap market in Accra. Their results were presented in Table 4.27. From the table it was observed that the average concentration in (mg/kg) for rock sample, in this work corroborates with the results of those researchers.

Table 4.28: Heavy Metal indices in Rock samples

Metal	Concentration Factor (CF)			Geochemical accumulation Indices (I)			Ecological Risk Index (ERI)			Hazard Quotient (HQ)		
	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.
Cr	-	-	-	-	-	-	-	-	-	-	-	-
Zn	0.748	1.640	0.442	-0.355	-0.058	-0.585	20.036	31.734	22.023	0.500	0.610	0.423
Cu	0.797	1.040	0.636	0.006	1.312	-0.718	0.748	1.640	0.402	48.257	105.800	25.900
Cd	0.868	1.058	0.734	-0.530	-0.124	-0.834	3.948	5.199	3.178	5.991	7.820	4.780
Pb	-	-	-	-	-	-	-	-	-	-	-	-

4.3.3 Heavy Metal indices in Rocks samples

The heavy metal indices in Rock samples around the Obajana Cement Plant were determined as shown in Table 2.28, using the following parameters.

(a) Contamination Factor (CF)

The Contamination factor was determined from equation (3.27). the CF for Zn ranged from (0.442 – 1.640) with mean value of 0.748, CF for Cu ranged from (0.636 – 1.040) with mean value of 0.797, and CF for Cd ranged from (0.734 – 1.058) with mean value of 0.868. The mean value of the contamination factor for all the analyzed heavy metals in the rock samples falls within the low level as shown in Table 2.2.

(b) Geochemical Accumulation Indices (I)

The Geochemical Accumulation Indices (I) was determined from equation (3.28). The Geochemical Accumulation Indices (I) ranged from (-0.585 – -0.058), (-0.718 – 1.312), (-0.834 – -0.124) with mean value of -0.355, 0.006, and -0.530, for Zn, Cu and Cd respectively. The Geochemical Accumulation Indices of all the analyzed heavy metals falls within the Non – Contamination level as shown in Table 3.2.

(c) Ecological Risk Index (ERI)

The Ecological Risk Index (ERI) was determined from equation (3.29). The Ecological Risk Index (ERI) ranged from (22.023 – 31.734), (0.402 – 1.640), (3.178 – 5.199) with mean value of 20.036, 0.748, and 3.984, for Zn, Cu and Cd respectively. All the analyzed heavy metals except Zn, were below the toxic response value. This may be due to geological formation of the area.

(d) Hazard Quotient (HQ)

The Hazard Quotient was determined from equation (3.31), the HQ for Zn ranged from (0.423 – 0.610) with mean value of 0.500, CF for Cu ranged from (25.900 – 105.800) with mean value of 48.257, and CF for Cd ranged from (4.780 – 7.820) with mean value of 5.991.

Table 4.29: Comparison of heavy metals indices concentrations in Rock Samples.

Metals	Contamination Factor (CF)	Geo-accumulation index (I)	Ecological Risk index (ERI)	Hazard Quotient (HQ)
Zn	Low	Non-Contaminated	Above Toxic Response value	Normal
Cu	Low	Non-Contaminated	Below Toxic Response value	Normal
Cd	Low	Non-Contaminated	Below Toxic Response value	Normal
Pb	N/A	N/A	N/A	N/A
Cr	N/A	N/A	N/A	N/A

N/A means not available

Table 4.30: Quality Control of the Data Obtained with NIST 1633c (Coal fly ash)

Element	Certified value	This work	Variance (error)%
As	186.2 ± 3.0	185 ± 1.48	0.64
La	87.0 ± 2.6	86.44 ± 0.692	0.64
Sm	19.0 ± 0	18.88 ± 0.169	0.63
U	9.25 ± 0.45	9.19 ± 1.305	0.65
Sc	37.6 ± 0.6	42.47 ± 0.169	12.95
Cr	258 ± 6	321.9 ± 7.081	24.77
Co	42.9 ± 3.5	44.871 ± 0.62	4.59
Rb	117.42 ± 0.53	140.8 ± 10.419	19.91
Cs	9.39 ± 0.22	9.203 ± 0.672	1.99
Nd	87.0 ± 0	85.07 ± 5.444	2.22
Eu	4.67 ± 0.07	5.741 ± 0.385	2.293
Yb	7.7 ± 0	7.413 ± 0.244	3.73
Lu	1.32 ± 0.03	3.088 ± 0.083	3.394
Hf	6.0 ± 0	8.448 ± 0.456	4.08
Ta	1.58 ± 0.03	0.973 ± 0.163	3.841
Th	23.0 ± 14.0	28.87 ± 0.519	2.552

Table 4.31: Concentration of Elements in Soil by INAA

ELEMENT	SS1	SS2	SS3	SS4	SS5	SS6	Average
Na	1796 ± 14.37	14340 ± 43.02	21110 ± 42.22	25370 ± 50.74	12950 ± 38.85	15450 ± 46.35	15169.333
K	16900 ± 861.9	77310 ± 1631.241	90340 ± 1084.08	86910 ± 1738.2	103500 ± 1656	108000 ± 1080	80493.333
La	188.7 ± 0.943	218 ± 1.09	274.1 ± 1.371	203 ± 1.218	173.7 ± 1.042	138.7 ± 0.971	199.367
Sm	40.1 ± 0.241	BDL	45.03 ± 0.225	32.22 ± 0.226	29.31 ± 0.205	26.98 ± 0.189	34.728
U	16.08 ± 1.222	31.49 ± 2.236	42.23 ± 2.365	30.47 ± 2.041	33.78 ± 1.723	33.13 ± 1.723	31.1967
Sc	2.773 ± 0.039	2.476 ± 0.054	1.525 ± 0.031	1.483 ± 0.033	1.499 ± 0.031	1.456 ± 0.030	1.869
Cr	19.57 ± 2.485	12.59 ± 2.531	6.597 ± 1.695	6.559 ± 1.594	6.03 ± 1.514	9.782 ± 1.848	10.188
Fe	16620 ± 249.3	15230 ± 289.37	3071 ± 70.633	6832 ± 163.968	6642 ± 179.334	5472 ± 164.16	8977.833
Co	3.826 ± 0.245	4.549 ± 0.268	3.212 ± 0.238	1.724 ± 0.315	5.012 ± 0.246	2.682 ± 0.179	3.501
Rb	25.91 ± 6.167	155.5 ± 8.708	144.3 ± 7.071	172 ± 6.192	254.9 ± 7.901	234.6 ± 7.742	164.535
Sb	0.243 ± 0.046	1.241 ± 0.073	BDL	BDL	0.125 ± 0.036	BDL	0.5363
Cs	BDL	BDL	1.281 ± 0.328	1.774 ± 0.296	BDL	2.205 ± 0.258	1.753
Ba	292.9 ± 33.391	1390 ± 58.38	1483 ± 44.49	1374 ± 42.594	917.4 ± 36.696	778.5 ± 32.697	1039.3
Nd	BDL	31.72 ± 3.299	28.78 ± 2.418	BDL	BDL	BDL	30.25
Eu	0.863 ± 0.146	93.2 ± 10.162	1.034 ± 0.149	0.664 ± 0.145	0.641 ± 0.152	BDL	19.280
Tb	2.302 ± 0.409	BDL	2.977 ± 0.366	2.239 ± 0.378	24.3 ± 3.9366	2.268 ± 0.281	6.817
Yb	4.5 ± 0.153	2.058 ± 0.171	3.679 ± 0.143	2.679 ± 0.139	2.833 ± 0.167	2.935 ± 0.153	3.114
Lu	0.654 ± 0.023	37.49 ± 2.887	0.448 ± 0.021	0.333 ± 0.019	0.299 ± 0.019	0.333 ± 0.022	6.593
Hf	8.274 ± 0.206	13.87 ± 0.291	12.31 ± 0.234	8.242 ± 0.214	6.381 ± 0.204	8.432 ± 0.202	9.585
Ta	BDL	136 ± 0.952	0.732 ± 0.213	BDL	1.031 ± 0.176	1.311 ± 0.165	34.769
Th	0.127 ± 0.002	22.89 ± 0.320	23.57 ± 0.282	BDL	25.96 ± 0.286	20.17 ± 0.302	18.543

BDL: Below Detection Limit

Table 4.32: Comparison of present Study with concentrations (mg/kg) of other related Studies and Standard.

Locations	Heavy Metals (mg/kg)						References
	Fe	Co	Cr	As	Cd	Pb	
Obajana	8977.83	3.50	10.19	-	-	-	Present Study
Ewekoro (Nigeria)	91.60	112.0	0.04	-	0.03	0.84	Majolagbe <i>et. al.</i> 2013
Ethopia	897.1	55.6	40.4	98.5	-	7.0	Samuel <i>et. al.</i> 2012
Saudi Arabia	14970	-	22.7	22.6	5.07	20.7	Abdurasoul <i>et. al.</i> 2011
Dutch	-	24	3.8	4.5	0.76	55	Crommentuijn <i>et. al</i> 1997
FAO/WHO	-	-	0.3	-	3.0	300	WHO 1996

4.4 Concentration of Elements in Soil by INAA

The concentration of elements in Soil samples obtained around the factory were determined using Neutron Activation Analysis (NAA) technique. Relative method was employed for the determination process. The samples were irradiated together with standard reference (coal fly ash NIST 1633c) materials under the same scheme of irradiation and counting technique. The values results obtained in this study for the reference standards were compared with the certificate values as shown in Table 4.30. The tables clearly showed that majority of the elements investigated were in excellent agreement with the certified (literature) values of the standards with maximum deviation error of 24.77% in Cr.

Twenty-one elements were detected in the soil samples as shown table 4.31. The dominant elements detected correspond with common metals found on the earth crust (Lentech, 2009). Na (15169.333 mg/kg), K (80493.333 mg/kg), Ba (1039.3 mg/kg) and Fe (8977.83 mg/kg) were among the most widely distributed element in nature and found in small quantities part of raw materials such as Alkalis ($\text{NaO} + \text{K}_2\text{O}$), Clay (Fe_2O_2) and Bauxite BaCO_3) used in cement production. Therefore, the soil around the factory has high concentration of common and low toxic metals (i.e. Na, K, Ba and Fe).

High concentration of two Toxic Metals Cr (10.188 mg/kg) and Co (3.501 mg/kg) were detected, this might be due to settlement of Cement dust particles from the factory to the surrounding soils. Most of the heavy metals concentration in soil close to the factory have high concentration values than other soil located about 2 km from the factory.

The average concentration of most heavy metals around the study area compared favorably with other related published studies for soil around Cement Factory

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 Summary

The potential radiological and heavy metal concentration due to Cement production activities around Obajana cement factory were studied, based on the initial Objectives of this research.

The mean activity concentration of primordial radionuclides (^{226}Ra , ^{232}Th and ^{40}K) in soil, Mining site, Cement finished product and cultivated tuber crop (Cassava) were, (47.2956, 77.5699, 601.8127) Bqkg^{-1} , (26.84435, 59.98768, 362.3639) Bqkg^{-1} , (36.0011, 49.2077, 146.6098) Bqkg^{-1} , and (20.3514, 37.4710, 164.4322) Bqkg^{-1} respectively. The mean activity concentration of the analyzed samples compared favorably with world standard and other related studies. The potential radiological hazard indices were determined from the activity concentration. Most of the radiological hazard indices were below the world standard.

The mean activity concentration in the soils were higher than that of the cultivated tuber crops, indicating a low Transfer Factor (TF) of natural radionuclide from soil to the selected cultivated crops around the farms closed to the factory. The TF varies in order of $^{232}\text{Th} > ^{226}\text{Ra} > ^{40}\text{K}$. All the Transfer Factor were below the world standard of Unity. There exists strong positive correlation ($p < 0.05$) relationship between $^{226}\text{Ra}_{\text{soil}}$ and $^{226}\text{Ra}_{\text{food}}$ ($r = 0.9699$), there exist weak positive correlation between $^{40}\text{K}_{\text{soil}}$ and $^{40}\text{K}_{\text{food}}$ ($r = 0.3610$) and $^{232}\text{Th}_{\text{soil}}$ and $^{232}\text{Th}_{\text{food}}$ ($r = 0.1061$). The positive correlation found among the ^{226}Ra radionuclides between the soil and food samples suggest that these radionuclides originated from the same source for individual environmental matrix. This might be due to Cement Production activities around Obajana factory.

Alpha and Beta activity concentration were determined in the water samples, using the low background Gas-less Alpha/Beta counting system (MPC 2000DP), calibrated with alpha (^{239}Pu) and (^{90}Sr) standards. The alpha and beta geometric mean of the whole samples were found to be 0.0156 ± 0.01487 Bq/l and 10.9 ± 13.8373 Bq/l respectively. All the samples were below the regulation for gross alpha activity in portable water. Also, about 20% of the samples were below and 80% of the samples have violated regulation for gross beta activity in portable water as recommended by (ICRP, 1997).

The alpha activity might be due to present of natural alpha-emitting radionuclide (e.g. ^{226}Ra and ^{210}Po) and high beta activity might be due to present of natural beta-emitting radionuclide (e.g. ^{210}Pb and ^{228}Ra) in the analyzed water sample. The radionuclide could not be determined due to limited function of the detector. Therefore, water from the sampled location might pose high risk due to cement production and present of natural radionuclide, if adequate measures is not taken.

The elemental composition of the Water and Rock Samples for some selected heavy metals were determined using Atomic Absorption Spectroscopy (AAS). The highest average concentration corresponds to Zn (12.87 mg/l, 48.26 mg/Kg) for (water, rock) samples respectively. The increasing trend was in the order of $\text{Zn} > \text{Cu} > \text{Cd} > \text{Pb} > \text{Cr}$. The heavy metals were detected at varying concentrations in the samples except for Cr and Pb, were not detected in some samples due to the detection limit of the machine used. The rock and water samples were below the recommended values and compared favorably with other related studies.

The soil around the factory has high concentration of common and low toxic metals Na (15169.333 mg/kg), K (80493.333 mg/kg), Ba (1039.3 mg/kg) and Fe (8977.83 mg/kg), high concentration of two Toxic Metals Cr (10.188 mg/kg) and Co (3.501 mg/kg) were detected. The

average concentration of most heavy metals around the study area compared favorably with other related published studies for soil around Cement Factory.

Microsoft (Excel, 2016) was the statistical package used for statistical analysis in this research.

5.2 Conclusion

The mean activity concentration of primordial radionuclides (^{226}Ra , ^{232}Th and ^{40}K) of the soil samples (47.2956, 77.5699, 601.8127) BqKg^{-1} were slightly above world standard (32, 45, 420) BqKg^{-1} , while the other analyzed sample compared favorably with world standard and other related studies. Most of the potential radiological hazard indices determined from the activity concentration were below the recommend standard.

The Transfer Factor (TF) of natural radionuclide (0.428, 0.531, 0.398) for (^{226}Ra , ^{232}Th and ^{40}K) respectively, from soil to crops were below world standard of Unity and varies in order of $^{232}\text{Th} > ^{226}\text{Ra} > ^{40}\text{K}$. There exists strong positive correlation ($p < 0.05$) found among the ^{226}Ra radionuclides between soil and food samples. Which suggests that the radionuclides originated from the same source for individual environmental matrix.

The alpha and beta geometric mean of the whole samples were found to be 0.0156 ± 0.01487 Bq/l and 10.9 ± 13.8373 Bq/l respectively. All the water samples were below the regulation for gross alpha activity in portable water. About 80% of the water samples were above regulation limit for gross beta activity in portable water recommended by (ICRP, 1997). The high beta activity might be due to natural beta emitting radionuclide sample (e.g. ^{210}Pb and ^{228}Ra) in the analyzed water (EPA, 1999). It was observed that all the sampling area exceed the Recommended reference dose level (RDL) of 0.1 mSv from 1 year consumption of drinking water. The water from sampled location might pose high risk due to cement production activities, if adequate measures is not taken.

Elemental composition of water and Rock samples of some selected heavy metals increases in the order of Zn > Cu > Cd > Pb > Cr. The highest average concentration corresponds to Zn (12.87 mg/l, 48.26 mg/Kg) for (water, rock) samples respectively. The average activity concentration of heavy metals in both samples were below the recommended values and compared favorably with other studies.

Soil around the factory has high concentration of common low toxic metals (i.e. Na, K, Ba and Fe).The soil around the factory has high concentration of common and low toxic metals Na (15169.333 mg/kg), K (80493.333 mg/kg), Ba (1039.3 mg/kg) and Fe (8977.83 mg/kg), high concentration of two Toxic Metals Cr (10.188 mg/kg) and Co (3.501 mg/kg) were detected. The average concentration of most heavy metals around the study area compared favorably with other related published studies for soil around Cement Factory.

5.3 Recommendation

Based on the findings of this study, the following recommendations were made to safeguard Obajana cement company and other Factories from contamination and pollution of the environment.

- i. More detail studies based on geology and soil type of the study should be carried out in areas observed to have high activity concentration of ^{226}Ra , ^{232}Th and ^{40}K and heavy metals for continuous monitoring and radiation protection purposes.
- ii. Investigation of Beta and Alpha emitting radionuclide responsible for high beta found to present in water samples around the area.
- iii. There should be continuous periodic monitoring of water quality used for domestic purpose, for efficient planning and management of water sources around the area.

- iv. The monitoring by government and other environmental agencies, in order to check Cement production activities and to protect the environment from radiological effect, contamination and hazardous pollutants.

5.4 Contribution to Knowledge

This study investigate the radiological and heavy metal concentration around the Obajana cement factory.

- i. The activity concentration of ^{226}Ra , ^{232}Th and ^{40}K in soil, marble mining site, cement finished product and selected cultivated cassava around the factory were determined.
- ii. The radiological hazard indices in the selected sample, compared with the world standard and other related studies.
- iii. Monitoring the back ground exposure rate (external radiation) around the sampling area using digital Survey meter.
- iv. The radionuclide transfer level from soil to cultivated crops were determined.
- v. Asses the Gross Alpha and Beta concentration in water sources, used for domestic purposes around the area.
- vi. Verified if there are elevated levels of trace element in soil, water and rocks samples collected around the study area using Neutron Activation Analysis (NAA) and Atomic Absorption Spectrometry (AAS).

REFERENCES

- Abdurasoul M. A., Salem E. E., Mahmoud E.A. N., Ali M. E., and Salem M.I. A. (2011). Impact of Cement Dust on Some Soil Properties Around the Cement Factory in Al-Hasa Oasis, Saudi Arabia. *American-Eurasian J. Agric. & Environ. Sci.*, 11 (6): 840-846, 2011.
- Abdurahman, K., Abdelhakim, H. and Benamar, D. (2013): Measurement of Natural radioactivity in cement of Tlemcen-Algeria by using well-shape NaI(Tl) detector. *Journal of Natural Sciences Research*. Vol.3: 182-191.
- Addo M.A, Darkol E.O., Gordom C., Davor P., Gbadago J.k., Faanu A., Kpeglo D. and Ameyaw S. (2014): Assessment of airborne ^{238}U and ^{232}Th exposure and dust load impact on people living in the vicinity of a cement factory in Ghana. *Radiation Protection and Environment*. Vol. 37: 120-131.
- Addo, M.A., Darko, E., Gordon, C., and Nyarko B.J.B.(2013): A preliminary study of natural radioactivity ingestion from cassava grown and consumed by inhabitants around a cement production facility in the Volta region, Ghana. *International Journal of Environmental Sciences Volume 3 (6): 2312 – 2323*.
- Adekoya, O. I., and Odundare, F. O. (2015): Gross alpha and gross beta radioactivity in surface soil and drinkable water around a steel processing facility. *Journal of radiation research and applied sciences. Elsevier*. 8(2015): 411-417.
- Ademola J. A. (2008): Assessment of natural radioactivity contents of cements used in Nigeria. *J. Radiol. Prot.* 28:581-588.
- Agbalagba, E.O., Osakwe, R. O. A., and Olarinoye, I. O. (2014): Comparative assessment of natural radionuclide content of Cement brands used within Nigeria and some countries in the world. *Journal of Geochemical Exploration* 142 (2014) 21 - 28.
- Agblagba, E. A.U. (2012). Gamma-Spectroscopy measurement of natural radioactivity and assessment of radiation in soil samples from oil fields environment of Delta State, Nigeria. *Elsevier, Journal of Environmental Radioactivity* 109: 64 -70.
- Abimbola, A.F., Ajibade O.M. and Kolawole T. (2007): Assessment of heavy metals in soils around automobile mechanics workshops in Ibadan, southwestern Nigeria. *Aquaterra Journal of Africa Water Resources and Environment*.87-88, 77, 2007.
- Adak, M. D., Adak, S. and Purohit K. M. (2007). Ambient air quality and health hazards near min-cement plants. *Pollution Research* 26(3): 361- 364.

- Ahmad, K., Khan, Z. I., Ashfaq, A., Ashraf, M., and Yasmin, S. (2014): Assessment of heavy metal and Metalloid Levels in Spinach (*Spinacia oleracea*) grown in waste soil of Sarghoda, Pakistan. *Pak. J. Bot.* 46(5) :1805-1810.
- Ajayi, J.O., Balogun, B.B. and Olabisi, O. (2012): Natural Radionuclide Contents in Raw Materials and the Aggregate Finished Product from Dangote Cement Plc, Obajana, Kogi State, North Central Nigeria. *Research Journal of Environmental and Earth Sciences* 4(11): 959-961.
- Alsop, P. A., 2007: Cement Plant Operation Hand Book, for Dry Process. 5th ed., International Cement Review. Tradeship Publications Ltd. UK, 317P.
- Arogunjo, A.M., Ofuga, E.E. and Afolabi, M.A., (2005): Levels of natural radionuclides in some Nigerian cereals and tubers. *J. Environ. Rad.* 82: 1- 6.
- Avwiri, G.O., Agbalagba, E.O., (2007): Survey of gross alpha and gross beta radionuclide activity in Okpare-Creek Deltal State Nigeria. *Asian network for scientific information. J. Appl. SC.* 7 (22), 3542 - 3546.
- Bello, I. A. (2012). External Dose Assessment from the Measured Radioactivity in Rock, Sediment and Clay samples of Sikiti, Oyo State, Nigeria. Ibadan, Nigeria: Unpublished M.Sc. Thesis, University of Ibadan.
- Bello, I. A., Jibiri, N.N. and Momoh, H.A. (2014): Determination of External and Internal Hazard Indices from Naturally Occurring Radionuclide in Rock, Sediment and Building Samples collected from Sikiti, Southwestern Nigeria. *Journal of Natural Sciences Research. Vol.4, No.12: 74-81.*
- Boadu Theophilus Marfo, Heavy Metals Contaminations of soil and water at Agboglobshie Scrap Market, Accra, Unpublished Thesis. Kwame Nkrumah University of Science and technology. M.Sc Thesis May, 2014
- Bower, H., (2002): Artificial recharge of groundwater; Hydrology and Engineering; *Hydro-geologist Journal* 10(1): 121-142.
- Cardoso, L. X., Cardoso, S. N. M., Alhanati, C. E., Ciolini, R., and Souza, S. O. (2013): Assessment of Environmental Radioactivity in Soil, Water and Food consumed in the Northeastern state of Sergipe – Brazil. *International Nuclear Atlantic Conference - INAC 2013 Recife, PE, Brazil, November 24-29, 2013.*
- CEC (1982): “1st Ring Test: Tespirometry Method. Degradation/Accumulation,” Sub-Group, 1982.

- Cember, H. (1996): *Introduction to Health Physics*. McGraw- Hill Health Professions Division, New York.
- Chad-Umoren, Y.E., Umoh I.I. (2014): Baseline radionuclides distribution pattern in soil and radiation hazard indices for Abak, Nigeria. *Adv. Phys. Theor. Appl.* 32:69–79.
- Crommentuijn T., Polder M. D., and Van de Plassche (1997): Maximum Permissible Concentrations and Negligible Concentrations for metals, Taking Background Concentration into Account (RIVN Report 601501001), Bilthoven Netherlands.
- Damla, N., Cevik, U., Karahan, G., & Kobya, A. I. (2006). Gross alpha and beta activities in tap water in eastern black sea region of Turkey. *Chemosphere*, 62(937), 957-960.
- Davison, C. M. (1974): Interaction of Gamma Radiation with Matter In: Siegbahn Kai (Editor) (1974): Alpha, Beta and Gamma Ray Spectroscopy. 4th Edition, vol. 1. North-Holland Publishing Company, Amsterdam, London. pp 37-78
- Diab, H. M and Nouh.SEL-Taher. A. (2008). Evaluation of natural radioactivity in a cultivated area around a fertilizer factory. *Nuclea. Rad. Phys.* 53-62.
- Ekwueme, B. N.,(2003). The Precambrian geology and evolution of the southwestern Nigeria Basement Complex; *University of Calabar press*.
- Ele Abiama. P., Ben-Bolie, G. H., Amechmachi, N., Najib, F., El Khoukhib, T., and Owono Atebac, P. (2012): Annual intakes of ²²⁶Ra, ²²⁸Ra and ⁴⁰K in staple foodstuffs from a high background radiation area in the southwest region of Cameroon. *Journal of Environmental Radioactivity* (110): 59 – 63.
- EPA 2009: The Environmental protection agencies web-page on beta particles (www.epa.gov/radiation/understand/beta.html).
- Ewa, I.O.B., Oladipo. M.O.A. and Umar, I.M. (2006). Trace Element Levels in Terrestrial and Aquatic Environments Near The Nigerian Research Reactor. *Journal of Environmental Systems, Bay wood Publisher, New York, USA*. Vol.32(1): 17-26.
- Ezepue, M. C. and Odigi, M. I.,(1993):*Journal of mining and geology*, vol. 29, No. 1
- Fagbote E.O and Olanipekun E.O (2010): *European Journal of Scientific Research*. Vol.41, nos.3,pp.373-382.
- Gbadebo, A.M., 2011. Natural radionuclides distribution in the Granitic rocks and soils of abandoned quarry sites, Abeokuta, Southwestern Nigeria. *Asian J. Applied Sci.*, 4: 176-185.

- Girigisu, S., Ibeanu, I.G.E., Adeyemo, D.J., Onoja, R.A., Bappah, I.A., and Okoh, S. (2014): Assessment of Radiological Levels in Soils from Artisanal Gold Mining Exercises at Awwal, Kebbi State, Nigeria. *Res J Appl Sci Eng Tech* 7(14):2899–2904.
- Gorur, F. K., Keser, R., Akcay, N., As, N., & Dizman, S. (2011). Annual effective dose and concentration levels of gross alpha and beta in Turkish market tea. *Iran Journal of Radiation Research*, 10(2): 67-72.
- Hakanson I., (1980): Ecological risk index for aquatic pollution control, a sedimentological Approach. *Water resources*, 14; 975-1001
- Harikumar P.S, U. P Nasir and M. P. Mujeebu Rahma, (2009): “Distribution of heavy metals in the core sediments of a tropical wetland system,”*International Journal. Environmental Science Technology*, Vol. 6, No. 2, 2009, pp.225-232.
- IAEA (1989): Guide book of the fall-out of radioactivity monitory in the Environment and food Programme. Technical Report series No. 295, IAEA, Vienna.
- IAEA. (20011). Extent of Environmental Contamination by Naturally Occurring Radioactive Material (Norm) and Technological Options for Mitigation. Technical Reports SeriEs No.4I9.
- Ibeanu I.G.E. (2002). Tin mining and processing in Nigeria: cause for concern. *Journal of environmental radioactivity*.Published by Elsevier Science Ltd. Vol. 60(1): 59-66.
- Ibeanu, I. G. E. (1999): Assessment of Radiological Effects of Tin Mining Activities in Jos and its Environments. Ph.D Thesis, Ahmadu Bello University, Zaria, Nigeria.
- Ibrahim, U., Akpa T.C., and Daniel, I.H. (2013): Assessment of radioactivity concentration in soil of some mining areas in Central Nasarawa State, Nigeria. *Sci World J* 8(2):7–12.
- ICRP (2000). The 2000 Recommendation of the International Commission of Radiological Protection, 21-23 *Elsevier Health Sciences*, USA.
- ICRP. (1997). Annals of the ICRP publication 103. The 2007 Recommendations of the International Commission on Radiological Protection.
- ICRP (1991). The 1990 Recommendation of the International Commission of Radiological Protection,ICRP Publication 60. 21-23 *Elsevier Health Sciences*, USA.
- ICRP (Publication 60 (1990); international commission on radiological protection.
- International Atomic Energy Agency, IAEA, (1989): Measurement of Radionuclides in Food and the Environment. *Technical Report Series*, No. 29. In Mu’azu, I. (2001): Radioactivity

- Measurement in Soils and Rocks from Phosphate and Gypsum Mines in Sokoto State, Nigeria. MSc. Thesis Ahmadu Bello University, Zaria.
- Isinkaye, M.O. (2012): Distribution of heavy metals and natural radionuclide in selected mechanized agricultural farmlands within Ekiti State, Nigeria. *Arab J Sci Eng* 37:1483–1490.
- Jabbar T, Akhter P, Khan K, Jabbar A, Saleem K (2009) Radiological impact of composite food served at PINSTECH. *Food Chem Toxicol* 47:1205–1208
- Jibiri N.N, Farai I.P and Alausa S.K (2007): Activity concentration of Ra-226, Ra-228 and K-40 in food crops from a high background radiation area in Bisichi Jos, Plateau State. *Nigeria radiation environmental biophysics*,46:53-59.
- Jibiri, N.N., and Agomuo, J.C. (2007). Trace elements and radioactivity measurements in some terrestrial food crops in Jos-plateau, north central, Nigeria. *Radiprotection*. Vol42: 29-42.
- Jibiri, N. N., and Abiodun, H. T. (2012): Effects of Food Diet Preparation Techniques on Radionuclide Intake and Its Implications for Individual Ingestion Effective Dose in Abeokuta, Southwestern Nigeria. *World Journal of Nuclear Science and Technology*. (2): 106-113.
- Jibiri, N.N, Olukorede O.A. and Egunjobi K.A. (2010): Variation of Mean Radiation Dose with Distance of Sites proximal to Purechem Cement Factory, Onigbedu Ogun State Nigeria. *The Pacific Journal of Science and Technology*. Vol. 11, No.2 (2010), 671-673.
- Jenkins, E. N. (1979): *Radioactivity: A Science in its Historical and Social Context*. Wykeham Publication (London) Ltd, pp. 34-40.
- Jonah, S. A. (2005): Gamma Ray Spectroscopy, Lecture Notes for the Training of Staff of NAFDAC on Radioactivity Measurement in Food Stuff, 24-28 January, 2005.
- Jonah, S.A., Umar, I.M., Oladipo, M.O.A., Balogun, G.I. and Adeyemo, D.J. (2006). Standardization of NIRR-1 irradiation and counting facilities for Instrumental neutron activation Analysis. *Appl. Radiat. Isot.*64: 818-822
- Khopkar, S.(1998). Basic Concepts of analytical chemistry. New Delhi, India: *New Age International*. Pp 267-280.
- Knoll, Glenn. F., (2000): Radiation Detection and Measurement. Third Edition. John Wiley & Sons, Inc. 48-52, 307-312.

- Kpeglo, D. O., Lawluvi, H., Faanu, A., Awudu, A. R., Deatanyah, P., Wotorchi, S.G., Arwui, C. C., EmiReynolds, G., and Darko, E. O. (2011): Natural Radioactivity and its Associated Radiological Hazards in Ghanaian Cement. *Research Journal of Environmental and Earth Sciences* 3(2): 161-167.
- Lentech (2009). Drinking Water Standards. Lentech Water Treatment and Air Purification Holding B.V (1998-2009). Retrieved from www.who.eu-waterstandards.htm. 09/10/2016.
- Majolagbe, A. O., Yusuf K. A., and Duru A. E., (2013). Trace metals characterization in Environmental media: A case study of Cement production area, Ewekoro, Southwest, Nigeria. *European Scientific Journal*. vol.3: 208-213.
- Malanca, A. Pessina, V. and Dallara, G. (1993): Radionuclide content of building materials and gamma-ray dose rates in dwellings of RioGrande Do-Norte Brazil. *Radiat. Protect. Dosim.*, 48:199-203.
- McMahon, G. (2007). Analytical instrument: A guide to laboratory, portable and miniaturized instruments. West Sussex, England. *John Willey and Sons Limited*. Pp 52-54.
- Momoh, A.H., (2013). Assessment of Radiation Exposure at E-waste Dumpsite around Alaba International Market Lagos, Nigeria. Unpublished MSc Thesis, University of Ibadan, Ibadan, Nigeria.
- Mu'azu, I. (2001): Radioactivity Measurement in Soils and Rocks from Phosphate and Gypsum Mines in Sokoto State, Nigeria. MSc. Thesis Ahmadu Bello University, Zaria.
- Muhanned, R.A.A. (2013). Qualitative, Quantitative and Radiological Assessment of Marl Layer in the Euphrates Formation for Portland Cement Industry in Kufa Cement Quarry at Al-Najaf Governorate. Published MSc Thesis, College of Science, University of Baghdad, Iraq.
- Musa, O.K., Shuibu, M.M., and Kudamnya, E.A. (2013). Heavy Metal Concentration in Groundwater around Obajana and Its Environs, Kogi State, North Central Nigeria. *American International Journal of Contemporary Research* Vol. 3 No. 8; 170-177.
- Ndontchueng M.M; Simo I. A; Nguelem E.J.M, Njinga R. L., Beyala J.F.; Kryeziu D. (2013): Preliminary Investigation of Naturally Occurring Radionuclide in Some Six Representative Cement Types Commonly used in Cameroon as Building Material. *International Journal of Science and Technology*. Volume 3 No.10 pp. 365 – 371.
- Neiler, J. H. and Bell, P. R. (1974): Scintillation Method. pp 245-302. In: Siegbahn Kai (Editor) (1974): Alpha, Beta and Gamma Ray Spectroscopy. 4th Edition, vol. 1. North-Holland Publishing Company, Amsterdam, London.

- Nada, A. et al. (2009). Distribution of radionuclides in soil samples from a petrified wood forest in El-Qattamia, Cairo, Egypt. *Appl. Radiat. Isot.*, 67, 643–649.
- Nollet M. (2011). Hand book on analysis of edible animal by product. New York, USA: *Taylor and Francis*. Pp 193-197.
- Okojie, L.O. (2014). Cement Production and Sustainable Rural Farming Livelihood in Nigeria: Striking a Sensible Balance through Environmental Legislation and Enforcement. *European Journal of Sustainable Development*. 3 (3): 251-262.
- Oladipo, M.O.A. (2012). Natural occurring radioactive substances [Power point slides]. Nuclear Science programme, Nuclear Technology Centre, Sheda, Abuja.
- Olayiwola, O. A. (2013): Accumulation and contamination of heavy metals in soils and Vegetation from industrial Area of Ikirun, Osun state, Nigeria, *Global Journal of Pure and Applied Chemistry Research* Vol.1 Issue No.1 pp.25-34, June, 2013.
- Olowoyo J.O., Mugivhisa L.L and Busa G.N. (2015): Trace metal in Soil and Plants around a cement factory in Pretoria, South Africa. *Pol. J. Environ. Stud.* Vol. 24, No. 5 (2015), 2087-2093.
- Omeje, C.U. (2009). Naturally Occurring Radioactive Materials (NORM) and Trace Element Measurements for Part of Sheet 102S.W. Zaria. Unpublished PhD Thesis Proposal, Ahmadu Bello University, Zaria, Nigeria.
- Onoja, M.A. (2015). A Study of Environmental Pollution around the Kaduna Refinery using Nuclear and Related Techniques. Unpublished PhD Thesis, Ahmadu Bello University, Zaria, Nigeria.
- Onoja, R.A. (2011). Determination of Natural Radioactivity and Committed effective dose calculation in Borehole water supply in Zaria, Nigeria. Unpublished PhD Thesis, Ahmadu Bello University, Zaria, Nigeria.
- Parry, S.J. (1991). *Activation Spectrometry in Chemical Analysis*. John Wiley and Sons: New York, NY.
- Qingjie G, Jun D (2008): Calculating pollution indices by heavy metals in ecological geochemistry assessment; a case study in parks of Beijing. *J Chin Univ Geosci* 19(3):23–41
- Rahaman, M. A., (1976) Review of basement geology of southwestern Nigeria: In geology of Nigeria (C. A. Kogbe, Ed.). Elizabethan publishing Co., Lagos.

- Rahib, H., Seema, A., Khattak, M. Tahir, S., and Liaqat, A. (2015): Multistatistical Approaches for Environmental Geochemical Assessment of pollutants in soils of gadoon Amazai Industrial Estate, Pakistan. *J. soils Sediments* (2015) 15:1119-1129.
- Reference values trace elements in soil, Monitorul oficial al romaniei, No.303 bis /6XII 1997 (in Romanian).
- Rizzo, S., Brai, M., Basile, S., Bellia, S., and Hauser, S. (2001). Gamma activity and geochemical features of building materials: estimation of gamma dose rate and indoor radon levels in Sicily. *Appl. Radiat. Isot.*, 55: 259-265.
- Sajo-Bohus, L., Gomez, J., Capote, T., Greaves, D., Herrera, O., Salazar, V., & Smith, A. (1996): Gross alpha Radioactivity of Drinking water in Venezuela. *J. Environ. radioactivity. Elsevier*. Vol. 35, No. 3 pp. 305-312, 1997.
- Samuel E., and Aynalem D., (2012): Assessing the Effect of Cement Dust Emission on Physiochemical Nature of Soil around Messebo area, Tigray, North Ethopia. *Int. j. econ. env. geol.* Vol:(3) 12–20.
- Shyamal, R.C., Rezaul, A., Rezaul-Rahman, A.K.M. and Rashmi, S. (2013). Radioactivity Concentrations in Soil and Transfer Factors of Radionuclides from Soil to Grass and Plants in the Chittagong City of Bangladesh. *Journal of Physical Science*, Vol. 24(1), 95–113, 2013.
- Sultan, A.M. (2006). Health hazards of cement dust. Department of Physiology, College of Medicine, King Saud University Riyadh, Kingdom of Saudi Arabia. Pp. 1-20.
- Taskin, H.M., Karavus, P., Touzogh, S., and Karahan, G. (2009). Radionuclide concentration in soil and excess lifetime cancer risk due to gamma radioactivity, Turkey. *Journal of Environmental Radioactivity*, 100, 49-53
- Tchokossa, P., Olomo, J.B., Osibota, O.A., (1999): Radioactivity in the community water supplies of Ife-central and Ife-East L.G.A.'S Osun State, Nigeria. *Nucl. Instr. Meth. Phys. Res.* A422, 780 -784.
- Van Lieshout, R., Wapstra, A. A., Ricc, R. A., and Girgis, R. K. (1974): Scintillation Spectra Analysis. In: Siegbahn Kai (Editor) (1974): Alpha, Beta and Gamma Ray Spectroscopy. 4th Edition, vol. 1. North-Holland Publishing Company, Amsterdam, London. Pp 501-538.
- UNSCEAR, United Nations Scientific Committee on the Effects of Atomic Radiation, Sources and effects of ionizing radiation, Report to General Assembly, with Scientific Annexes, United Nations, New York, 1993.

- United Nations Scientific Committee on Effects of Atomic Radiation,(UNSCEAR) 2000. Sources and Effects of Ionizing Radiation (Report to the General Assembly) New York: United Nation). *UNSCEAR Report, New York*.
- White, G.R. 1981. Concrete Technology, 3rd Ed. John . Delmar Publishers, USA, 18 – 19.
- World Health Organization (WHO). World Health Organization Guidelines for drinking water quality.1996; 2nd Ed, Vol.2, *Health Criteria and Supporting Information*, WHO, Geneva.
- WHO. (2004). Guidelines for drinking-water quality. Sixty-first meeting, Rome, 10–19 June 2003. Joint FAO/WHO Expert Committee on Food Additives.
- WHO and GoP, (2005). Quality Drinking Water: Guidelines and Standards for Pakistan. Ministry of Health Service Academy, Islamabad, Pakistan.
- Yang YB and Sun LB. (2011): Status and control countermeasures of heavy metal pollution in urban soil. *Environmental protection Science*, 35(4): 79-81.

APPENDIX A

Calibration of NaI(Tl) Gamma Spectrometry

Table 1.0: Spectral energy windows used in the Analysis

<i>Isotope</i>	<i>Gamma Energy (Kev)</i>	<i>Energy Window (Kev)</i>
<i>R-226</i>	<i>1764.0</i>	<i>1620-1820</i>
<i>Th-232</i>	<i>2614.5</i>	<i>2480-2820</i>
<i>K- 40</i>	<i>1460.0</i>	<i>1380-1550</i>

Table 1.1: Table of Energy Calibration for quantitative Spectral Analysis

<i>Isotope</i>	<i>Calibration Factors</i>		<i>Conversion Factors(Bq Kg⁻¹)</i>	<i>Detection Limits</i>	
	<i>10⁻³ (cps/ppm)</i>	<i>10⁻⁴ (cps/ppm)</i>		<i>ppm</i>	<i>Bq/Kg</i>
<i>⁴⁰K</i>	<i>0.026</i>	<i>6.431</i>	<i>0.032</i>	<i>454.54</i>	<i>14.54</i>
<i>²²⁶Ra</i>	<i>10.500</i>	<i>8.632</i>	<i>12.200</i>	<i>0.32</i>	<i>3.84</i>
<i>²³²Th</i>	<i>3.612</i>	<i>8.768</i>	<i>4.120</i>	<i>2.27</i>	<i>9.08</i>

APPENDIX B

CALIBRATION OF GAS FIELD PROPORTIONAL COUNTER

Table 2.0: Calibration of Gas filled Proportional Counter

Calibration Result	Alpha	Beta
Detector Efficiency	87.95%	42.06%
Detection limit	0.16cpm	1.47cpm
Detector Background	0.14cpm	77.82cpm