QUANTIFICATION OF HEAVY ELEMENTS AND RADIATION EFFECTS OF TRONA, SOLD IN ZARIA MARKETS, KADUNA STATE, NIGERIA

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QUANTIFICATION OF HEAVY ELEMENTS AND RADIATION EFFECTS OF TRONA, SOLD IN ZARIA MARKETS, KADUNA STATE, NIGERIA

BY

Hannatu Jura IBRAHIM, BSC. (ABU) 2012

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SEPTEMBER, 2018

DECLARATION

I declare that the work in this Thesis entitled "**Quantification of Heavy Elements and Radiation Effects of Trona, Sold in Zaria Markets,Kaduna State,Nigeria."** has been carried out by me in the Department of Physics. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any otherInstitution.

_____ _____

Ibrahim Hannatu Jura Date
(P15SCPY8021)

CERTIFICATION

This Thesis entitled **"QUANTIFICATION OF HEAVY ELEMENTS AND RADIATION EFFECTS OF TRONA, SOLD IN ZARIA MARKETS, KADUNA STATE, NIGERIA",** by Hannatu Jura IBRAHIM meets the regulations governing the award of degree of Master of Science (M.Sc.) Radiation Bio Physics of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation**.**

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DEDICATION

I dedicate this work to my Late Dad Mr. Ibrahim Yakubu Maisamari Jura.

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ABSTRACT

This study was carried out to quantify the heavy metals level and Radioactivity concentration in some selected varieties of Trona namely Farar Balma, Jan Balma, Ngurnu, Jan Kanwa, Farar Kanwa, Yar Agadez, Dan Libya, Manda, all sold in Zaria markets of Kaduna State,Nigeria. Elemental analysis of Trona, was determined by atomic absorption spectrometry (AAS). Elements analyzed were Cadmium (Cd), Manganese (Mn) Chromium (Cr), Nickel (Ni), Copper (Cu), Zinc (Zn), Cobalt (Co) and Iron (Fe). Also, the samples were analyzed for Potassium (K). Results indicate that concentrations of the toxic metals (Cd, Zn, Cr, Cu, Co, Pb, Mn & Ni) in the samples were 0.0028±0.0006,0.0151±0.0033,1.1500±0.2286,0.0020±0.0006,0.3200±0.2354,0.7606±0.0143, 0.1717±0.0504 and 0.1368±0.0765 respectively. The concentrations of all the elements were found to be within World Health Organization Recommended Dietary Intake. The specific activity of the naturally occurring radioactive materials (Ra-226, Th-232, K-40) in the Trona was also analyzed. The specific activity of K-40, Ra-226 and Th-232 ranged from 1143.50 Bq/kg - 43.34Bq/kg, 151.02 Bq/kg - 1.80 Bq/kg and 65.85 Bq/kg -1.03 Bq/kgrespectively with mean values of 455.28±10.56, 11.96±1.41, 42.904±4.54 for K-40, Th-232 & Ra-226 respectively. Parameters such as radium equivalent activity and Ingestion effective dose where computed. The values of the radiological parameter showed that radium equivalent activity ranged from 213.73Bq/kg -9.35Bq/kg with a mean value of 95.05±3.62Bq/kg and this amount is less than the permitted amount, which is 370 Bq/kg (UNSCEAR 2000). Likewise, the result of the analysis revealed that, the ingestion effective dose in all Trona samples were lower than the permissible limits of 1 mSv/y recommended by (ICRP 1996). Therefore Observations from this study reflects that there is a low risk of heavy metal and radiological intoxication to the consumer, except for continuous consumption of Trona exceeding the recommended daily intake which would result to endangering consumers.

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Total elemental concentrations of Co, Pb, Cd, Zn, Cr, Cu, Mn, Ni, and K

ABBRIATIONS

BFT=Borno Farar kanwa Trona

NJT= Niger JanKanwa Trona

LDT=Libya DanLibya Trona

SB_JT= Sokoto JanBalma Trona

KM_GT= Kano Mangul Trona

CNT= Chad Ngurnu Trona

CJT= Chad JanKanwa Trona

SB_FT= Sokoto FararBalma Trona

NAT= Niger Agadez Trona

JM_NT = Jigawa Manda Trona

JB_fT= Jigawa FararBalma Trona

K_AM_NT= Katsina Manda Trona

YFT= Yobe FafarKanwa Trona

NFT= Niger FararKanwa Trona

WHO= World Health Organization

RDI=Recommended dietary Intake

NARICT=National Research Institute for Chemical Technology

IAEA= International Atomic Energy Association

LET=Linear Energy Transfer

NIRPR= Nigerian Institute of Radiation Protection and Research

NNRA= Nigerian Nuclear Research Institute

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

Heavy elements are metallic elements which have a high atomic weight and a density much greater (at least 5 times) that of water (Victor, 2011). There are more than 20 heavy metals and these heavy metals are highly toxic and can cause damaging effects even at very low concentrations. They tend to accumulate in the food chain and in the body and can be stored in soft (e.g., kidney) and hard tissues (e.g., bone). Being metals, they often exist in a positively-charged form and can bind on to negatively-charged organic molecules to form complexes (Victor, 2011).

The body has need for approximately 70 friendly trace element heavy metals, but there are another 12 poisonous heavy metals, such as Lead, Mercury, Aluminum, Arsenic, Cadmium, Nickel, etc., that act as poisonous interference to the enzyme systems and metabolism of the body. No matter how many good health supplements or procedures one takes, heavy metal overload will be a detriment to the natural healing functions of the body (Victor, 2011).

It is tangible from recent scientific reports that there is an increased use of geological mineral substances in human and animal foods (Aribido *et al.*, 2001)1. In Nigeria, the renewed government interest in solid mineral exploration and exploitation may possibly explain the reason for the use of naturally occurring inorganic salts for diverse purposes (Aribido *et al.*, 2001). Based on this, the beneficial effects of these mineral additives in plant residue and animal nutrient utilization for animal productivity increase have been reported by Mees and Merchen, 1985. Though some natural products such as alum were also used in water processing for home and industrial needs, likewise Trona called Kanwa

in northern part of Nigeria are used for these purposes. Trona, is traditionally known as **kaun** among the Yoruba, **kanwa** among the Hausa and **akanwu** among the Igbos and **Okanwa** among Igalas and **Ikoro** among Egbira people of Nigeria. "Trona" is erroneously called potash although it contains low amount of potassium compared to sodium, it is the second most commonly used salt in Nigeria. Makanjuola and Beetlestone, (1977) reported that the level of potassium in Trona is quite below detection in most of the specimen analyzed. This indicates that its chemistry is misunderstood by those describing it as 'potash'. These findings with other existing facts show that potash as a mixture of various salts with other earth impurities may be toxic which raises doubt on its ingestion safety by humans. The biochemical and physiological effects of potash have been investigated but data scarcity still exists, concerning its dietary effects in humans (Oyeleke, 1988). Although potash is widely used in Cameroon, Ghana, Nigeria and several other West African countries, little information has been reported of its radiological content, however, studies have shown its elemental compositions.

This research aims at contributing to literature in the following ways:

- The data obtained can be used as a future reference material since to the best of my knowledge, such information on radioactivity in Trona has not been investigated.
- That the result obtained can be used as a guide on the consumption of Trona.
- It can serve as a base line data on the levels of radioactivity concentration in Trona.

1.2 Aim and Objectives

The aim of this thesis work is to quantify heavy elements and radiological concentration of the different varieties (Balma, Farar Kanwa, Jan Kanwa, Dan Libya, Yar Agadas, Ngurnu, Manda, Mangul) of mined Trona sold in markets within Zaria.

The following objectives are used to achieve the above set aim:

1. To determine the different elemental concentration of the samples.
2. To determine the activity concentration of K-40, Th-232 and Ra-226 in the samples.
3. To determine the radiological implications (dose estimate, radium equivalent activity and effective dose) of the above radionuclides.

1.3 Statement of Problem

Trona minerals are radioactive because of the presence of the radioactive ^{40}K isotope. (Donald 2015). Literature has reported that the high concentration of potassium in foods and drinking water could be detrimental to human health (Davidson,1974).

The popularity of Trona is such that in some parts of the world, it is ranked next in importance to the common table salt. However, the fact still remains that it contains certain level of radioactive K-40. (Makanjuola and Beetlestone, 1977).

1.4 Justification of Research Work

Natural background radiation comes from radioactive elements normally present in the soil. Natural terrestrial radionuclide sources in soil, food, air and drinking water are the major contributors to worldwide radiation exposure (Fasae, 2013). Although the concentration of NORMs in most natural substances is low, almost any operation in which any material is extracted from the earth and processed can have NORM, in product, by-product, residue or waste streams.

Similarly, sources of heavy metals in the environment include man made sources due to advancement in technology such as mining. Mining introduces toxic elements to the environment and this leads to the toxic substance contained in the mined rock or area easily exposed (Paul *et al.*, 2014). These findings with other existing facts show that potash as a mixture of various salts with other earth impurities may be toxic which raises

doubt on its ingestion safety to humans. Hence there is a need to carry out analysis on Trona so the public and relevant authority will have a better knowledge on its radioactivity concentration as well as its heavy metal composition.

As such it has become paramount to analyze mined consumables to ascertain the concentration of heavy metals and NORMs.

1.5 Scope and Limitation

This research work covered majorly mined Trona sold in Samaru, Sabon gari, Kwangila, Dan magaji, Tudun wada, Shika and Bassawa markets within Zaria namely. All the different varieties (Balma, Farar Kanwa, Jan Kanwa, Dan Libya, Yar Agadas, Ngurnu, Manda, Mangul) of Trona sold in these markets in Zaria where collected for analysis. The research therefore will cover the quantification of heavy elements found in the Trona samples gotten from the market. Furthermore, the radiological concentrations of these samples will be identified and documented accordingly. Instruments situated at NARICT BASSAWA in Zaria and National Institute for Radiation Protection and Research at the University of Ibadan will be used for the analysis. The analysis carried out in these places involved Atomic Absorption Spectrometer and High Pure Germanium detectors respectively.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Radioactivity

Radioactivity in the environment comes from both natural background and man-made sources. Natural abundant radionuclides (Ra-226, Th-232 and K-40) in the environment, and release from fertilizers, agro chemicals, research and medical facilities form the bulk of radionuclides in the environment (Wisser *et al.*, 2003). Natural occurring radioactivity is due to bedrock formations which are weathered, resulting in mineral leaching that leads to contamination, (Martin *et al.*, 1995). These contaminations have health effect that poses great danger to human and other living organism in the biosphere.

Many radionuclides are known to decay by alpha, beta and other form of emission which happen to pose a hazard when ingested. Among which are Cesium-137, Chromium-51, Cobalt-60, Iodine-131, Lead-210, Phosphorus-32, Radium-226, Radon-222, Scandium-46, Strontium-90, Thorium-232, Tritium, Uranium-238, Zinc-65 and Zirconium-96, (Cember, 2009). Exposure to ionizing radiation represents a potential hazard to humans and radioactivity is known to trigger deterministic and stochastic effects (Hall and Giaca, 2006). Alpha radiation, for instance was recognized to be the most dangerous type of radiation when incorporated in the human body. This is due to the high mass and Linear Energy Transfer (LET) of alpha particles (Knoll, 1989). Thus all radiobiological damaging effects begin with the consequence of radiation interactions with the atoms forming the cells.

This has made it essential to access the presence of radionuclides in consumables as generally recommended by bodies like World Health Organization (WHO), and International Atomic Energy Agency (IAEA) that set an International Basic Safety

Standard (BSS) for protection against ionizing radiation and for safety of radiation sources.

2.2 Natural Radioactivity

Radioactivity is a natural phenomenon. It is the spontaneous emission of ionizing radiation particles (alpha, beta and gamma rays) following the disintegration of certain atomic nuclei. The main contributors of radioactivity to natural background radiation are external radiation from both cosmic and terrestrial sources, and internal radiation from internally deposited radioactive materials such as radon, carbon-14 and potassium-40. The table 2.1 shows a mean annual natural background radiation in certain areas of the world from both external and internal sources.

These natural radioactive substances are responsible for the phenomenon of natural radioactivity in the environment. When these substances disintegrate, they undergo nuclear transition from one nuclear state to the other, emitting radiations. Only the gamma components contribute significantly to the external natural background radiation fields. (UNSCEAR, 1977).

Table 2.1: Average contribution of different sources of natural background radiation to the yearly dose to the population

Source	Dose (mSv/y)
External radiation	
Terrestrial radiation	(Rock,soil) 0.45(20mSv/yr: India, Brazil)
Cosmic radiation	0.36 (1.2mSv/yr, Denver, USA)
Internal radiation	
^{14}C in the body produced by cosmic radiation	0.02
Other nuclides produced by cosmic radiation	0.01
^{40}K in the body	0.18
Uranium and thorium decay nuclides within the body	0.16
Radon and radon progeny	2.00
Total	3.00

Source: Ibeanu, 2016

2.3 Norms (Naturally Occurring Radioactive Materials).

NORM is the acronym for Naturally Occurring Radioactive Material, which includes all radioactive elements found in the environment. However, the term is used more specifically for all naturally occurring radioactive materials where human activities have increased the potential for exposure compared with the unaltered situation. Concentrations of actual radionuclides may or may not have been increased; if they have, the term

Technologically-Enhanced (TENORM) may be used (World Nuclear Association 2016). All Minerals and raw materials contain radionuclides of natural origin. The most important for the purposes of radiation protection are the radionuclides in the U-238 and Th-232 decay series. For most human activities involving minerals and raw materials, the levels of exposure to these radionuclides are not significantly greater than normal background levels and are not of concern for radiation protection. However, certain activities can give rise to significantly enhanced exposures that may need to be controlled by regulation. Material giving rise to these enhanced exposures has become known as naturally occurring radioactive material (World Nuclear Association 2016).

2.3.1 NORM sources

The list of isotopes contributing to natural radiation can be divided into those materials which come from the ground (terrestrial sources – the vast majority) and those which are produced as a result of the interaction of atmospheric gases with cosmic rays (cosmogenic). NORM levels are typically expressed in either Becquerel per kilogram (or gram) and it indicates level of radioactivity generally or due to a particular isotope, while parts per million (ppm) indicates the concentration of a specific radioisotope in the material. (World Nuclear Association 2016).

2.3.2 Terrestrial NORM

Terrestrial NORM consists of radioactive material that originates from the Earth's crust and mantle, and where human activity results in increased radiological exposure. The materials may be original (such as uranium and thorium) or decay products thereof, forming part of characteristic decay chain or series, or potassium-40. The two most important chains providing nuclides of significance in NORM are the thorium series and the uranium series (World Nuclear Association 2016).

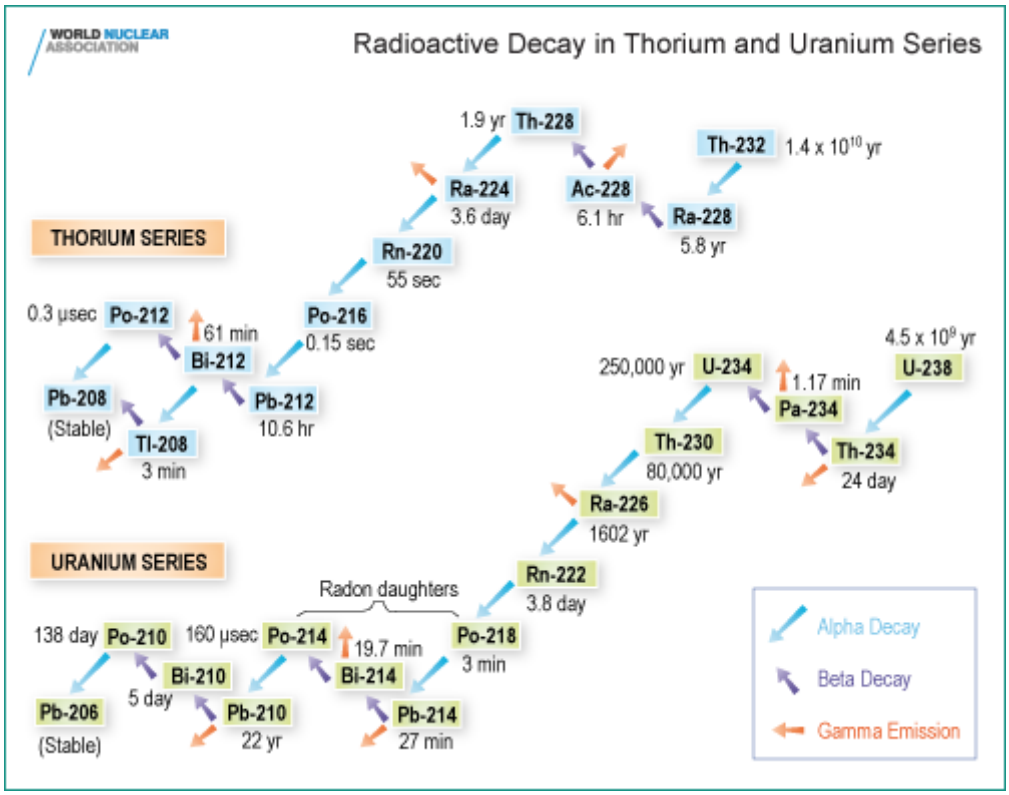


Plate I: Radioactive Decay in Thorium and Uranium Series.

(World Nuclear Association, 2016).

Another major source of terrestrial NORM is potassium 40 (K-40). K-40 has a long half-life of (1.25 billion years) meaning it still exists in measurable quantities today. It beta decays, mostly to calcium-40, and forms 0.012% of natural potassium which is otherwise made up of stable K-39 and K-41. Potassium is the seventh most abundant element in the Earth's crust, and K-40 averages 850 Bq/kg there. It is found in many foodstuffs (bananas for example), and indeed fills an important dietary requirement, ending up in our bones. (Humans have about 65 Bq/kg of K-40 and along with those foods are therefore correspondingly radioactive to a small degree (World Nuclear Association, 2016).

2.4 Some uses of Trona

Trona mostly occurs in the northern part of Nigeria, particularly in Yobe, Borno and Maiduguri areas, extending to border countries like Chad and Niger (Ajiboye *et al*., 2013, Omajali, 2010).According to Makanjuola and Beetlestone 1977, it is the second most commonly used salt in Nigeria. It is next important table salt and very low amounts of potassium as compared to sodium (Ekanem, 1977). Trona is used for many purposes in Nigeria. In powdery form, when mixed with tobacco it is used as snuff. In the Northern part of Nigeria, it is also administered in large doses by the 'Hausas' in the form of guinea corn and millet porridges called 'kunun kanwa' which is administered to women immediately after delivery for the purpose of increasing the quality and quantity of breast milk (Davidson, 1974). It is also used as a tenderizer, flavoring agent, food preservative, as well as improving protein digestibility of cowpea (Uzogara *et al*., 1988 and Omueti *et al*., 1992). Tron*a is* a major food supplement in most rural and urban home areas including food industries in Nigeria and medicine (Omajali and Sanni., 2010). Every home uses Trona as food supplement or as medicine in human and animals. It had great significance for use as medicines, culinary purposes, tanning of leather, and other uses (Paul, 2011). It has also been taken as a medicine in humans for various ailments long time ago in Northern Nigeria, like skin infection, respiratory problem, gastrointestinal problem, reproductive problem, *etc* (Alawa *et al.*, 2000). Trona is used as salt licks for animals and the salt earth could be marketed for animal's nutrient supplements (Paul, 1986). It is mostly taken by nursing mothers in pap to boost breast milk (Ekanem, 1977). Traditionally, Tronais used as an aid in childbirth postnatal care and employed in the treatment of menstrual disorders (Alawa *et al.*, 2000). It is used in concoctions for the treatment of reproductive ailments such as retained placenta and difficulty in urination

(Paul, 1986). In addition, *farar kanwa and jar kanwa* , varieties of Trona were used in various mixtures to treat dandruff, problems related to pregnancy, eye disorders, infertility, and as an ingredient in herbal concoctions (Paul, 2011).

The standard Hausa millet porridge, for example, could be made with various grades of *farar kanwa, ngurnu*, and jar *kanwa* salt (Uzogara *et al.*, 1990). *Trona* is extensively used in the tanning industry and in the preparation and enhancement of flavor of local beverages and snuff (Buchanan and Pugh, 1969).

In addition, the salts are extensively used in food preservative to hinder growth of microorganisms that cause food spoilage (Uzogara *et al.*, 1990). Boiling leafy vegetables with *Trona* minimizes losses of importance minerals and tenderise the leaves and make it more attractive by conserving the attractive green colour found in the fresh vegetable (Richard, *et al.*, 2000). Also, *farar kanwa* was also used in making local soap known as "*sabulun solo*" that is used in bathing.

Reports of its use as softener for food and vegetables such as cowpea, okra and **ewedu** have been attested to by Ankrah and Dolvo, (1978). Apart from being taken in food, it is also used as a component by some Nigeria medicinal concoctions and sometimes it is chewed raw (Sodipo *et al.*, 1992) with high potency in cough, tooth and stomach aches and constipation. Studies have indicated that the high level of potash in foods and drinking water could be detrimental to human health (Davidson *et al.*,1974, Bello, 1988).

Mining of Trona occurs at depths ranging from 800 feet to 1600 feet below the surface in Trona beds that are 8 to 14 feet thick. The Trona ore is recovered utilizing dry or wet methods. Dry mining is similar to underground coal mining; the mine workings are developed using room-and-pillar and long wall mining techniques. The mining cycle

includes shearing the Trona from the face with either a long wall shearer or continuous miners and then loading it onto conveyor belts. The conveyor belts move the Trona to ore skips that carry it to the surface through vertical shafts. The recovered Trona ore is stockpiled on the surface to be used as feed for the processing plant. Wet mining (solution mining) is done by injecting a solution from the surface into the Trona deposit using a series of bore holes as injection wells. This is done in either previously unmined ground or in the mined-out areas of active operations. In both cases, the injected solution dissolves the Trona ore which saturates and enriches it. Subsequently, the saturated solution is pumped to the surface through recovery wells for further processing into soda ash. Some mine operators use dry recovery methods for primary ore extraction and then wet mining methods for secondary recovery. This technique results in maximum recovery of the trona reserve, some of which was previously considered unminable (Davidson *et al.*,1974.)

2.5 Dosimeric Model for Radioactivity

Recommendations of ICRP for intake or ingestion limit of radionuclide are based on a simple Dosimetric model: the maximum allowed body burdens were set by comparing the dose equivalent due to delivery of radionuclide to specific organ by radiation. Deposition in a given organ may be considered to be instantaneous with respect to time that the nuclide will be cleared from the organ at a rate determined by the effective half-life (T_E).

2.5.1 Effective half-life

Effective half-life may be calculated by integrating the dose rate over the required time interval. In making this calculation, two factors must be considered, namely:

(a.) In situ radioactive decay of the radionuclide and

(b.) Biological elimination rate of the radionuclide.

In most instances, biological elimination follows first-order kinetics. In this case, the equation for the quantity of radioactive material within an organ at any time t after deposition of a quantity Q_0 is given by

$Q = Q_0\, e^{-\lambda_P t}(e^{-\lambda_B t})$……2.1

Where λ_P is the radioactive decay constant and λ_B is the biological elimination constant.

The two exponentials in Eq. 1, may be combined

$Q = Q_0 e^{-(\lambda_P + \lambda_B)t}$……2.2

and, if

$\lambda_E = \lambda_P + \lambda_B$,……2.3

we have

$Q = Q_0 e^{-\lambda_E t}$……2.4

where λ_E is called the *effective* elimination constant. The effective half-life is then

$T_E = \frac{0.693}{\lambda E}$

From the relationship among λ_E, λ_P, and λ_B, we have; $\frac{1}{TE} = \frac{1}{TP} + \frac{1}{TB}$ Or

$T_E = \frac{TP \times TB}{TP + TB}$……2.5

2.5.2 Total dose: dose commitment

The retention of the radionuclide in the body is described by (Cember, 2009) as:

The dose dD during an infinitesimally small period of time dt at a time interval t after an initial dose rate $\dot{D}_0$ is

dD = initial dose rate × dt.= $\dot{D}_0 e^{-\lambda_E t}dt$.……2.6

The total dose during a time interval t after deposition of the radionuclide is

$D = \dot{D}_0 \int \int_0^t e - \lambda \mathrm{E} t \mathrm{d}t$……2.7

which, when integrated, yields

$$D = \frac{\dot{D}0}{\lambda E}(1 - e^{-\lambda E t}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.8$$

For an infinitely long time—that is, when the radionuclide is completely gone

Eq. 2.8, reduces to

$$D = \frac{\dot{D}0}{\lambda E} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2.9$$

For practical purposes, an "infinitely long time" corresponds to about six effective half-lives. It should be noted that the dose due to total decay is merely equal to the product of the initial dose rate $\dot{D}_0$ and the average life of the radionuclide within the organ $1/\lambda_{E.}$ that is, the limiting value is reached after about six half-lives for practical purposes. At this stage the amount of activity deposited in the critical organ is equal to the amount of activity eliminated.

2.5.3 Annual Limit on Intake (ALI)

An Annual Limit on Intake (ALI) is defined as that activity of a radionuclide or Derived limit for the amount of radioactive material taken (inhaled or ingested) into the body of a Reference Man (ICRP 1975) in a year. In other words, it is the smaller value of intake of a given radionuclide in a year by reference man that would result in:

•a committed effective dose equivalent of 5 rem or

•a committed dose equivalent of 50 rem to any individual organ or tissue.

The AL1 for a particular radionuclide is therefore, the largest value of annual intake, I, that satisfies the following constraints:

$Ih_{E,50} < 5$rem,

$I\ h_{T,50} < 50$ rem, for all T ,

2.5.4 Derived Air Concentration (DAC)

This is defined as that concentration of radionuclide in air which, if breathed by Reference Man (ICRP 1975) for a work-year, would result in the intake of one ALI. That is the concentration of a radionuclide in air is limited by $\int C(t)\, Bdt \leq ALI$. Where C(t) is the concentration of the radionuclide in air at time t, B is the volume of air breathed by a worker per unit time, and the integration is carried out over a 2000 hour work-year. For the special case of constant air concentration, the DAC is related to the AL1 through

DAC (Bq/m^3) = $\frac{AL\,1\,(Bq)}{2.4\ x:\ 103\,(m3)}$ based on a normal breathing rate B of 0.020 m^3/min. (Herman 2009).

2.6 Gamma Ray Interactions in a Detector

The process of detection of radiation is initiated when an incident gamma ray enters the crystal of the detector. The energy of the gamma ray is totally absorbed under ideal conditions. This is accomplished by three main interactions between gamma ray and the crystal. These interactions are photoelectric effect Compton scattering, and pair production.

2.6.1 Photoelectric effect

Photoelectric effect is an interaction between a low energy incident photon and an inner shell orbital electron. The energy of the incident photon is totally absorbed and used to eject the orbital electron from its orbital shell. This electron is known as photoelectron. This happens if the incident photon energy exceeds the binding energy of the electron. The ejected electron leaves a vacancy in the inner orbital shell causing the emission of characteristic x-rays or auger electron when an outer shell electron full fills this vacancy (Sorenson & Knoll, 2000).

2.6.2 **Compton** scattering

The interaction process of Compton scattering takes place between the incident gamma ray photon and an electron in the detector material (Adams and Dams, 1970). The incoming gamma ray photon is deflected through an angle Θ with respect to its original direction and hence the photon transfers part of its energy and momentum to a free electron, creating a recoil electron. Since all angles of scattering are possible, the energy transferred to the electron can vary from zero to a large fraction of the gamma ray energy (Knoll, 2000).

2.6.3 Pair production

This interaction mechanism occurs in the intense electric field near the protons of the nuclei in the absorbing medium (detector) and corresponds to the creation of an electron-positron pair at the point of complete annihilation of the incident gamma-ray photon. For this process to take place, the gamma ray energy should exceed twice the rest mass energy of the electron (1.022MeV). Both positron and electron disappear and are replaced by two annihilation photons of energy m_0c^2 (0.511MeV) each emitted back to back (Knoll, 2000).

2.7 Description of Some Heavy Metals Studied

Some heavy metals that were studied in the samples collected are:

2.7.1 Lead (Pb): Lead is a toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world. It is a cumulative toxicant that affects multiple body systems, including the neurological, haematological, gastrointestinal, cardiovascular and renal systems. Children are particularly vulnerable to the neurotoxic effects of lead, and even relatively low levels of

exposure can cause serious and, in some cases, irreversible neurological damage. (IPCS 1995, Fewtrell *et al.*,2003).

2.7.2 Chromium: The toxic effects of chromium to both plant and human health are well known. Depending on the mode of exposure to chromium, several medical conditions may result, including dermatitis, skin ulcers, irritation of the air ways, cough, chest pain, abdominal pain, diarrhea, heart failure, as well as damaging of the gut, liver and kidneys (Assem and Zhu 2007).

2.7.3 Nickel**:** According to (Das *et al.*,2008), nickel is a known haematotoxic, immunotoxic, neurotoxic, genotoxic, reproductive toxic, pulmonary toxic, nephrotoxic, hepatotoxic and carcinogenic agent. Soils naturally contain between 4 and 8 ppm of nickel, except for mining and other nickel related industrial areas where the concentration can be as high as 9,000 ppm.

2.7.4 Copper**:** Exposure to excess copper can result in nasal and throat irritation, nausea, vomiting, diarrhea, liver and kidney damage, and possible death (Group, 2010).

2.7.5 Zinc**:** Zinc is also an essential element needed by the body in small amounts. The average daily intake of zinc through food sources is about 5.2 to 16.2 mg in the US. If as large as ten to fifteen times the recommended daily allowance (RDA) of zinc is ingested, even for a short period of time, it can lead to stomach cramps,nausea and vomiting. If ingested for longer periods, anaemia, damage to the pancreas and low birth weight may occur (ASTDR 2000).

2.7.6 Cobalt**:** Cobalt can be used to treat anaemia in pregnant women because it stimulates production of red blood cells. High concentrations of cobalt above 1 mg can result in vomiting and nausea, asthma, pneumonia, damage to the thyroid, and vision and heart problems (Lenntech (2013).

2.7.7 Cadmium**:** Cadmium exerts toxic effects on the kidney, the skeletal system and the respiratory system and is classified as a human carcinogen (ICPS 1992).It is generally present in the environment at low levels; however, human activity has greatly increased those levels (ICPS 1992).Lower concentrations are found in vegetables, cereals and starchy roots. Human exposure occurs mainly from consumption of contaminated food, active and passive inhalation of tobacco smoke and inhalation by workers in the non-ion compound industries (W.H.O 2007).

2.7.8 Manganese: Manganese is an essential element for humans and other animals. Adverse effects can result from both deficiency and overexposure. Manganese is known to cause neurological effects following inhalation exposure, particularly in occupational settings, and there have been epidemiological studies that report adverse neurological effects following extended exposure to very high levels (W.H.O 2007).

2.8 Previous Works

Uba (2016) carried out an analysis on the physicochemical parameters (solubility, density, pH, conductivity, moisture content, hydrosorption and elemental analysis) of the samples each of (Balma, Kanwarbai-bai, Jan kanwa and Fararkanwa) in Sokoto State using standard procedures. The sodium (Na) content was high in all the samples > 20750 mg/kg which was higher than the permissible limit (6065 mg/kg). The potassium content was >1666 mg/kg. Copper was not detected in all the samples while manganese and iron were detected in moderate concentrations. The result of the study indicated that trona may be a potential source of essential elements required for growth and development.

Imafidon *et al* (2016) carried out a research to evaluate Trona for metal content, acute toxicity and biochemical effects on vital organs such as the liver and the kidney of rats.

Samples were purchased at Uselu market, Benin City, Edo state. Elemental analyses revealed the presence of high levels of sodium and iron, the presence of heavy metals such as cadmium, zinc and lead were also detected.

Sudi *et al.*, (2016) determined the essential elemental composition of natural potash deposits obtained in Yusufari Local Government Area of Yobe state . The samples were obtained in three areas namely; Madukuri, Kotufa and Kirba. The highly concentrated essential elements were potassium followed by sodium.). The next essential components were Ca followed by Mg. The levels of essential component decrease in the order as K >> Na >> Ca> Mg.

Paul *et al.*, (2014) determined the mineral and toxic element constituents of Dutsen Dan Libya (DDL) by atomic absorption spectrometry (AAS). Parameters analyzed were Calcium (Ca), Sodium (Na) and Magnesium (Mg). Others include Chromium (Cr), Nickel (Ni), Copper (Cu), Zinc (Zn), Cobalt (Co) and Iron (Fe). Results indicated that concentrations of the mineral elements and the toxic metals were within the World Health Organization's Recommended Daily Intake

Ochei *et al* (2010) carried out an analysis on the effect of potash on the hearts of rabbits as a result of the toxicity cases that had been observed in potash intake. The study was done to determine the effect of potash on the hearts of rabbits. Twenty rabbits were used for the study. Animals were grouped into 4 (A, B, C and D). Group A served as the control while groups B, C, and D were the treatment groups. The study revealed that continuous consumption of potash resulted to some varying degrees of distortion and disruption of the cytostructure of the heart, as compared to the control group which slow normal cellular

and continuous consumption of potash on the heart with that of the group D appearing more remarkable.

Inegbenebor and Inegbenor (2004) reported the composition of elements in trona samples from localities in: North Eastern zone of Nigeria (Yobe, Borno and samples from Libya in North Arica). A total of thirteen samples (mangul, manda, kanwar Libya, kafikafi, kanwa1, kanwa2, kanwa3,Gassaba, Morso, Jan kanwa, Nuku, wadudum farin kanwa, gurro) were analysed for Na, K; Zn, Pb, AI, .Mg, Ca. Fe, S and P. All the samples contained sodium, lead, alumium, calcium, phosphorus and carbon dioxide. The grey samples (kafikafi, gurro, mangul and Kanwa3) had high concentration of calcium and zinc at 4.6% and 1.95% respectively. The samples also had high concentration of iron 2.8%.

Buchanan and Purgh(1969) observed by that potash can be administered as medicine for all sorts of ailments. As medicine, in its grounded form, it is mixed with tobacco and used as snuff. In the Northern part of Nigeria, it is also administered in large doses by the 'Hausa' majority in the form of porridge of guinea corn and millet in what is popularly called kunun Kanwa. This is administered to their women immediately after delivery as a medicine to increase the quality and quantity of breast milk (Davidson *et al.*, 1974).

Davidson (1974) also reported that, the toxic nature of potash was noticed in the nursing mothers around Zaria and Malunfashi areas of Northern Nigeria due to the intake of 30mg per day

Edijala (1980) determined the effects of potash on cooking time since it is commonly used by most Nigerians in the rural areas for cooking vegetables and legumes. It was observed that it increases the green color and texture of vegetables as well as reduces the cooking

time of legumes. Cowpea which is noted for its prolonged cooking time of 40-65 minutes was reduced to 10-15 minutes when cooked with a high concentration of potash.

Oyeleke (1988) reported that, from documented literature, it has observed that increased potash intake leads to decreased food and water intake in experimental animals which was followed by the presence of wrinkled skin with some hair losses

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

This chapter explains the procedure in which the samples were taken to collect the samples and also procedure for analysis.

3.2 Materials and Sample Collection

The materials used in this work are

Trona samples	Analytical balance
Polyethylene bags	Marinelli beakers
Table ceramic mortar and pestle	Pulverizer
Filter papers	Hand gloves
Digestion tubes	Weighing balance
Acetone	Digital camera
Tape recorder	Field notebooks

Samples of Trona where purchased from eight (8) different markets in Zaria on their market days, taking note of initial point of whole sale purchase so as to know the exact state or country responsible for mining and distributing the collected sample. The simple random sampling method was used for sample collection. A simple random sample is a sample selected in such a way that every possible sample of the same size is equally likely to be chosen.

The samples were packed into doubled polyethylene bags and properly labeled for documenting and taken to the Geography Department of Ahmadu Bello University Zaria for preparation. Gamma spectroscopy count and analysis at National Institute for

Radiation Protection and Research (N.I.R.P.R) at the University of Ibadan using a High purity Germanium detector with specifications.

Detector Model: GC 8023, manufactured by CANBERRA

Serial Number: 9744

Pre Amplifier Model: 2002csl

Pre Amplifier Serial Number: 13000742

Standard Source Used For Calibration: Multi-Gamma Ray Standard (Mgs6m315)

Counting Time 10,800 Seconds

Detector Diameter: 78 Mm

Detector Length: 69.8 Mm

Resolution (FWHM): 2.3 keV, ^{60}Co at 1.33mev.

Relative Efficiency: 80%

Type of Detector: P-Type

No of Channel Detector: 16k

Software for Analysis: Genie 2k,

Also some samples were taken to Nigerian Research Institute of Chemical Technology (N.A.R.I.C.T) Bassawa Zaria for the elemental analysis using the spectrometer with model: Shimadzu AAS 6800 model.

3.3 Sample Preparation for Gamma Spectroscopy

A total of fourteen (14) samples were collected. The collected samples of Trona were ground to fine powder to ensure equal representation of samples and packed into fill labeled cylindrical plastic containers of height 6.5cm by 8cm diameter and labeled before putting inside the detector. These filled containers where tightly covered to prevent radon escape and stored for 30 days for short lived radionuclides to attain secular equilibrium.

3.4 Elemental Concentration

The elemental concentration was analyzed using the atomic absorption spectrometry methodology. Below is the principle behind the analysis carried out.

3.4.1 Atomic absorption spectroscopy (AAS)

Atomic absorption spectrometry (AAS) is a spectro-analytical procedure for qualitative and quantitative assessment of chemical elements based on the absorption of light (optical radiation) by free atoms in the gaseous state. It is used to determine the concentration of a particular element in a sample. AAS can be used to determine over 70 different elements in a single sample. It was first used as an analytical technique in the second half of the 19th century. The modern form of AAS was largely developed during the 1950s by a team of chemists in Australia.

Atomic absorption spectroscopy is based on standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and on the Beer-Lambert Law. The electrons in the atomizer can be placed in an excited state for a period of nanoseconds by absorbing the radiation of a given wavelength. This wavelength is specific to a particular electron transition in a particular element, so each wavelength corresponds to only one element, and the width of an absorption line is only a few picometers (pm), which gives the technique its elemental selectivity. The radiation flux with or without a sample in the atomizer measured and the ratio between the two values is converted to analyte concentration or mass using the Beer-Lambert Law.

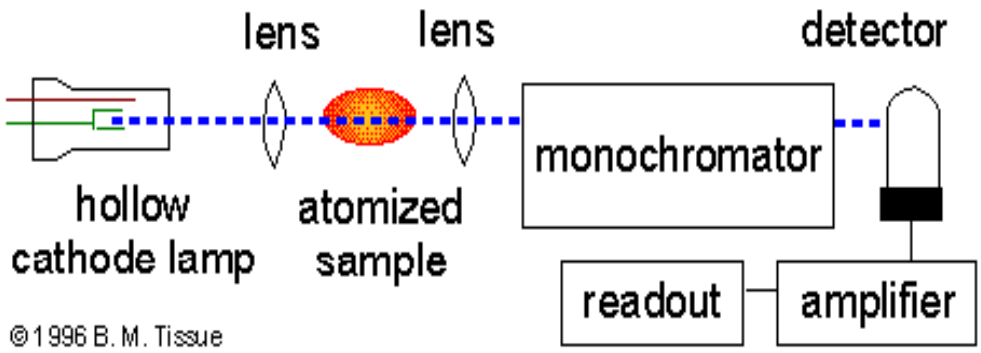


Plate II: **Schematic of an atomic-absorption experiment**

(Source: http://www.the British museum.ac.uk/science/techniques/sr-tech-aas.html).

3.4.2 Principle of atomic absorption spectrometer

The primary sources of radiation in atomic absorption are **hollow cathode lamps**. These lamps are composed of a cathode and an anode sealed in a tube with an inert gas (argon or neon). The cathode is made of the element to be determined. When a high voltage is applied the atoms of the inert gas are ionized and attracted by the cathode. These ions hit the cathode and excite the atoms of the elements used to make the cathode. Once the atoms are excited, radiation is emitted at the characteristic wavelength of the element. The light from the hollow cathode lamp passes through the flame **(Burner/nebulizer)** where the sample is atomized. This fine mist of the sample is sprayed into the nebulizer. Atoms of the elements are formed from the sample mist and are able to absorb some of the light from the lamp at the wavelength set for that particular element. The light passed through the flame is received by the **monochromator,** which is set to accept and transmit radiation at the specified wavelength. The light emerges from the monochromator exit slit and falls on the **photomultiplier detector**. At this point an output current, proportional to the incident light, is intensified, amplified, processed electronically and finally presented to a **readout device, that is**. printer, digital display. (Garcia, 2012)

3.4.3 Procedure for digestion

1.0g of each of the samples was accurately weighed and transferred into digestion tubes; 10ml of hydrochloric acid was added into the weighed sample. The mixed substance was then placed on a hot plate at 100 degree Celsius for at least 45-1hr until a clear solution is obtained. The solution was allowed to cool down for at least 15mins. Insoluble materials present inside was filtered using filter paper. The filtered liquid was poured into sample bottles of 60ml and distilled water added to ensure the content equals 60ml and stirred gently. The digest of each sample was then transferred into different well stopper rubber container which was then ready for atomic absorption spectrometric analysis.

3.4.4 Atomic absorption spectrometry measurement

Total elemental concentrations of the 10 selected elements was determined using shimadzu Japan Model 6800 AAS equipped at a time when each of the hollow cathode lamps required for the elements selected. The lamps were fixed on the AAS machine and each of these processes was done with a flame type consisting of air/acetylene. (Tessier *et al.*, 1979).

The elemental concentration was calculated using the equation below:

$$\text{Content (mg/kg)} = \frac{\text{conc . (mg /l)} \times \text{V (ml)}}{m\ (g)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.1)$$

Where conc (mg/l) is the concentration due to AAS, V(ml) is the volume of the digested sample and m(g) is the weight of the sample used for digestion. (Guilaume, 2012).

3.5 Detection and Measurement of Gamma Radiation

Gamma radiation can be measured by detecting atomic disintegrations that occur in a sample and counting the number of these events that occur during a specific time period.

Scientific instruments employ one of several technologies including HPGe crystal detection, proportional counting, among others. HPGe crystal counting was used in this work. HPGe detector was chosen for the determination of activity concentrations of gamma emitting radionuclides because the HPGe has better counting efficiency and energy resolution for measurement of gamma ray energies above several hundred keV compared to the only other detector category of major importance available for such measurements - NaI(Tl).

3.6 Theory of HPGe-Based Gamma-Ray Spectrometry

HPGe-based gamma-ray spectrometry is a technique that can be used to detect and measure gamma ray photons from radionuclide sources. The HPGe detector system consists of a lead shielded HPGe detector, a multi-channel analyzer (MCA) and analysis software on a desktop computer. The HPGe detector has a much greater thickness and narrower band gap compared to other detectors because it is constructed from ultra-pure germanium so as to improve depletion depth. These characteristics give it better counting efficiency and high energy resolution, making it very convenient for use in gamma-ray spectroscopy. Because of its small band gap (0.7eV), room-temperature operation of germanium detectors of any type is impossible due to the large thermally induced leakage current that would result (Knoll,1997). The HPGe detector must be cooled to reduce the leakage current to the point that the associated noise does not compromise its good energy resolution. Normally, the temperature is reduced to 77 K through the use of an insulated dewar in which a reservoir of liquid nitrogen is kept in thermal contact with the detector, or other cooling alternatives. However, the HPGe detector can be allowed to warm up to room temperature between measurements without any problem unlike the Ge(Li) which must be continuously maintained at low temperatures to prevent a catastrophic

redistribution of the drifted lithium that will rapidly take place at room temperature. This operational advantage is the major reason that the HPGe detectors have supplanted Ge(Li) configurations. Fabrication techniques have been developed to the point that modern HPGe detectors will withstand indefinite cycling of the temperature. Modern HPGe systems incorporate a preamplifier as part of the cryostat package. This is important in order to locate the preamplifier as close as possible to the detector so as to minimize capacitance. The input stages of the preamplifier normally are also cooled along with the detector to reduce electronic noise. The figure below (3.2) shows the arrangement of the components of HPGe based spectrometry. Germanium detectors have excellent energy resolution for gamma-ray spectroscopy compared to other detector types for this range of energies (Knoll,1997). This allows for the separation of many closely spaced gamma-ray energies which remain unresolved in other detectors like NaI(Tl); HPGe can resolve up to two gamma rays that are within 0.8 keV of each other (Randolph,1996).



Plate III: **Diagram of the equipment set-up of HPGe Detector Spectrometry**

The MCA, which may be considered as a series of single channel analyzers (SCA) with incrementing narrow windows, consists of an ADC, control logic, memory and display. The MCA achieves pulse height analysis by sorting successive signal pulses into parallel amplitude channels. The ADC converts analog signals (pulse amplitudes from detector) to equivalent digital signals (numbers). An input gate controls movement of pulses from the detector into the ADC by blocking pulses from reaching the ADC during the time period when it is busy digitizing a previous pulse. The control logic picks memory locations for storage of the digitized signals, holds the input gate open when the ADC is not busy, and closes it when the ADC is busy. The memory stores the digitized pulses and has addressable locations corresponding to the maximum number of channels into which the recorded spectrum can be divided. The number of channels to be used for measurements depends on the degree of resolution required and the total number of counts that can be obtained. Having very few number of channels results in distortions and loss of resolution in the spectrum, while having too many channels leads to a low number of counts per channel resulting in large statistical fluctuations (noise) which could obscure small additional peaks. Depending on the resolution of a detector, the optimum number of channels should be 4 per FWHM of peak (Knoll,1997).

The resolution of a detector improves as the response function gets narrower. R is dimensionless and conveniently expressed as a percentage or simply as the FWHM.

The time during which a MCA cannot take in an analog pulse is called its dead time (τ). τ comprises of the processing time of the ADC and the memory storage time, and can be worked out as expressed in equation 3.2 (Knoll,1997)

$\tau = N\,(1/\nu) + B$ ……..3.2

Where N is the channel number in which the pulse is stored, ν is the frequency of the clock oscillator and B is the pulse storage time.

3.7 System Calibration

The calibration of an analytical system is one of the most important tasks required of any analyst. If the calibration is incorrect then all the result produced will be inaccurate. The essential requirements of a calibration are to establish an energy / efficiency / resolution relationship (G.A Sutton, 1993). For gamma-ray measurement with germanium detector, the position of photo peak (full energy peak) is relevant for energy measurements.

3.7.1 Energy calibration

Energy calibration is important for the qualitative analysis of the samples containing radioactive nuclide. The exact identity of photo peak present in the spectrum produced by the detector system is a necessary requirement for the measurement of gamma-emitters. The **calibration** results in a relationship that allows you to associate a given channel number with its appropriate **energy**. In other words, the energy calibration is the establishing of the number of the channels present in a multi-channel analyzer (MCA) or pulse height analyzer in relation to gamma-rays energy (IAEA, 1989).

3.7.2 Efficiency calibration

Efficiency Calibration is important for the quantitative analysis of the samples containing radioactive nuclides. Efficiency calibration is the relationship between the number of counts and the disintegration rates, and the efficiency of gamma spectrometer is a measure of how many pulses occur for a given number of gamma-rays. To accurately determine activity concentrations, correct and reliable determination of the efficiency curve is of great importance. Detection efficiency is a complex function of the energy, spectrometer

characteristics, measurements geometry, volume and density of the sample, etc. In order to calibrate the spectrometer properly, calibration standards should be prepared with matrices with similar density, similar concentration for the relevant radionuclides, and in the same geometry and counting configuration as the real samples.

3.7.3 Energy resolution

The resolution of a spectrometer is a measure of its ability to resolve two peaks that are fairly close together in energy. This is usually expressed as the width of the photo peak at half of its maximum height (F.W.H.M). The energy resolution can be calculated by:

$R = (FWHM/ H_o) \times 100\%$. Where: Ho is the peak centroid (Knoll2000).

3.7.4 Secular equilibrium

Total activity of a radionuclide undergoing a radioactive process is calculated by considering a long-lived parent decaying into a short-lived daughter whom in turn decays into a stable nuclide. In this case the half-life of the two radionuclides - the parent and the daughter, are such that the half-life of the parent (T_1) is far much greater than that of the daughter (T_2); $T_1 >> T_2$. The total activity at any time is the sum of the parent radionuclide and daughter radionuclides. The rate of decay of daughter atoms ($- dN_2/dt$) is equal to the rate at which they are produced.

The relationship between the activity of the parent radionuclide (A_1) and that of the daughter radionuclide (A_2) at any time t is given by the equation 3.3

$$A_2 = A_1 [1-\exp(-\lambda_2 t)] + A_2 0 \exp(-\lambda_2 t) \quad \text{.....3.3}$$

Where λ_2 is the decay constant of the daughter radionuclide, t is the time lapse, and $A_2 0$ is the initial activity of the daughter radionuclide.

The activity A_2 then builds up after several daughter half-lives to the point when $A_2 = A_1$ at which time the daughter activity is equal to that of the parent (Gordon, 2008). This

condition is termed secular equilibrium between the parent radionuclide and its decay products. This means that a chain of short lived daughter radionuclides can be in secular equilibrium with a long lived parent. The activity of each member of the chain is equal to that of the parent. Hence, any member of the chain can be used to present the activity concentration of the parent radionuclide.

3.7.5 Identification of radionuclides

The table 3.1 gives the centroid channel energies which were used to identify and quantify the radionuclides of interest in the samples

Table 3.1: Recommended energy lines for gamma-ray analysis of environmental samples (IAEA, 2003)

Element or radionuclide	Isotope used	Spectral line/Energy (Kev)
K-40	40K	1460.81
Th-232	212Pb	238.63
	228Ac	911.21
U-238 (226Ra)	214Pb	351.92
	214Bi	609.31
		1764.7

3.8 Activity Concentrations of Radionuclides from Gamma-Ray Spectra

Because of the different types of gamma interactions that take place inside the detector, energy from the photons is not always completely absorbed by the detector, which results in variations in detector efficiency. There occur peaks representing total absorption of gamma rays from the source and other peaks that represent partial absorption. Based on the measured count rates under the photo peaks corresponding to the gamma rays of ^{40}K and other radionuclides in the ^{232}Th and ^{235}U decay series, the activity concentrations of

relevant radionuclides in the samples can be determined. The procedure for quantification relies on the establishment of secular equilibrium between ^{226}Ra and the short-lived decay products of radon in the samples (Mohanty *et al.,* 2004). The activity concentration of ^{232}Th is determined from the average concentrations of ^{212}Pb and ^{228}Ac in the samples while that of ^{226}Ra (^{238}U equivalent) is determined from the average concentrations of ^{214}Pb and ^{214}Bi . The well-known spectral interference between the gamma lines of ^{226}Ra (186.20 keV) and ^{235}U (185.70 keV) is inevitable, especially in the presence of a relatively high uranium concentration, and therefore the 186.20 keV line is normally not used for the determination of activity concentration of ^{238}U equivalent.

The activity concentrations of natural radionuclides in the samples (A_s) are computed after spectral deconvolution by custom software on a computer linked to the spectrometer. Several quantification methods are available for use. The comparative method uses the following relation (Mustapha, 1999);

$$\frac{AsMs}{Is} = \frac{ArMr}{Ir} \quad \text{..... (3.4)}$$

Where A_s, M_s and I_s are radionuclide activity concentration, mass and radionuclide intensity of sample while the right hand side are the same quantities for the reference standard. The second method involves efficiency calibration of the detector and uses the following relation (Arogunjo, 2007):

$$As = \frac{A}{\varepsilon PrM} \quad \text{..... (3.5)}$$

Where A is radionuclide intensity in counts per second, Ɛ is the detector efficiency for particular gamma-ray energy, P_r is the transition probability of gamma decay and M is mass of the sample. Another method also involves efficiency calibration of the detector system and uses the relation (Otwoma *et al.*, 2013)

$A_s = \frac{C}{\varepsilon t f}$ …… (3.6)

were C is radionuclide intensity in counts per second, Ɛ is detector efficiency, t is counting time in seconds and f is the branching ratio i.e. number of photons per hundred disintegrations of the radionuclide of interest.

The gamma-ray detector is normally calibrated for energy and detection efficiency using certified reference materials and standard reference sources. Equation (3.5) was used in this work.

The activity concentrations in the samples was obtained using the equation bellow (Obed, et al., 2005; Jibril *et al.*, 2007)

$A = \frac{N}{\varepsilon P \gamma M s}$ …… (3.7)

were A is the activity concentration of the radionuclide in the sample given in Bq/kg. N is the count rate under the corresponding peak, ε is the detector efficiency at the specific γ-ray energy, P_γ is the absolute transition probability of the specific γ-ray, and M_s is the mass of the sample in kilogram.

3.9 Radiation Hazard Associated with NORMs (Radiation Hazard Indices).

In this study, radiological parameters such as the dose estimate, radium equivalent activity, activity concentration and ingestion effective dose, were used to assess the potential radiation hazards associated with the consumption of Trona.

3.9.1 Radium equivalent activity **(Ra_{eq})**

To represent the activity levels of Ra-226, Th-232 and K-40 by a single quantity, which takes into account the radiation hazards associated with them, a common radiological index has been introduced called Radium equivalent activity. This is used to access the

hazards associated with materials that contain the above listed radionuclides. And it is mathematically defined by Beretka and Mathew, 1995 & UNSCEAR 2000 as;

$$Ra_{eq}\,(Bq.kg^{-1}) = A_{Ra} + 1.43A_{Th} + 0.077A_K \quad \text{(3.8)}$$

were A_{Ra} , A_{Th} and A_K are the activity concentration of Ra-226, Th-232 and K-40 respectively.

In the above relation, it has been assumed that 10Bq/kg of Ra-226 7Bq/kg of Th-232 and 130 Bq/kg of K-40 produce equal gamma dose.

3.9.2 Dose estimate: From the activity concentration obtained from the Trona samples, **the dose estimate** to humans was calculated using equation 19 below (Jibiri 1999, ICRP 1996)

$$E = (U_{Ra}C_{Ra} + U_{Th}C_{Th} + U_K C_k).M \quad \text{(3.9)}$$

Were M is the annual average quantity of Trona consumed per person in Nigeria (9.13kg/capita/year) (Paul,2014). C is the specific activity concentration of radionuclide in Trona determined in this work, and U refers to the effective dose coefficients measured for the radionuclides (Sv/Bq) for different age groups (IAEA BSS 1996).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Varieties and Uses of Trona

This chapter displays and discusses the results obtained in the cause of this work. The varieties of Trona in Zaria markets and its uses are discussed below

There are eight (8) different varieties of Trona sold in the markets within Zaria. Namely:

4.1.1 Jan kanwa: Jan Kanwa is used for cooking most of herbs consumed to cure ailments. Also used to wash the stomach and also used for skin treatment.



Plate IV: Jan Kanwa

4.1.2 Farar Kanwa: Used for preparing waina, masa and kunun kanwa. Also used to treat Gastro Intestinal infection.



Plate V: Farar kanwa

4.1.3 Dan libya: Name gotten from the origin of the sample. This is administered to any person suffering from stomach ache, jaundice, diarrhea, fever, cold, no matter what form, it is believed to cure the pains. It is also used to treat Gastro intestinal problems.



Plate VI: Dan Libya

4.1.4 Ngurnu: Used for soups and food. E.g. to cook beans, make okra soups, to tenderize any hard substance that takes long to cook and reduces cooking time, it is also used for treating infections and wound healing.



Plate VII: Ngurnu

4.1.5 Manda: Administered to someone who has lost much blood in the body or has no blood in the body. It is cooked with moringa roots, boiled for some minutes and given to the patient to drink. It is believed to add blood to the body other than blood transfusion. This is also used for skin treatment and wound healing.



Plate VIII: Manda

4.1.6 Mangul: Used to melt any form of blood clot in the body, especially women who just delivered. It is administered to help remove or melt the blood clot for easy removal

from the body. Also doctors recommend those who do not eat salt to use manda as substitute for salt.

4.1.7 Balma: Further divided into Jan balma (physically looks red in colour by modifying its color, according to the sellers, this is just to enhance its physical look and nothing more), and Farin balma which looks grey in color. This is administered to animals to help them eat well and expand their stomach capacity. Also it restores appetite to a pregnant animal that do not eat well as a result of loss of appetite.





Plate IX Jan Balma

Plate X: Farar Balma

4.1.8 Yar Agadas: This is used for cooking some special hausa delicacies as it enhances the taste of the food cooked. It is also mixed with animal fodder to feed them with it.



Plate XI:: Yar Agadez

4.2 Toxic Metals Concentration

Table 4.1 presents and summarizes the concentration in mg/kg of the 8 toxic metals (Mn, Cr,Ni,Pb,Co,Zn,Cd,Cu) analyzed in the Trona samples. They were detected at varying concentrations in the samples samples even though, some elements such as Co, Zn, Cr,Cu, Mn, Ni and K where present in some samples and absent in some due to the concentrations been below the detection limit of the machine used.

Table 4.1: Elemental concentrations of Co, Pb, Cd, Zn, Cr, Cu, Mn, Ni, and K in mg/kg

S/N	**Toxic metal**	**Mean**	**Minimum**	**Maximum**	**Standard deviation**
1	Cd	0.0028	0.0006	0.0072	0.0006
2	Zn	0.0151	0.0023	0.0326	0.0033
3	Cr	1.1500	0.1066	2.2579	0.7583
4	Cu	0.0020	0.0003	0.0035	0.0007
5	Co	0.3200	0.0024	1.0133	0.2354
6	Pb	0.7606	0.6629	0.8463	0.0143
7	Mn	0.1717	0.0187	0.5958	0.0504
8	Ni	0.1368	0.0008	0.5933	0.0765
9	**K**	**2.1004**	**0.2930**	**2.7433**	**0.3202**

Note: Potassium (K) is not a heavy metal.

Table 4.2 (i- ix) Comparison of elemental concentration for different varieties of Trona

(i) ELEMENTAL FOR FARAR BALMA

SAMPLE CODE	Co	Pb	Cd	Zn	Cr	Cu	Mn	Ni	K
JB_fT (T/WADA)	BDL	0.8276	0.0019	0.0095	BDL	BDL	0.4174	0.0118	0.2930
SB_FT (SAMARU)	BDL	0.7682	0.0018	0.0326	0.5491	BDL	0.5958	BDL	BDL
W.H.O RDI(mg/kg)	**3**	**2.3**	**8**	**42**	**30**	**4700**	**2100**	**10**	**200**

All elements were found to be below the W.H.O RDI allowance

(ii) ELEMENTAL FOR FARAR KANWA

SAMPLE CODE	Co	Pb	Cd	Zn	Cr	Cu	Mn	Ni	K
BFT(d/MAG)	0.0520	0.6639	0.0024	0.0084	BDL	0.0007	0.1731	0.5933	1.9442
YFT (SABO)	BDL	0.7630	0.0013	0.0193	0.1255	BDL	0.4042	0.0168	BDL
NFT	BDL	0.7859	0.0006	BDL	0.3159	BDL	0.0575	0.0114	BDL
W.H.O RDI(mg/kg)	**3**	**2.3**	**8**	**42**	**30**	**4700**	**2100**	**10**	**200**

All elements were found to be below the W.H.O RDI allowance

(iii) ELEMENTAL FOR NGURNU

SAMPLE CODE	Co	Pb	Cd	Zn	Cr	Cu	Mn	Ni	K
CNT(SAM)	BDL	0.7786	0.0072	0.0025	2.0631	0.0022	0.1407	BDL	BDL
W.H.O RDI(mg/kg)	**3**	**2.3**	**8**	**42**	**30**	**4700**	**2100**	**10**	**200**

All elements were found to be below the W.H.O Recommend Dietary Intake allowance

(iv) ELEMENTAL FOR JAN KANWA

SAMPLE CODE	Co	Pb	Cd	Zn	Cr	Cu	Mn	Ni	K
NJT (SABO)	0.0024	0.6629	0.0022	0.0253	0.5936	0.0003	0.0952	0.1232	BDL
CJT (T/WADA)	BDL	0.7796	0.0018	0.0023	0.1066	BDL	0.0610	BDL	BDL
W.H.O RDI(mg/kg)	**3**	**2.3**	**8**	**42**	**30**	**4700**	**2100**	**10**	**200**

All elements were found to be below the W.H.O Recommend Dietary Intake allowance

(v) ELEMENTAL FOR MANDA

SAMPLE CODE	Co	Pb	Cd	Zn	Cr	Cu	Mn	Ni	K
JMnT(D/MAG)	BDL	0.7734	0.0050	0.0206	1.9625	BDL	0.0959	0.0008	BDL
K_aMnT (T-W)	BDL	0.8463	0.0006	0.0065	BDL	BDL	0.0929	BDL	2.6069
W.H.O RDI(mg/kg)	**3**	**2.3**	**8**	**42**	**30**	**4700**	**2100**	**10**	**200**

All elements were found to be below the W.H.O Recommend Dietary Intake allowance

(vi) YAR AGADEZ

SAMPLE CODE	**Co**	**Pb**	**Cd**	**Zn**	**Cr**	**Cu**	**Mn**	**Ni**	**K**
NAT (SHIKA)	BDL	0.7901	0.0015	BDL	1.2493	BDL	0.0478	BDL	2.2015
W.H.O RDI(mg/kg)	**3**	**2.3**	**8**	**42**	**30**	**4700**	**2100**	**10**	**200**

All elements were found to be below the W.H.O Recommend Dietary Intake allowance

(vii) JAN BALMA

SAMPLE CODE	Co	Pb	Cd	Zn	Cr	Cu	Mn	Ni	K
SBjT(SHIKA)	1.0133	0.7703	0.0053	BDL	0.9185	0.0035	0.0187	BDL	2.6575
W.H.O RDI(mg/kg)	**3**	**2.3**	**8**	**42**	**30**	**4700**	**2100**	**10**	**200**

All elements were found to be below the W.H.O Recommend Dietary Intake allowancE

(viii) MANGUL

SAMPLE CODE	Co	Pb	Cd	Zn	Cr	Cu	Mn	Ni	K
JMnT(D/MAG)	BDL	0.7734	0.0050	0.0206	0.9625	BDL	0.0959	0.0008	BDL
W.H.O RDI(mg/kg)	**3**	**2.3**	**8**	**42**	**30**	**4700**	**2100**	**10**	**200**

All elements were found to be below the W.H.O Recommend Dietary Intake allowance

(ix) DAN LIBYA

SAMPLE CODE	Co	Pb	Cd	Zn	Cr	Cu	Mn	Ni	K
JMnT(D/MAG)	BDL	0.7734	0.0050	0.0206	0.9625	BDL	0.0959	0.0008	BDL
W.H.O RDI(mg/kg)	**3**	**2.3**	**8**	**42**	**30**	**4700**	**2100**	**10**	**200**

All elements were found to be below the W.H.O Recommend Dietary Intake allowance.

The mean and standard deviations of the concentrations(mg/kg) of Cd, Zn,Cr,Cu,Co,Pb,Mn and Ni in the samples were found to be 0.0028±0.0006, 0.0151±0.0033,1.1500±0.7582,0.0020±0.0007,0.3200±0.2354,0.7606±0.0143,0.1717±0.0504 and 0.1368±0.0765 respectively. With the highest concentration (mg/kg) corresponding to Cr and the lowest corresponding to Cu. The increasing trend was in the order: Cr>Mn>Ni>Pb>Co>Zn>Cd>Cu. Also,the Trona samples were found to contain a significant amount of Potassium. The most abundant element in the samples was found to be Potassium.

The concentration of Potassium in the samples analyzed ranges between 0.0293-2.7433 mg/kg with an overall mean concentration of 2.1004mg/kg .The recommended dietary allowance for K by W.H.O is 4700mg, its excess leads to hyperkalemia. The concentration of Potassium in this work does not exceed the R.D.A.

The concentration of Copper in this research ranges between 0.0003mg/kg-0.0035 mg/kg, with an overall average of 0.0020 mg/kg. It was suggested by W.H.O (1993) that Cu a concentration greater than 3mg/kg is associated with gastrointestinal effect. The result obtained in this work is within the limit set by W.H.O.

The concentration of Manganese was between 0.0187mg/kg-0.5958 mg/kg, with an overall average concentration of 0.1717mg/kg. For Mn, the RDA is 2.3mg/kg and its excess causes Manganism, a toxic condition resulting from over exposure to Manganeese. The result obtained in this work is within the acceptable limit limit set by (WHO 1993; 1996).

The concentration of Zinc was between 0.0023mg/kg-0.0326 mg/kg with a mean value of 0.0151mg/kg, The RDA for Zn is 2100 mg/kg (WHO, 1967).The result obtained is within the acceptable limit Even though, if greater than the recommended daily allowance of zinc is ingested, even if it's for a short period of time, it can lead to stomach cramps,nausea and vomiting. If ingested for longer periods, anaemia, damage to the pancreas and low birth weight may occur.

Lead concentration detected in the samples ranged between 0.6629mg/kg-0.8463mg/kg with a mean concentration of 0.7606 mg/kg which is below the maximum recommended value of 10mg/kg set by WHO (1967)

The concentration of Nickel in this work ranged between 0.0008mg/kg-0.5933 mg/kg. It is reported BY W.H.O, 1967, to be toxic at concentration equal or greater than 8mg/kg.

Nickel is a known toxic to the: red blood cells, immunes system, neurons, reproductive system, genes and also a carcinogenic agent. The result obtained in this work is below the recommended allowance by W.H.O.

The concentration of Cadmium in this work ranged between 0.0006mg/kg-0.0072 mg/kg with an overall average concentration of 0.003mg/kg. it is reported by W.H.O 2007 that, Cadmium, at a concentration of 200 mg/kg or more, exerts toxic effects on the kidney, the skeletal system and the respiratory system and is classified as a human carcinogen. The result obtained in this work is also bellow the recommended allowance of 200mg/kg set by W.H.O 1967.

The concentration of Cobalt in this study ranged between 0.0024mg/kg-1.0133 mg/kg, with an overall mean of 0.3200mg/kg. High concentrations of cobalt above 30 mg/kg can result in vomiting and nausea, asthma, pneumonia, damage to the thyroid, and vision and heart problems (WHO 1993). The result obtained in this work is below the recommended dietary allowance.

The concentration of Chromium was found to range between 0.1066mg/kg-2.2579 mg/kg with an overall average concentration of 1.1500mg/kg. Depending on the mode of exposure to chromium, several medical conditions may result, including dermatitis, skin ulcers, irritation of the air ways, cough, chest pain, abdominal pain, diarrhea, heart failure, as well as damaging of the gut, liver and kidney (WHO 1967). The result obtained in this work is below the World health organization (1967) recommended dietary allowance (42mg/kg).

Table 4.3: Comparison of Present Study on Concentration (mg/kg) With That of Other Researchers and W.H.O RDI

Name	Cu	Mn	Ni	Cr	Co	K	Zn	Pb	Cd
This work	0.002±0.001	0.172±,0.050	0.137±0.077	1.15±0.229	0.32±0.235	2.101±0.320	0.015±0.003	0.761±0.014	0.003±0.001
Paul	0.00860	-	0.0092	0.0004	0.0068	-	0.0100	-	-
Uba	-	-	-	-	-	>1666 mg/kg	-	-	-
W.H.O RDI	3mg/kg	2.3mg/kg	8mg/kg	42mg/kg	30mg/kg	4700mg/kg	2100 mg/kg	10mg/kg	200 mg/kg

4.3 Radiological Assessment

The radiological concentration of the samples was analyzed and the results discussed below.

4.3.1 Activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K.

The specific activity of the naturally occurring radionuclide in the Trona samples collected from the markets has been displayed in the Table. 4.3. The specific activity of K-40, Ra-226 and Th-232 ranged from 1143.50 Bq/Kg - 43.34Bq/Kg, 151.02 Bq/kg - 1.80Bq/kg and 65.85Bq/kg-1.03Bq/Kg with mean values of455.28±10.56, 11.96±1.41, and 42.904±4.54 respectively.

Table 4.4: Efficiency Calibration Values for the HpGe Detector

S/N	Radionuclide	Energy (keV)	Efficiency
1	Eu- 155	60 .0	0.006169
2	Eu- 155	86.5	0.029740
3	Eu- 155	105.3	0.042728
4	Sb-125	176.3	0.059553
5	Sb-125	427.9	0.041428
6	Sb-125	600.6	0.034679
7	Mn- 54	834.8	0.027683
8	Zn- 65	1115.5	0.023075
9	K- 40	1460.8	0.025431

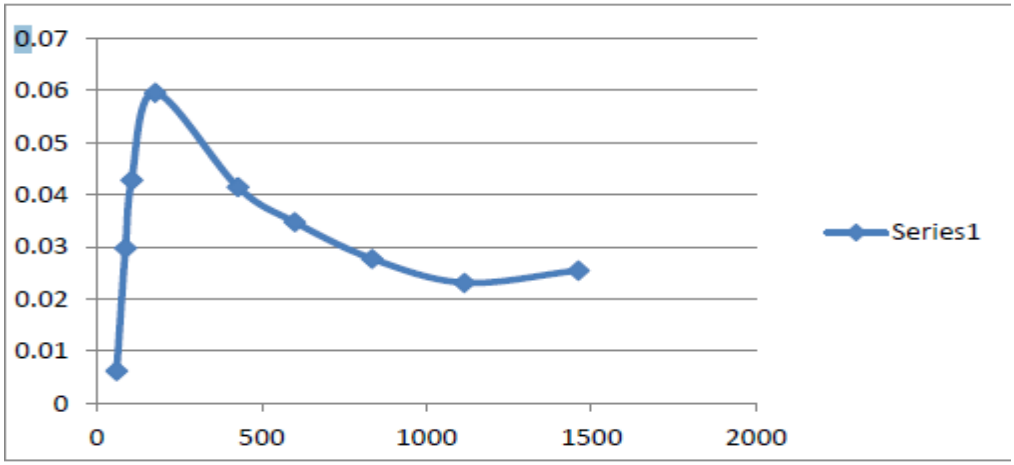


Fig. I: Results of efficiency calibration for HPGe detector. (NIRPR Ibadan 2017)

Table 4.5 The Specific Activity of The Samples Measured

SAMPLE CODE& LOC.	Ra-226(Bq/kg)	Th-232(Bq/kg)	K-40(Bq/kg)
FT(D/MAG)	122.70 ± 7.01	3.61 ± 0.48	43.34 ± 2.40
NJT (SABO)	11.51±2.81	1.62 ± 0.31	86.21 ± 3.44
LDT SABO	1.20±0.30	1.03 ± 0.39	1420.71 ± 27.67
SB_JT (SHIKA)	1.80±0.47	2.09 ± 0.42	59.20 ± 2.87
KM_GT SHIKA	14.98±2.63	1.82 ± 0.56	1237.33 ± 24.64
CNT SAMARU	24.40 ± 4.27	1.33 ± 0.26	207.2 ± 6.03
CJT (T/WADA)	14.67±2.93	1.16±0.25	110.94 ± 4.17
JB_fT (T/WADA)	29.82 ± 4.76	17.57 ± 2.47	409.44 ± 10.12
NAT (SHIKA)	35.07 ± 4.14	6.91 ± 1.02	113.11 ± 4.29
JMnT(DAN/MAG)	84.02 ± 8.96	65.85 ± 5.32	461.58 ± 10.87
SB_FT (SAMARU)	10.40 ± 3.16	13.36 ± 1.92	378.04 ± 9.20
K_aMnT (T-W)	67.56 ± 8.91	39.79 ± 4.36	469.77 ± 11.74
YFT (SABO)	31.50 ± 5.33	6.18 ± 1.14	1143.50 ± 23.26
NFT (T/WADA)	151.02 ± 7.81	5.17 ± 0.88	233.58 ± 7.11
Average±S.D	42.904±4.54	11.96±1.41	455.28±10.56
World Average	33	45	420

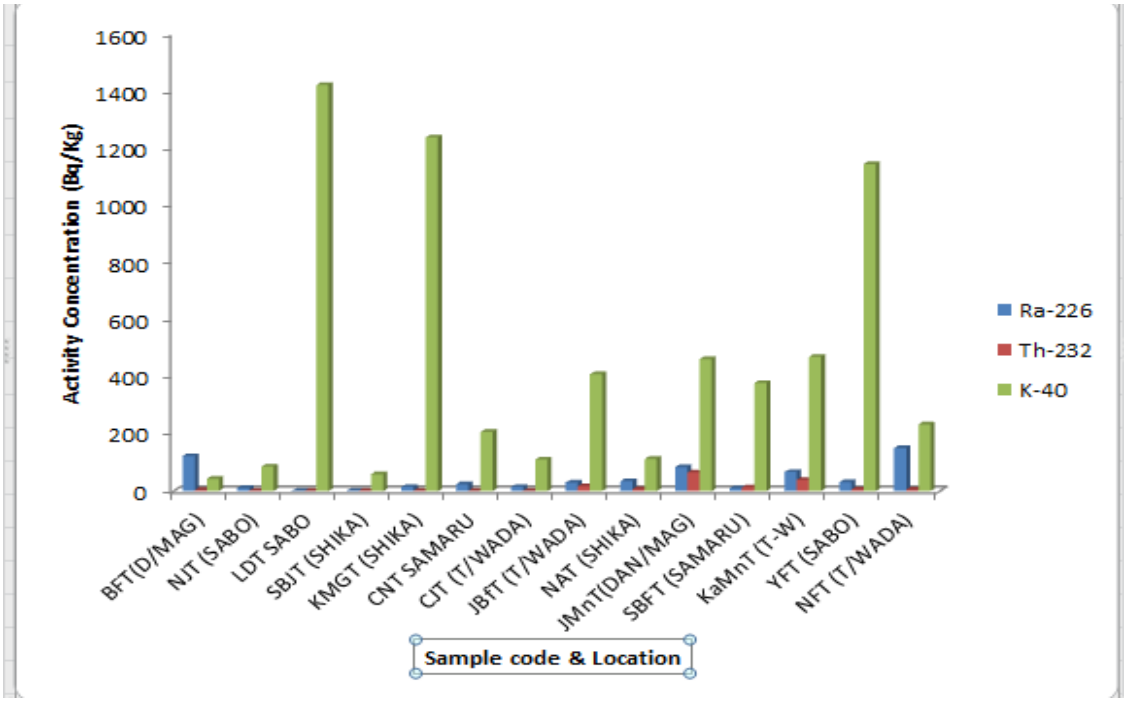


Fig.II : Comparison of radiological concentration for all Trona samples collected.

Table 4.6 (a-i) the Specific Activities Classified According To Varieties

(a) FOR FARAR BALMA

SAMPLE CODE	Ra-226(Bq/Kg)	Th-232(Bq/Kg)	K-40(Bq/Kg)
JB_fT (T/WADA)	29.82 ± 4.76	12.61 ± 2.00	17.57 ± 2.47
SB_FT (SAMARU)	10.40 ± 3.16	7.19 ± 0.60	13.36 ± 1.92
Average ± S.D	**20.11± 3.96**	**9.9± 1.3**	**15.465± 2.195**
World average	**33**	**45**	**420**

The concentration of Ra-226, Th-232 and K-40 where all found to be below the world average.

(b) FOR FARAR KANWA

SAMPLE CODE	Ra-226(Bq/Kg)	Th-232(Bq/Kg)	K-40(Bq/Kg)
BFT(d/MAG)	122.70 ± 7.01	3.61 ± 0.48	43.34 ± 2.40
NFT (T/WADA)	151.02 ± 7.81	5.17 ± 0.88	233.58 ± 7.11
YFT (SABO)	31.50 ± 5.33	6.18 ± 1.14	1143.50 ± 23.26
Average± S.D	**101.74**	**4.986± 0.833**	**473.47± 10.92**
World average	**33**	**45**	**420**

The concentration of Th-232 was found to be below the world average while the concentration of Ra-226 and K-40 where found to be above the world average value and this could be attributed to the geological formations of the mining areas.

(c) **FOR MANDA**

SAMPLE CODE	Ra-226(Bq/Kg)	Th-232(Bq/Kg)	K-40(Bq/Kg)
JMnT(D/MAG)	84.02 ± 8.96	65.85 ± 5.32	461.58 ± 10.87
K_aMnT (T-W)	67.56 ± 8.91	39.79 ± 4.36	469.77 ± 11.74
Average± S.D	**75.79± 8.94**	**52.82± 4.84**	**465.68± 11.31**
World Average	**33**	**45**	**420**

The concentration of Ra-226, Th-232 and K-40 where all found to be above the world average value and this could be attributed to the geological formations of the mining areas.

(d) FOR JAN KANWA

SAMPLE CODE	Ra-226(Bq/Kg)	Th-232(Bq/Kg)	K-40(Bq/Kg)
CJT (T/WADA)	14.67±2.93	1.16±0.25	110.94 ± 4.17
NJT (SABO)	11.51±2.81	1.62 ± 0.31	86.21 ± 3.44
average± S.D	**13.09± 5.74**	**1.39± 0.28**	**98.58± 3.81**
World average	**33**	**45**	**420**

The concentration of Ra-226, Th-232 and K-40 where all found to be below the world average.

(e) FOR NGURNU

SAMPLE CODE	**Ra-226(Bq/Kg)**	**Th-232(Bq/Kg)**	**K-40(Bq/Kg)**
CNT SAMARU	24.40 ± 4.27	1.33 ± 0.26	207.2 ± 6.03
World average	**33**	**45**	**420**

The concentration of Ra-226, Th-232 and K-40 where all found to be below the world average.

(f) FOR JAN BALMA

SAMPLE CODE	**Ra-226(Bq/Kg)**	**Th-232(Bq/Kg)**	**K-40(Bq/Kg)**
SBJT (SHIKA)	1.80 ± 0.47	2.09 ± 0.42	59.20 ± 2.87
World average	**33**	**45**	**420**

The concentration of Ra-226, Th-232 and K-40 where all found to be below the world average.

(g) FOR AGADEZ

SAMPLE CODE	Ra-226(Bq/Kg)	Th-232(Bq/Kg)	K-40(Bq/Kg)
NAT (SHIKA)	35.07 ± 4.14	6.91 ± 1.02	113.11 ± 4.29
World average	**33**	**45**	**420**

The concentration of Ra-226, Th-232 and K-40 where all found to be below the world average.

(h) FOR MANGUL

SAMPLE CODE	Ra-226(Bq/Kg)	Th-232(Bq/Kg)	K-40(Bq/Kg)
KM_GT SHIKA	14.98±2.63	1.82 ± 0.56	1237.33 ± 24.64
World average	**33**	**45**	**420**

The concentration of Ra-226 and Th-232 where found to be below the world average except that of K-40 which was above the world average value.

(i) DAN LIBYA

SAMPLE CODE	Ra-226(Bq/Kg)	Th-232(Bq/Kg)	K-40(Bq/Kg)
LDT SABO	1.20± 0.30	1.03 ± 0.39	1420.71 ± 27.67
World average	**33**	**45**	**420**

The concentration of Ra-226, Th-232 and K-40 where all found to be below the world average**.**

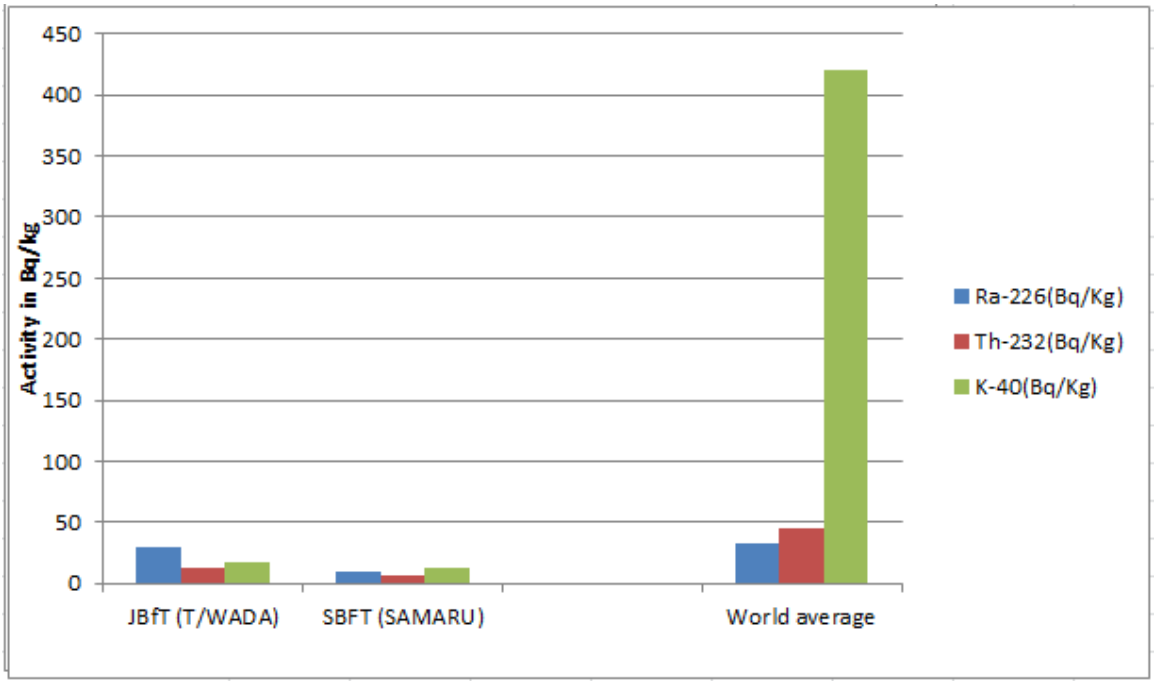


Fig. III: Comparison of radiological concentration for all FARAR BALMA

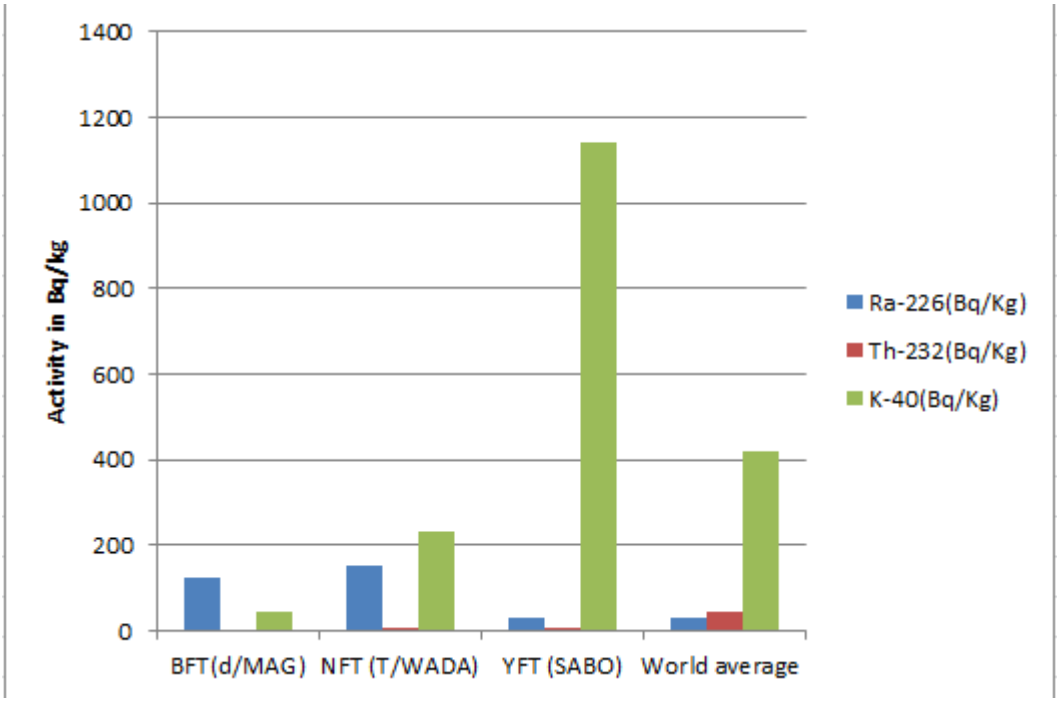


Fig. IV: Comparison of radiological concentration for all FARAR KANWA

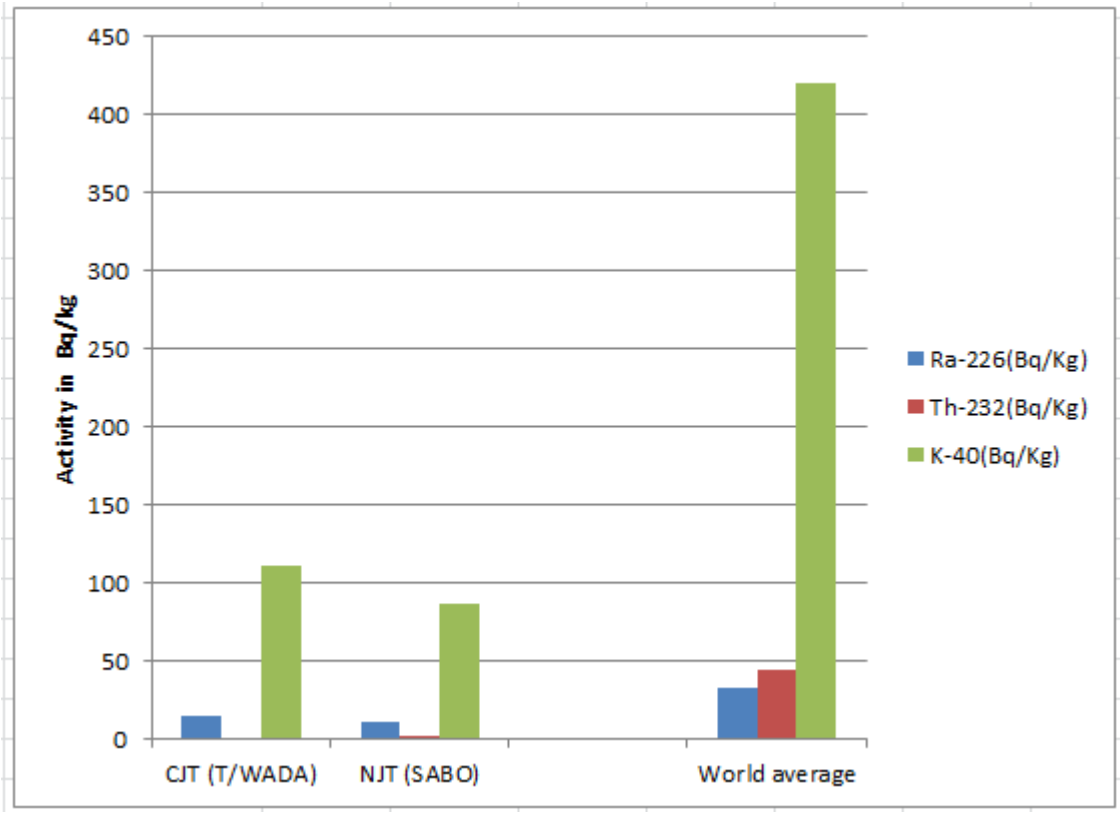


Fig. V: Comparison of radiological concentration for all JAN KANW

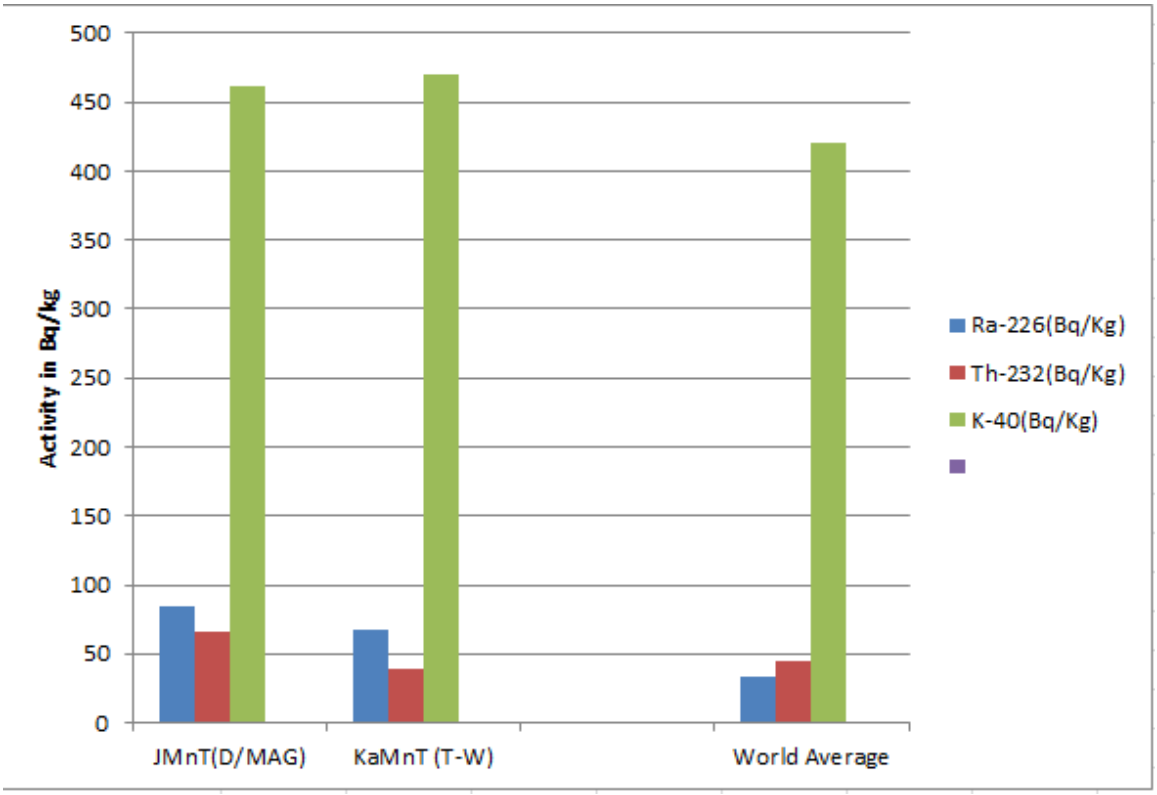


Fig. VI: Comparison of radiological concentration for all MANDA

4.3.2 Radiological hazard implication

The hazard associated with these radionuclides was calculated and presented below.

4.3.2.1 *Radium equivalent activity (Ra_{eq}).*

The values of the radiological parameter showed that radium equivalent activity ranged from 213.73Bq.kg^{-1}-9.35Bq.kg^{-1}with a mean value of 92.27Bq/kg. The highest value corresponded to NFT (T/WADA) with concentration value of 176.39 Bq/kg and the lowest value corresponding to SB$_J$T (SHIKA) with a concentration value of 9.35 Bq/kg. The result is displayed below.

Table 4.7: Radium Equivalent Activity Values

SAMPLE CODE	^{226}Ra-(Bq/Kg)	^{32}Th(Bq/Kg)	^{40}K-(Bq/Kg)	Ra_{eq} (Bq.kg^{-1})
BFT(D/MAG)	122.70 ± 7.01	3.61 ± 0.48	43.34 ± 2.40	131.19
NJT (SABO)	11.51±2.81	1.62 ± 0.31	86.21 ± 3.44	20.47
LDT SABO	1.20±0.30	1.03 ± 0.39	1420.71 ± 27.67	112.07
SB_JT (SHIKA)	1.80±0.47	2.09 ± 0.42	59.20 ± 2.87	9.35
KM_GT SHIKA	14.98±2.63	1.82 ± 0.56	1237.33 ± 24.64	112.86
CNT SAMARU	24.40 ± 4.27	1.33 ± 0.26	207.2 ± 6.03	42.26
CJT (T/WADA)	14.67±2.93	1.16±0.25	110.94 ± 4.17	24.67
JB_fT (T/WADA)	29.82 ± 4.76	17.57 ± 2.47	409.44 ± 10.12	86.47
NAT (SHIKA)	35.07 ± 4.14	6.91 ± 1.02	113.11 ± 4.29	53.66
JMnT(D/MAG)	84.02 ± 8.96	65.85 ± 5.32	461.58 ± 10.87	213.73
SB_FT (SAMARU)	10.40 ± 3.16	13.36 ± 1.92	378.04 ± 9.20	58.61
K_aMnT (T-W)	67.56 ± 8.91	39.79 ± 4.36	469.77 ± 11.74	160.63
YFT (SABO)	31.50 ± 5.33	6.18 ± 1.14	1143.50 ± 23.26	128.39
NFT (T/WADA)	151.02 ± 7.81	5.17 ± 0.88	233.58 ± 7.11	176.39
AVERAGE				**92.27±17.9**

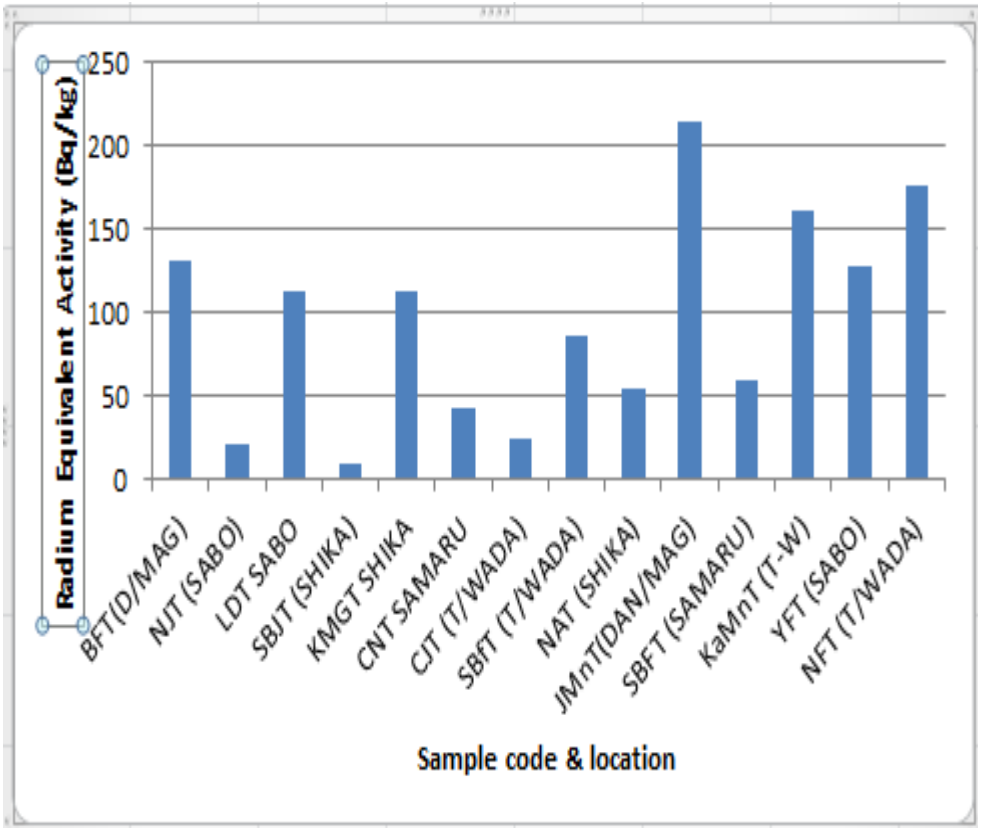


Fig VII: Radium Equivalent Activities and their respective sample collection location

4.3.2.1 *Ingestion effective dose (mSv/yr).*

The table below shows the results of the Ingestion effective dose in (mSv/y) for different age range due to specific activity of ^{238}U, ^{232}Th and ^{40}K in the Trona samples which was calculated. The range of summation of the Ingestion effective dose was observed to vary as follows. For age <1Yr: 0.0068-0.002. For age 1-2Yrs: 0.0001-0.0014, for 2-7yrs: 0.0001-0.0009, for 7-12Yrs: 0.002-0.0001 for 12-17Yrs: 0.0001-0.003 >17Yrs: 0.0001-0.0009.

Table 4.8: Calculated Effective Doses and Their Corresponding Sample Codes

S/N	SAMPLE I.D	<1YR	1-2YRS	2-7YRS	7-12YRS	12-17YRS	>17YRS
1	BFT(D/MAG)	0.0054	0.0011	0.0007	0.0020	0.002	0.0004
2	NJT (Sabo)	0.0006	0.0001	0.0009	0.0002	0.002	0.0004
3	LDT (Sabo)	0.0008	0.0006	0.0003	0.0001	0.0001	0.0009
4	SB_JT (Shika)	0.0002	0.0005	0.0003	0.0003	0.0003	0.0001
5	KM_GT (Shika)	0.0014	0.0006	0.0003	0.0003	0.0002	0.0001
6	CNT (Samaru)	0.0012	0.0003	0.0002	0.0005	0.0030	0.0005
7	CJT (T/Wada)	0.0007	0.0002	0.0001	0.0002	0.0002	0.0005
8	JB_fT (T/Wada)	0.0023	0.0005	0.0003	0.0004	0.0004	0.0001
8	NAT (Shika)	0.0019	0.0004	0.0002	0.0005	0.0005	0.0001
10	JMnT(DAN/MAG)	0.0066	0.0010	0.0008	0.0012	0.0010	0.0003
11	SB_FT (Samaru)	0.0012	0.0003	0.0002	0.0003	0.0030	0.0002
12	K_aMnT (T-W)	0.0048	0.0009	0.0006	0.0009	0.0030	0.0002
13	YFT (Sabo)	0.0023	0.0007	0.0004	0.0006	0.0009	0.0002
14	NFT(T/Wada)	0.0068	0.0014	0.0009	0.0020	0.0006	0.0004
	Average ±S.D	0.0003±0.0006	0.0006 ±0.0004	0.0004 ±0.00007	0.0006 ±0.0001	0.0001 ±0.0003	0.0003 ±0.00006

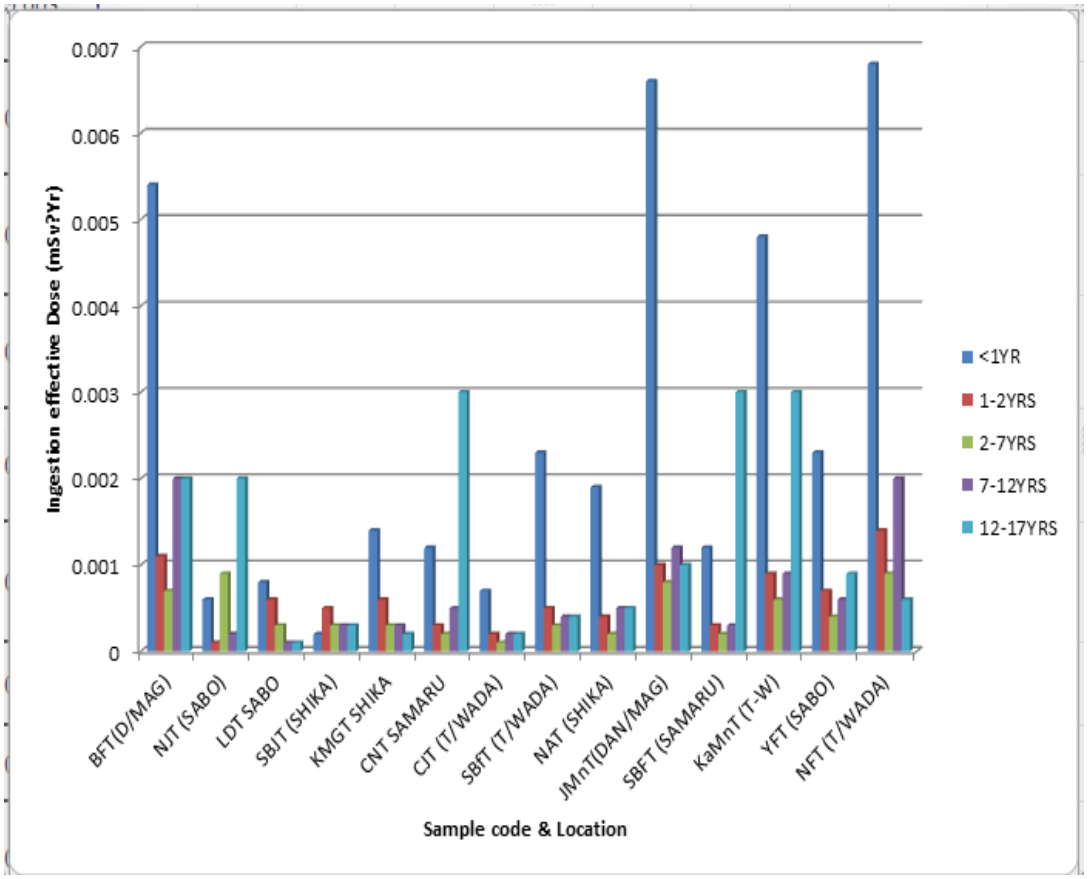


Fig VIII: Ingestion effective dose and their respective sample code

CHAPTER FIVE

5.0 SUMMARY, CONCLUSION AND RECOMENDATION

5.1 Summary

The aim of this research work was to assess the heavy elements and activity concentrations of the different varieties of Trona sold in markets within Zaria.

5.1.1 Elemental analysis

Result of the elemental analysis revealed that all the elements analyzed where present in some samples even though minute, while below detection limit in some samples. The element with the highest concentration was chromium, with a concentration of 2.2579mg/kg while the elements with the lowest concentration were copper with a concentration of 0.0003 mg/kg. Comparing with the work of other researchers, Cu, Ni, Cr, Co and Zn concentrations where found to be greater than the concentration observed by Paul (2014) even though it is within limit and poses no health risk.

All elements were found to be within the W.H.O Recommended dietary intake for heavy elements and safe for consumption.

5.1.2 Activity concentration analysis

Radioactivity in 14 samples of Trona was determined by gamma spectrometry. Investigated radionuclides include ^{226}Ra, ^{232}Th and ^{40}K. Average concentration of ^{226} Ra was found to be 42.904±4.54 $Bq.kg^{-1}$. The mean value of ^{232} Th concentrations was 11.96±1.41 $Bq.kg^{-1}$, also, mean activity concentration of ^{40}K was equal to 455.28±10.56 $Bq.kg^{-1}$. The average activity concentration due to ^{226}Ra was found to be slightly greater than the world average of 33 Bq/kg which raises a brow of concern, the average activity due to ^{232}Th was also found to be below the world average value of 45

Bq/kg, whereas the average activity concentration due to ^{40}K was found to be far greater than the world average value of 420 Bq/kg. ^{40}K being an isotope of potassium, which is an important nutrient for man and is naturally available in abundance is expected to be more, compared to other radionuclides. However it poses no risk to the consumer as the human body system normally undergoes Potassium Homeostasis.

5.1.3 Radium equivalent activity analysis

Activity concentrations together with Trona consumption rate were used to estimate radium equivalent dose to consumers. The radium equivalent activity ranged from 213.73Bq.kg^{-1}-9.35Bq.kg^{-1}with a mean value of 95.05Bq/kg. This amount is less than the permitted amount, which are 370 Bq/kg.

5.1.4 Ingestion effective dose analysis

Activity results and Trona consumption rate were used to estimate ingestion effective dose from these radionuclides. The total average ingestion effective dose for age (7-12y) was found to be: For age **<1Yr**: 0.0068mSv/yr-0.002 mSv/yr. For age **1-2Yrs**: 0.0001mSv/yr -0.0014mSv/yr, for age**2-7yrs**: 0.0001mSv/yr -0.0009mSv/yr, for **7-12Yrs**: 0.002mSv/yr -0.0001mSv/yr. for **12-17Yrs**: 0.0001mSv/yr -0.003mSv/yr. For age **>17Yrs**: 0.0001-0.0009mSv/yr. The overall average ingestion effective dose in all Trona samples was observed to be lower than the permissible limits of 1Sv/y recommended by (ICRP 1996).

Observations from this study reflects that even though the geological location of the areas in which the Trona is mined may likely influence the concentration of the heavy elements and radionuclides in the samples analyzed, it is seen not to pose any serious health burden as the concentrations were found to be below the standards limit .

Hence it is concluded that there is a low risk of heavy metal and radiological intoxication to the consumer, except for continuous consumption of Trona exceeding the recommended daily intake would result to endangering consumers.

5.2 Conclusion

All elements were found to be within the W.H.O Recommended dietary intake for heavy elements and safe for consumption elemental wise.

^{226}Ra in some samples (Farar kanwa & Manda) was found to be slightly greater than the world average of 33 Bq/kg which raises a brow of concern.

Likewise the average activity concentration due to ^{40}K in some samples (Farar kanwa, Manda Mangul) was found to be far greater than the world average value of 420 Bq/kg.

^{40}K being an isotope of potassium, which is an important nutrient for man and is naturally available in abundance is expected to be more, compared to other radionuclides. However it poses no risk to the consumer as the human body system normally undergoes Potassium Homeostasis. Concentration of all NORMS analyzed in Manda were far greater than the world average and also a concern on its ingestion safety.

The radium equivalent activity amount is less than the permitted amount, which are 370 Bq/kg.

Observations from this study reflects that even though the geological formation of the areas in which the Trona is mined may likely influence the concentration of the heavy elements and radionuclides in the samples analyzed, it is seen not to pose any serious health burden as the concentrations in most samples were found to be below the standards limit except for Farar kanwa, Manda & Mangul. Hence we conclude that there is a low

risk of heavy metal intoxication to the consumer, except for continuous consumption of Trona exceeding the recommended daily intake would result to endangering consumers

5.3 Recommendations

After a detailed survey, it was observed that Trona is consumed by a lot of individuals due to various reasons, hence it is recommended that:

a) Trona sample collections should be done directly from the site of mining, because it is a more reliable indicator which considers the geological formation of the area in which these samples are mined from and could explain reasons why some elements might be present or absent.

b) Although, the study has shown a low degree of biological efficacy, the minerals should be used with caution.

c) In the case of further future similar work, the concentration state of the Trona samples at varying intervals should be known or analyzed so as to ascertain if radioactivity and elemental concentration increases or decreases with depth of mining.

d) The results obtained in the present study covers only eight varieties of Trona sold in "Zaria markets". There is a need to expand the scope so as to cover other varieties (if any) sold **outside** Zaria.

e) Further studies should be carried out on the metals" concentrations in Trona (using other methods such as NAA or XRF method in other to monitor the discrepancies in the concentration level.

f) Further studies should be carried out in order to justify other uses such as anti-inflammatory, anti-ulcer etc.

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