

**ASSESSMENT OF NATURALLY OCCURRING RADIONUCLIDES IN DOMESTIC
WATER OF THREE SETTLEMENTS IN THE KETU SOUTH MUNICIPALITY**

BY

CLEMENTINE AYIVI- DORKENOO

10640973

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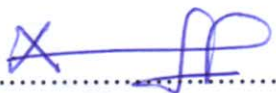
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DECLARATION

This dissertation is the result of research work undertaken by Clementine Ayivi - Dorkenoo in the Department of Nuclear Sciences and Applications, University of Ghana, under the supervision of Dr .Joseph Korbla Gbadago and Prof. Emmanuel O. Darko both of the School of Nuclear and Applied Sciences.



Clementine Ayivi- Dorkenoo



Date



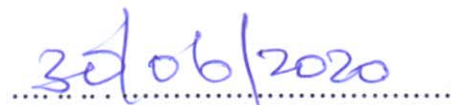
Dr. Joseph Korbla Gbadago
(Principal Supervisor)



Date



Prof. Emmanuel O. Darko
(Co- supervisor)



Date

ABSTRACT

This study was carried out to determine the concentration of naturally occurring radionuclides (^{226}Ra , ^{228}Ra , ^{232}Th and ^{40}K) in water from hand dug wells and few mechanized boreholes used domestically by the people of Aflao, Denu and Agbozume -Klikor communities of Ketu South Municipality. The concentrations of radionuclides from these water sources were measured using gamma spectrometry. The annual effective dose they are exposed to as a result of the consumption was estimated for various age groups. The risk associated with the radionuclides as a result of usage was also estimated. The physico-chemical parameters such as pH, temperature, TDS, conductivity, Ca^{2+} , Mg^{2+} alkalinity and Cl^- were measured using portable water kits analyzer and titrimetric method to determine any possible influence on the radionuclide distributions. Water from three hand dug wells and three mechanized boreholes were sampled in each of the communities. The mean Activity concentrations of ^{226}Ra , ^{228}Ra , ^{232}Th and ^{40}K recorded from the wells and boreholes water in the three communities were, Aflao: ^{226}Ra 3.44 ± 1.07 Bq/l, ^{228}Ra 1.59 ± 0.5 Bq/l, ^{232}Th 1.17 ± 0.11 Bq/l, and ^{40}K 17.98 ± 1.78 Bq/l, Denu: ^{226}Ra 1.973 ± 0.60 Bq/l, ^{228}Ra 1.065 ± 0.38 Bq/l, ^{232}Th 2.16 ± 0.36 Bq/l, and ^{40}K 6.38 ± 1.20 Bq/l and Agbozume obtained ^{226}Ra 0.70 ± 0.12 Bq/l, ^{228}Ra 0.12 ± 0.03 Bq/l, ^{232}Th 0.65 ± 0.10 Bq/l and ^{40}K 2.20 ± 0.28 Bq/l. Generally, almost all the radionuclides measured in both Wells and Boreholes water exceeded the maximum allowable world limits of 1 Bq/l for $^{226}\text{Ra}/^{228}\text{Ra}$ and ^{232}Th . Thorium isotopes are highly insoluble and therefore their contribution to radioactivity in water is negligible. ^{40}K is also not considered in the radionuclide standards. Hence the radionuclide of concern is ^{226}Ra , which has

recorded relatively significant concentrations. Therefore, any possible radiological impact as a result of usage of water in these localities would likely come from radium. The estimated total equivalent doses for the various age groups for Aflao ranges from 1.64 to 5.50 mSv/a; Denu ranges from 1.62 to 5.45 mSv/a; and Agbozume ranges from 0.01 to 0.58 mSv/a. The WHO (2004) limit for quality water is 0.1 mSv/a. This limit therefore suggests that the water quality in the wells of Aflao Second Low-cost and Aflao Well 5 do not meet the WHO reference limit, however, Aflao Beat-9 generally seemed to be nearer to the reference limit but, not good for infants at the age < 1a. Similarly, the water from Aflao Boreholes does not generally meet the WHO standards. Denu Well 1 does not meet the WHO standards but water from Well 2 was found to be generally within the limit. The Denu Boreholes generally do not meet the WHO reference limit. The Agbozume- Klikor Wells on the average, recorded slightly higher doses than the allowable limits especially for infants at the age < 1a. Similarly, for Agbozume boreholes, the doses recorded are above the world limits. The estimated fatal cancer risk values for Aflao, Denu and Agbozume were 2.31×10^{-3} , 1.22×10^{-3} and 0.46×10^{-3} respectively. The values obtained for Aflao is slightly higher than the world's average value of 1.45×10^{-3} . There is therefore the need for continuous monitoring of groundwater in these communities for early detection of any threat of radiological health hazards in the long term. The Wells in the Municipality have generally recorded doses lower than Boreholes. This difference may be due to the varying depths. The Wells are generally shallow compared to the Boreholes which are deeper. The Boreholes are possibly closer to the geological rocks than the Wells. Thus water from the Boreholes have higher chances of

interaction with the rocks than the Wells. Interaction with these geological materials increases the possibility of leaching the radionuclides into the water. The electrical conductivity and TDS recorded significantly high values in water from Aflao and Denu compared to water from Agbozume-Klikor. This indicated that, the high salinity of the domestic water in these localities has contributed to enhancing the concentration of the radionuclides in the various Wells and Boreholes water in the Municipality. Temperature and pH do not seem to have any significant impact on the domestic water in all the various locations. The result obtained for the Chemical parameters showed that for Aflao; Wells ASLW1, AW3 and Boreholes ASLBH1, AWWBH3 seemed to contain more radium than Ca^{2+} and Mg^{2+} , a possible indication of higher concentrations of $\text{CO}_3^{2-}/\text{HCO}_3^-$ which seemed to have improved the dissolution of radium in the water. However, in Well B9-AW2 and Borehole ASLBH2 of Aflao, Ca^{2+} and Mg^{2+} contents recorded higher values than the radium, an indication that there was relatively greater immobilization of Ra on the sediments by co-precipitation with the sulphates. Similar trends were repeated in the Denu and Agbozume-Klikor Wells and Boreholes. The higher values of Cl^- might be attributed to the proximity of the municipality to the sea and the Keta lagoon.

. DEDICATION

This work is dedicated to all the members of my family, more especially to my lovely husband Mr. Rowland Coffie Dorkenoo and my beautiful children John, Clairebelle and Nathan Dorkenoo, and the Ayivi family.

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LIST OF ABBREVIATIONS

ALK	-	Alkalinity
BDL	-	Below Detection Limit
Bq/L	-	Becquerel per Liter
BSS:	-	Basic Safety Standards
Ca ²⁺	-	Calcium
Cl ⁻	-	Chlorides
DCF	-	Dose Conversion Factor
EC	-	Electrical Conductivity
ELCR	-	Excess Lifetime Cancer Risk
EPA	-	Environmental Protection Agency
G.A.E.C	-	Ghana Atomic Energy Commission
HPGe	-	High Purity Germanium Detector
IAEA:	-	International Atomic Energy Agency
ICRP	-	International Commission on Radiological Protection
K	-	Potassium
KeV	-	Kilo Electrovolt
LE	-	Life Expectance
LLD	-	Lower Limit of Detection
MDA	-	Minimum Detectable Activity
Mg ²⁺	-	Magnesium
MOFA	-	Ministry of Food and Agriculture
MOH	-	Ministry Of Health
mSv/a	-	Millisievert per Annum

NORMs	-	Naturally Occurring Radioactive Materials
NRA	-	Nuclear Regulatory Authority
Ra	-	Radium
RF	-	Risk Factor
RPA	-	Radiation Protection Authority
TDS	-	Total Dissolved Solids
Th	-	Thorium
U	-	Uranium
UNSCEAR:	-	United Nations Scientific Committee on the Effects of Atomic Radiation
USEPA	-	United States Environmental Protection Agency
WHO	-	World Health Organization

CHAPTER ONE

INTRODUCTION

1.1 Background

Radioactive substances are everywhere on Earth. They contain radioactive isotopes (radionuclides), generating different types of ionising radiation in the course of nuclear transformations (Dinh et al., .2011). Radionuclides present in the environment can be grouped into several distinct classes with respect to their origin: Primordial radionuclides, Cosmogenic radionuclides, radionuclides produced in natural decay series and anthropogenic radionuclides. Primordial radionuclides comprise radioactive isotopes which have been present on Earth since its formation. Because of their very long half-lives, comparable with the age of the Solar system, they have not yet decayed beyond the point of their detection. The most prominent members of this group are the radioactive isotopes of ^{40}K , ^{238}U and ^{232}Th which contributes some percentage to the effective dose received by members of the global population due to ionising radiation originating from natural radionuclides (UNSCEAR, 1998:2008). In radioactivity decay, the unstable parent radionuclides are transformed into stable daughters, which end up in the release of energy (Zapeczka and Szabo, 1986). These daughter radionuclides have distinct chemical composition, mobility, solubility and half-life that differ from their parent radionuclides (Gilkeson et al., 1983). ^{238}U , and ^{232}Th are part of the matrix of rock, and they are distributed throughout underground rock formations. They are essentially insoluble in the reservoir fluids, and therefore immobile. However, the radium isotopes ^{226}Ra , and ^{228}Ra which are daughters of ^{238}U , and ^{232}Th respectively, are somehow soluble in water and

are therefore mobile. Radium may be produced within any water and its concentration present may depend on the nature of the formation, physical and the chemical conditions. Chemically, calcium, barium, and some strontium freely combine with radium, because they have similar properties and are more in abundance (Gbadago, 2010; and Bruzzi et al., 2000). The dissolved mineral may also occur naturally due to the migration of water through rocks containing high level of salt such as magnesium, potassium and sodium which are cations and anions such as chlorides, bicarbonates, carbonates and sulphates and can also occur as a result of human activities (WHO, 1996). Electrical conductivity measures how water is transported by an electric current and this is also related to the salinity in water, these may increase with increasing conductivity and total dissolved solids (Vengosh, 2003). Aside the recoil processes which plays a significant role in radionuclide release in water, leaching and dissolution remains the two main processes for radionuclide transport in underground water (Dinh et al., 2011), and it is greatly affected by the salinity of the water found mostly in the aquifer matrix. The ratio between adsorbed and dissolved radium depends on the salinity among other factors, and thus the concentration of dissolved radium typically increases with salinity (Miller and Sutcliffe, 1985; Herczeg et al., 1988; Krishnaswami et al., 1991; Moise et al., 2000; Sturchio et al., 2001; Vinson et al., 2009; Tomita et al., 2010; Vinson, 2011). Public water supply systems derive their water from both surface and underground water bodies, such as boreholes, streams, rivers, wells and the like for washing, bathing, flushing of toilets, drinking and so on in performing these activities, radionuclide may be released (Darko et al., 2010; UNSCEAR, 2000), and the human being can be exposed by both inhalation or ingestion of the radionuclides. When the cells of living organisms are exposed to this

ionized radiation, it may cause damage to the cells and if a large number of cells are affected then, the living organisms may end up developing cancer (Lahlou, 2000). For this reason, countries worldwide have reasoned together for standardized level of naturally occurring radioactive material in water above which measures are taken (WHO, 2004: 1996; DWAF 1999; Canadian GD 2000; NHMRC/ANZECC/ARMCANZ 2000). Over the years, a number of researchers have investigated into the occurrence of natural radioactivity in water and in other medium globally. A study of the radioactivity in ground water from Tanke-Ilorin, Nigeria, has been carried out. Ten water samples were analysed by gamma-ray spectroscopy to determine the ^{226}Ra and ^{228}Ra concentrations. The activity concentration values ranged from 0.81 ± 0.08 to 7.4 ± 2.2 Bq/l for ^{226}Ra and from 1.8 ± 0.3 to 5.6 ± 2.6 Bq/l for ^{228}Ra . The derived Annual Effective Dose received by the population as a result of the ingestion of ^{226}Ra was estimated to range from 0.08 ± 0.01 to 0.12 ± 0.07 mSv/y with an average of 0.39 ± 0.11 mSv/y and ^{228}Ra range from 0.50 ± 0.32 to 1.42 ± 0.70 mSv/y with an average of 0.91 ± 0.31 mSv/y. Consequently, the Annual Effective Dose received, as a result of the combined ingestion of ^{226}Ra and ^{228}Ra , was found to range from 0.81 to 1.74 mSv/y with an average of 1.30 mSv/y. The mean contribution of both ^{226}Ra and ^{228}Ra activities to the committed effective dose from a year's consumption of drinking water in the study area is, therefore, higher than the allowable level of 1 mSv/y to the general public for prolonged exposure as recommended by ICRP, and much more than the new WHO recommended level of 0.1 mSv/y for drinking water (Nwankwo, 2013).

Natural radioactivity measurements in drinking water from drilled wells, dug wells and waterworks in Finland, show that, the mean annual effective dose for the three different

source of ground water were 0.41 mSv, 0.05 mSv and 0.02 mSv respectively. The highest effective dose from drinking water was caused by ^{222}Rn constituting 75% and 60% of the total effective dose caused by all natural radionuclides for drilled-well and dug wells dug respectively. ^{210}Po and ^{210}Pb contributed the most to the effective dose caused by the long lived radionuclides. Contribution of the isotopes of radium (^{226}Ra and ^{228}Ra) to the total effective dose from drinking water was minor compared to the WHO (Vesterbacka, 2007). The activity concentrations of some radionuclides in tap water samples of the Eastern Black Sea region of Turkey were measured, and the concentration of the radionuclides ^{214}Pb , ^{214}Bi , ^{40}K , ^{226}Ra and ^{137}Cs were determined using high resolution gamma ray spectrometry. ^{222}Rn activity concentrations in tap water samples were also measured using Liquid Scintillation Counting. The mean specific activities of ^{214}Pb , ^{214}Bi , ^{226}Ra , ^{40}K , ^{137}Cs and ^{222}Rn in tap water samples were 6.73, 6, 19.16, 168.57, 5.45 mBq l⁻¹ and 10.82 Bq l⁻¹, respectively. These values are comparable with concentrations reported for other countries. The estimated effective doses were $6.878 \times 10^{-4} \mu\text{Sv y}^{-1}$ for ^{214}Pb , $4.800 \times 10^{-4} \mu\text{Sv y}^{-1}$ for ^{214}Bi , $3.916 \mu\text{Sv y}^{-1}$ for ^{226}Ra , $0.763 \mu\text{Sv y}^{-1}$ for ^{40}K , $0.052 \mu\text{Sv y}^{-1}$ for ^{137}Cs and $5.848 \mu\text{Sv y}^{-1}$ for ^{222}Rn (Cevik et al., 2005)

In Ghana, there are scanty of data on natural background radiation levels in drinking water. A study of the possible radiological impact of drinking water in two critical mining communities of Dumasi and Chujah at Bogoso in the Western Region of Ghana was carried out (Gbadago et al., 2011). Infants less than 1 year old in Chujah using treated water were found to be exposed to 10 % more than the WHO limit of 0.1mSv. Water samples collected from boreholes and treated water supplied by a gold mining company were analysed for important radionuclides such

as ^{238}U , ^{234}U , ^{226}Ra , ^{210}Po , ^{230}Th , ^{232}Th and ^{224}Ra , using extractive techniques in the Radio Analytical Laboratory of the South African Nuclear Energy Corporation. None of the radionuclide concentrations found exceeded the world averages in drinking water.

The $^{238}\text{U}/^{235}\text{U}$ ratios were also found to fall within those for natural environmental materials. The dose contributions of the radionuclides for different age groups were evaluated using the IAEA recommended dose conversion factors. The lifetime average dose for all the communities are lower than 0.1 mSv as recommended by WHO; however, if age group classification is considered, infants less than 1 year old in Chujah are exposed to 0.11 mSv when the treated water is used (Gbadago et al., 2011).

Preliminary studies have been conducted in Aflao, on the impact of naturally occurring radioactive materials (NORMs) on the environments and the public from the operational activities of Diamond Cement Factory in Ghana. Both water and soil sample were collected and their activities measured using gamma spectrometry system high purity germanium detector. The annual effective dose was found to vary from 0.022 to 0.186 mSv with an average of 0.094 ± 0.041 mSv for soil samples. That of the water samples varied from 0.094 to 0.287 mSv with an average of 0.179 ± 0.080 mSv. The average value of the equivalent dose of the soil samples was found to be lower than the world average soil annual equivalent dose of 0.7 mSv (Adukpo et al., 2011). However, this work was limited to the factory area in Aflao within the Ketu South Municipality. There is therefore the need to extend the studies to other major towns in the Ketu South Municipality such as Denu, Agbozume and areas not covered in Aflao. In this study, assessment of naturally occurring radionuclide contents in water in a large coverage area of the Ketu South Municipality could help in the identification of major point sources for

radionuclides. These potential point source(s) could be well understood through the various concentrations of radionuclides determined from the water sources located across large span of the Municipality.

1.2 Problem Statement

Major sources of water for domestic use in the Ketu South Municipal area are hand dug wells and few mechanized boreholes. Water from these sources does not undergo any treatment process before consumption and more so, some of the water sources have high salinity. High salinity is known to enhance the concentration of naturally occurring radionuclides and associated elements in a media (Gbadago, 2010). Aside human activities such as cement production and large applications of fertilizer for vegetable production in the municipality, geological formations could also be a source for natural radionuclides in ground water. The specific levels of naturally occurring radionuclides of terrestrial origin are related to the composition of each lithological separated area, and to the content of the rock from which the soils originate (Gbadago, 2010). The Ketu South Municipality consist of three main geological formations, namely, the Dahomenyan formation at the North consisting of tropical Grey and Black Earths soils, the Regosolic Groundwater Laterites and the littoral deposit comprising of marine sands and the Tertiary formation of Savannah Ochrosols for the soil type (Kesse, 1986). Cement production, large scale use of fertilizers and ground water interactions with the geologic formations coupled with high salinity would impact largely on the sources of drinking water. Radioactivity monitoring studies of drinking water resources so far, has established

that measurement of ^{226}Ra , and ^{228}Ra from the 2-decay chains are necessary to calculate the estimated annual dose with a high degree of certainty (Gbadago 2011; Faanhof and Louw 2001; Desideri et al. 2007; DWAF 1999). There is therefore the need to evaluate the radionuclide content of the drinking water sources in the municipality. The physico-chemical compositions were measured to determine any possible influence on the radionuclides distributions.

1.3 The objectives of the research

1.3.1 Overall Objectives

The primary objective is to assess the levels of naturally occurring radionuclides (^{226}Ra , ^{228}Ra , ^{232}Th and ^{40}K) in water from boreholes and mechanized boreholes and hand dug wells used domestically by the people of Aflao, Denu and Agbozume -klikor communities of Ketu South Municipality; and estimate the annual effective dose and its associated health risk. The physico-chemical compositions were measured to determine any possible influence on the radionuclide distributions

1.3.2 Specific Objectives;

- (a) To evaluate the Activity Concentration of important naturally occurring radionuclides (NORMs) in domestic water sources at Ketu south municipality;
- (b) To evaluate the Annual Dose and Annual Effective Dose;
- (c) To estimate the level of radiation exposure as a result of usage;
- (d) To estimate the risk associated with the radionuclides as a result of usage; and

(e) To determine any possible influence of physico-chemical parameters on naturally occurring radionuclides (NORMs) in domestic water sources at Ketu South Municipality.

1.4 Relevance and Justification of the Research

Long term injection of radionuclides from domestic water can threaten the health of humans including children and adults, there by affecting their internal organs. Exposure to ionizing radiation from these radionuclides could cause various cancers which could lead to death (UNESCEAR, 2017; Gbadago et al., 2011). Previous work done by (Boateng et al., 2006) indicated that the source of water for domestic used should be investigated since the ground water can move great distances through unseen aquifers. There is therefore the need to measure the activity concentration levels of important natural radionuclides in the domestic water system and estimate the average radiation exposures as a result of usage. The data obtained from this study will be added to the existing data and it will be useful in the determination of any regulatory approach.

1.5 Scope and Limitation of Research

The research is intended to measure some important naturally occurring radionuclides such as (^{226}Ra , ^{228}Ra , ^{232}Th and ^{40}K) in domestic water from hand dug wells and mechanical boreholes of Aflao, Denu and Agbozume - Klikor communities of Ketu South Municipality. Water samples were randomly collected from some particular areas of study. Gamma spectrometric analysis was used in the measurement of the abundance distribution of these NORMs. The data obtained was used in the estimation of annual effective dose and the risk associated with the exposure to these radionuclides. The physico-chemical parameters such as pH, temperature, TDS, conductivity, Ca^{2+} , Mg^{2+} ,

alkalinity and Cl^- were measured using portable water kits analyzer and titrimetric method to determine any possible influence on the radionuclide distributions. Tables and Statistical diagrams (histograms) were used to interpret any possible influence of the physico-chemical composition on the radionuclide. However the study covers only some few selected areas of the municipality, it would be necessary if the study is extended to cover the entire municipality.

1.6 Thesis Composition

The thesis is made up of five chapters. Chapter one consist of introduction brief information about the study. Chapter two is the literature review of previous works by some researchers on similar studies. Chapter three is the methodology and the analytical techniques involved to obtain accurate results. Chapter four is the evaluation and discussion of the analytical results. Chapter five is conclusions and recommendations depending on the analytical results.

CHAPTER TWO

LITERATURE REVIEW

2.1 Origin of Radionuclides

The classifications of radionuclides are based on their origin which are: primordial, cosmogenic and anthropogenic. Primordial radionuclides are radioactive materials that originate with the formation of the earth. They have very long half-lives compared with the age of solar system. Some of these primordial radionuclides are ^{238}U , ^{232}Th and ^{40}K ; ^{40}K the most common among them. Cosmogenic radionuclides are produced as a result of cosmic radiation interaction with the atmospheric constituents some examples of cosmogenic radionuclides are ^{26}Al , ^{14}C , ^{36}Cl , and ^3H . This occurs as a result of high energy from the cosmic rays. Anthropogenic radionuclides originate as a result of man-made activities which includes disposal of waste from nuclear plant operation (Dinh et al., 2011). Some examples of anthropogenic radionuclides are radon-22, strontium -90 and cesium-137. The presence and dominance of the primordial radionuclides ^{238}U , ^{235}U and ^{232}Th in natural materials coupled with long half-lives and toxicity make their study a fair representation of natural radionuclides.

During the decay process of these radionuclides as shown in Table 2.1 below, gamma rays from the nucleus are released alongside with alpha and beta particles (Zapecza and Szabo, 1986)

Table 2.1: Showing the three main decay series and their mode of decay (IAEA, 2003)

Radionuclides	Main mode of decay	Radionuclides	Main mode of decay	radionuclides	Main mode of decay
^{238}U	A	^{235}U	α, γ	^{232}Th	A
^{231}Th	β, γ	^{231}Th	B	^{228}Ra	B
$^{234\text{m}}\text{Pa}$	β, γ	^{231}Pa	A	^{228}Ac	β, γ
^{234}U	α, γ	^{227}Ac	B	^{228}Th	α, γ
^{230}Th	α, γ	^{227}Th	A	^{224}Ra	α, γ
^{226}Ra	α, γ	^{223}Ra	A	^{220}Rn	A
^{222}Rn	A	^{219}Rn	A	^{216}Po	A
^{218}Po	α	^{215}Po	A	^{212}Pb	β, γ
^{214}Pb	β, γ	^{211}Pb	B	^{212}Bi	α, β, γ
^{214}Bi	β, γ	^{211}Bi	A	$^{212}\text{Po (65 \%)}$	$\alpha,$
^{214}Po	α, γ	^{207}Tl	B	$^{208}\text{Tl (35 \%)}$	β, γ
^{210}Pb	β, γ	^{207}Pb	None	^{208}Pb	None
^{210}Bi	β, γ	-	-	-	-
^{210}Po	α	-	-	-	-
^{206}Pb	None	-	-	-	-

2.1.1 Uranium

Uranium is an important naturally occurring radionuclide, found in surface and ground water and abundantly occurs in different types of rocks due to its unlimited mobility (Zapecza and Szabo, 1986; Awan and Khan, 2015). Uranium occurs in rocks by weathering with a background value between 0.79 – 11 mg U kg⁻¹ relative to the parent rock (Kabata-Pendias and Pendias, 2001). It exists as a dense radioactive element in natural silver-white form with atomic number of 92 and atomic weight of 238 g/mol, ion size of 1.05 with six (6) valence electrons (Scott and Barker, 1962; Hess and others,

1985). Uranium has three radioactive isotopes, ^{234}U , ^{235}U and ^{238}U (Awan and Khan, 2015). ^{238}U is the most occurring isotope with the abundance of 99.27 %, half-life of 4.5×10^9 years (Sheppard et al., 2005) They have similar chemical reactions but exhibit small variation in their chemical behavior due to small differences in mass, same physical properties such as boiling and melting points and volatility. They have the same biochemical and biological influence on human health but possess different radioactive properties such as half-life, decay mode and specific activity with percentage abundance of 0.0054%, 0.72% and 99.27% (Awan and Khan, 2015) and half-lives of 244000 years, 170 million years and 4500 million years respectively. The longer half-life produces less radioactivity per mass of the material. ^{234}U is a daughter radionuclide of ^{238}U decay series with a shorter half-life and is in radioactive equilibrium with the parent ^{238}U radionuclide (Scott and Barker, 1962; Hess and others, 1985). Igneous rocks contain more concentration of uranium as compared to sedimentary rocks which are made up of clay segment with its concentration in several ppm. The same concentration is found in metamorphic rocks but maximum concentration of uranium is formed in black shales and phosphates. Uranium metal has the ability to form compounds with non-metal elements with the exception of the noble gases such as helium, argon, neon, xenon, krypton, radon and their compounds (Levy and Wilson, 1973). Uranium in the surface water can disperse over large distances. As in soil, the mobility of uranium in waters depends on factors such as pH, redox potential, sorting characteristics of sediments and the suspended solids in the water (Chen et al., 1986).

2.1.2 Thorium

Thorium is a natural radioactive element that comes about in low concentration in the rocks, soil, water, plants and animals, and is more abundant than uranium (Fernandes, 2018). The chemical symbol is Th. Thorium appears as a silvery white and soft metal and has atomic number of 90, a weight of 232 and a solid under normal conditions. Both natural and man-made forms of thorium are radioactive. Naturally occurring thorium exists as ^{232}Th , ^{230}Th or ^{228}Th radioisotopes which are short-lived and intermediates of the decay chain. Thorium has ionic radius of 1.10, melting point of 1,800 °C (3,300 °F) and boiling point of 4,500 °C (8,100 °F). Thorium is soluble in acids and reacts slowly with oxygen at room temperature; and at higher temperature it reacts rapidly with oxygen to form ThO_2 . Thorium, Phosphates and Chlorides nitrates can form complexes. The relative abundance and importance of individual complexes depends on the concentrations of these ions and on the pH of water.

Thorium has oxidation state of +4 in aqueous solution. Concentrations of thorium in crystal rocks are less than 100 ppm (Dinh et al., 2011). Thorium forms fluoride complexes in acidic water and reacts with water at pH greater than 8 to form $\text{Th}(\text{OH})_4$ which has the ability to precipitate. It forms Th^{+4} at pH less than 3.5 and forms complexes with carbonates, phosphates, chlorides and nitrates. Thorium is strongly adsorbed on iron hydroxides and humid substances (Dinh et al., 2011).

2.1.3 Potassium

Potassium (K) is found in most rocks and is a major component of the rock forming minerals. It occurs mostly as aluminosilicates and K-feldspars during weathering processes. K-feldspars is made up of orthoclase and microcline found in all granite rocks together with biotite and muscovite as the main rock forming mineral. The K_2O present in K-feldspars ranges from 11-15%. Ranges from 8 to 10% and 10 to 11% in both biotite and Muscovites respectively (Glover et al., 2012). A higher concentration of ^{40}K in shallow ground water may be as a result of intensive agriculture practices relating to the usage of fertilizer on the land for quick growth and more yield of crops.

Potassium-40 freely dissolves in ground water and the concentration of ^{40}K in water changes depending on the specific condition in the aquifer and the content of potassium present in the host rocks (Glover et al., 2012; Dinh et al., 2011).

2.2 Radionuclide release and transportation in underground water

The release and the transportation of radionuclides in ground water are based on the geology, hydrogeology and the geochemistry conditions of a particular area (Zapeczka and Szabo et al. 1986). The saturated zone beneath the water table contains ground water which continually interact with the solid matrix of the aquifer resulting into the release of chemical and radioactivity content in the direction of groundwater movement with varying physico-chemical parameters such as temperature, pH, electrical conductivity (EC), total dissolved solids (TDS) and the lithology of the aquifer matrix (Dinh et al., 2011). Radionuclide in the rock mass which is not disturbed for about 10^7 years is referred to as close system. In this case, the long-lived parent radionuclides are found to be in

secular radioactive equilibrium and both the parent radionuclide and all the intermediate successive daughter radionuclides would possess the same activity concentration and all activity ratio (AR) in this closed systems are equal to one (1). In the case where the rock mass is opened as a result of geological disturbance involving the interaction of groundwater flow, it causes a radioactive disequilibrium and the activity ratio is not equal to one (1). Radioactive disequilibrium occurs as a result of two processes such as fractionation brought by recoil and fractionation as a result of the changes in both physical and chemical properties of the radioactive elements of the decay series (Hoehn, 1998; Gunten, 1995).

In the transportation of natural radionuclide from rocks and soils, two major processes takes place and these are dissolution and leaching of the host rocks. This happens through the infiltration of groundwater aquifer (Zapecza and Szabo et al., 1986; Dinh et al., 2011). The movement of radionuclides in ground water depends on their solubility. For example, Uranium is more soluble and mobile in groundwater rich in oxygen in the presence of bicarbonate, phosphate and fluoride with low total dissolved solids (TDS). Uranium is less mobile in ground water with less oxygen containing gases such as hydrogen with less oxygen resulting into the adsorption of the uranium onto humic substances found in the aquifer while radium mobility is very high in groundwater which are rich in chloride reducing agent with high total dissolved solids content (Zapecza and Szabo et al., 1986). Thorium is immobile in groundwater. Thorium forms hydroxides which are absorbed by humid substances, this makes thorium to be absent from groundwater (Dinh et al., 2011). The physical removal of daughter radionuclides from the parent radionuclides during the decay process is known as decay recoil. This performs a

major role in the transportation and dissolution of the radionuclides. The gradual release of soluble components of radionuclides contaminant through the pore space of the host rock (solid matrix) into groundwater aquifer is termed as Leaching (Kim, 2005).

2.3 Physico-Chemical Parameters

Physico-Chemical Parameters are the physical and chemical constituents of water and their concentrations depending on the geological factors of a particular area or region. Industrial wastes and municipal solid wastes are the main sources of both surface and ground water pollution. Surface and groundwater quality depends on the physico-chemical parameters and it is important to test the quality of water before consumption. Some physical parameters are temperature, pH, Electrical Conductivity and TDS. The chemical parameters are alkalinity, chlorides, Total hardness, calcium and magnesium.

2.4 Effect of some Physico-Chemical Parameters on Radionuclides

2.4.1 pH

pH is important in the determination of how corrosive water is. The lower the pH, the higher the corrosive nature of water (Karanth 1987; Patil et al., 2012).

pH is the measure of how acidic or alkaline a solution is. A Positive correlation exists between pH, electrical conductivity and total alkalinity. pH plays a vital role in the solubility and mobility of some important radionuclides (Awan and Khan, 2015). A study done by a researcher revealed that under alkaline pH, Uranium (VI) reacts with carbonate to produce highly soluble complexes resulting into increasing mobility and

abundance of uranium in groundwater and soil. It is not easy to precipitate uranium as phosphate in excess carbonate under the same alkaline medium (Awan and Khan., 2015). Thorium forms Th^{+4} at pH less than 3.5 and forms complexes with carbonates, phosphates, chlorides.⁴⁰ K level in ground water is high at low pH and the concentration level is low, at a low pH (Seghour and Seghour, 2009). Thorium is soluble in acid, insoluble in water and behaves like rare earth metals (Zapeczka and Szabo., 1986).

U (VI) forms complexes like $[\text{UO}_2 (\text{CO}_3)_3]^{4-}$ in excess carbonate .under alkaline pH and in excess, precipitate the uranylene to form $\text{UO}_2 (\text{OH})^{-2}$.

2.4.2 Temperature

The rate of chemical reactions depend on temperature, Temperature promote chemical weathering of rocks, chemical reactions, dissolution of chemicals and radionuclides from the host rocks (Patil et al., 2012; Glover et al., 2012). Temperature also increases with increasing conductivity as well as TDS (Kubi, 2013). The reduction of uranium hexafluoride (UF_6) by oxygen occurs at room temperature (Levy and Wilson, 1973). Thorium slowly reacts with oxygen at room temperature and reacts rapidly with oxygen to form ThO_2 (Zapeczka and Szabo, 1986).

2.4.3 Electrical Conductivity (EC)

Electrical conductivity is a measure of the ability of water to transport or conduct electric current. Conductivity increases with increasing ion concentration and electrical current is transported by ions in solution. Conductivity can also be referred to as the total dissolved

constituent of water or total dissolved salts. Electrical Conductivity has a correlation with parameters such as temperature, pH, total dissolved solids, alkalinity, total hardness, calcium, chloride and iron concentration of water (Kumar and Sinha, 2010). Conductivity as well as TDS increases with increasing salinity (Kubi, 2013; Vengosh, 2003).

2.4.4 Total dissolved solids (TDS)

Total dissolved solids are the sum of all dissolved solid constituent or salt in water measured in milligram per liter. These materials are chlorides, organic matter, carbonate, sulphate, calcium, sodium, magnesium, bicarbonate and other ions. TDS increases with increasing salinity (Kubi, 2013). The solubility and mobility of radium is facilitated by the presence of salt in the groundwater and high TDS and salinity also causes the retention of some radionuclides in groundwater (Vengosh, 2003).

2.4.5 Alkalinity

Alkalinity is defined as measure of the ability of water to neutralize an acid and is an expression of buffering capacity. A buffer is an aqueous solution which does not change the concentration of H^+ ions when an acid is added. It absorbs the extra H^+ ions and helps the water body to have a steady pH. Alkalinity acts as a stabilizer for pH. Alkalinity, pH and hardness affect the toxicity of many substances in the water (Patil et al., 2012).

The alkalinity of underground water is identified by the soil and bedrock from which water passes. The actual sources of alkalinity are rocks formed by carbonate, bicarbonate, and hydroxide compounds. Borates, silicates and Limestone contain carbonates. Water

passing through limestone may have high alkalinity with good buffering capacity. Granites and sandstones may have low alkalinity. Calcium carbonate as well as magnesium carbonate donates carbonate ions to the buffering system. Alkalinity is related to hardness since the source of alkalinity is carbonate rocks (limestone) which is CaCO_3 . Calcium Carbonate (CaCO_3) relates to most alkalinity and hardness in CaCO_3 is equal to alkalinity. Hard water is made up of metal carbonates (CaCO_3) which is high in alkalinity. Carbonate is related to sodium or potassium but do not contribute to hardness. Soft water has low alkalinity and small buffering capacity (Patil et al., 2012). Uranium (VI) forms highly soluble complexes with carbonate in alkaline medium (Awan and Klan, 2015).

2.4.6 Chlorides

Chlorides exist in nature as salts of sodium, potassium and calcium such as NaCl , KCl and CaCl_2 respectively (Patil et al., 2012). Chlorides move from various rocks into soil and water by weathering. The chloride ion is highly mobile and can be taken to closed basins or oceans. A high content of chloride increases the electrical conductivity of water as well as the TDS. High salinity (salt) causes the retention of some radionuclides in groundwater and facilitates the solubility and mobility of radium (Vengosh, 2003; Vinson et al., 2013).

2.4.7 Calcium and magnesium

Calcium and magnesium are found in both surface and groundwater which originate from the dissolution of limestone CaCO_3 , gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and rocks containing

calcium and minerals. Groundwater aquifers contain higher concentrations of calcium ions from rocks and soil. Calcium carbonate is insoluble in water but dissolves more easily in water consisting of dissolved carbon dioxides. Calcium is present in water as Ca^{2+} (aq) and can also be in the form of CaOH^+ (aq), $\text{Ca}(\text{OH})_2$ (aq) or as CaSO_4 in seawater. Calcium and magnesium are the main cause of water hardness and calcium is a pH stabilizer since it has buffering properties and also determines the taste of water (Glover et al., 2012; Ayimah, 2014). Calcium, magnesium and radium belong to the same group 2 which are alkali earth metals. Radium and calcium have the same chemical and physical properties (Vengosh, 2003).

2.5 General health effect of radionuclides

Exposure to very high ionizing radiation for a short period of time can cause health effects such as skin burns, acute radiation syndrome also known as radiation sickness such as nausea and vomiting this can cause death and long-term health effects such as cancer and cardiovascular disease. . Exposure to low level radiation can cause a long-term effect (Stochastic Effect) such as cancer over a lifetime (WHO, 2011). As radiation exposure increases the chance of getting cancer also increases, and the risk increases as the dose increases: the higher the dose, the greater the risk. The risk of getting cancer from radiation exposure is low as the dose reduces. The radiation effect can be classified into two groups such as Deterministic and Stochastic effect. Deterministic effect depends on the exposure time, doses and type of radiation received and threshold of the doses; it is caused by a high radiation dose and its occurrence probability increases with increasing radiation dose.

2.5.1. Health effect of uranium

The absorption of uranium oxides increases with increasing solubility. Uranium oxides such as U_3O_8 and UO_2 are partially insoluble but uranium trioxide is more soluble. The uranium compound entering the organism via the gastric wall or lungs is changed in the body liquid. U^{4+} undergoes oxidation to produce hexavalent uranium and uranyl ions. Uranium chemical reaction occurs after the absorption resulting into the production of oxides and hydroxides or carbonates. The soluble uranium is absorbed within few days and is related to chemical toxicity. The soluble uranium compounds are renal toxins which manifest by the degeneration of the functional parts of the kidneys and cause damage to the gastrointestinal tract. The insoluble uranium is absorbed for a long period of time from months to years and is related to radiation toxicity. The insoluble uranium compounds are hazardous to the respiratory system. Therefore the degeneration of the lungs epithelium and hemorrhage and children are in danger when exposed to uranium (Oterreicher et al., 2015). Uranium in its natural form in groundwater and surface water may cause various cancers and its toxicity causes a long-term damage to an exposed organism resulting from the slow absorption of the uranium oxides by the lungs and the longtime retention of the uranium oxides in the visceral organ tissues (Oterreicher et al 2015). Chemical toxicity of uranium does not depend on its isotopic abundance but remain identical in their natural, enriched and depleted uranium forms. The chemical toxicity is regarded as the contributor to general health problems induced by changes in the kidneys, lungs, liver and the hematopoietic system (Oterreicher et al., 2015).

2.5.2 Health effect of Thorium on human

^{232}Th and ^{230}Th are natural radionuclides and at high radiation dose exposure, can result into lung, pancreas, hepatic, bone, kidney cancers and leukemia (USEPA, 2006a; Klu, 2015).

2.6. Diamond Cement Factory and its Radiological Impact in the Ketu South Municipality

Diamond Cement Ghana Limited is an Indian-owned Portland cement producing company. It is located 3 km north of Aflao Township in the Ketu South Municipality, Volta Region. The factory started production in 2002. The settlements around the factory area are scattered houses, about 300 m from the factory. The cement factory plays a very important role in the economy of Ghana (Adukpo et al., 2011). Portland cement is one type of a building in Ghana, that is preferred by most Ghanaians and also elsewhere where in other countries. Portland cement is known to produce more sustainable concrete and mortar design. It reacts chemically with water to obtain setting and hardening properties when used in blocks for the construction of buildings, concrete, roads, bridges, and other structures. The production of the cement is by calcination thus a mixture of a calcareous and an argillaceous material at a temperature around 1450 °C. Calcareous substances are of calcium oxide found in limestone (CaCO_3), chalk or oyster shells and argillaceous materials are silicate and aluminate substances found in clays. Shale and slags thus, Clinker is also produced by a calcination process which involves a well-proportioned mixture of argillaceous and calcareous substances. The clinker produced is mixed with a predefined ratio of gypsum and milled together in a ball miller to obtain the Portland cement (Bediako and Amankwah, 2015). Portland clinker and anhydrite can

lead to radiological effect on human life. Cement manufacturing can cause environmental contamination at all stages of its production process (UNSCEAR, 2000). Cement contains natural occurring radionuclides such as ^{238}U , ^{232}Th and ^{40}K , and their associated decay products.

Cement products contribute to environmental radioactivity in two ways thus external and internal exposures. The external radiation exposure is mainly caused by gamma radiation originating from ^{226}Ra , ^{232}Th and ^{40}K . In other way the internal radiation exposure is also caused by the short-lived daughter product of radon (^{222}Rn) following the decay of ^{226}Ra . The internal radiation exposure affect the respiratory tract .this is because, ^{218}Po which is progeny of radon-222 is electrostatic and has the ability to sticks to the dust in the environment and when inhaled it can affect the respiratory track and other tissues and organ in the body. (Kpeglo et al., 2011; Aslam et al., 2012 and Özdiş et al.2017).

2.7 Radiological characteristic of natural radioactivity in groundwater

According to UNSCEAR Report for 2008, groundwater consumption by human can result in internal exposures to ionizing radiation of which a small fraction of the average annual committed effective dose are from natural sources .The annual global mean dose was estimated for ionizing radiation received from drinking water and food and the value obtained was 0.29 mSv which was approximately 12% of the total committed dose from all natural sources estimated at 2.4 mSv. The concentration of ^{40}K is kept at a constant level in the body but has the highest part of the dose as 0.17 mSv/year. UNSCEAR

(2008) stated that natural decay series comprising of ^{238}U , ^{234}U , ^{226}Ra , ^{210}Po , ^{230}Th , ^{232}Th , and ^{224}Ra contribute significantly to the ingested dose received from the consumption of food and water. The calculation of the committed effective dose was done based on the reference concentration values of natural radionuclides in water and the reference annual intake of water by infants of age less than one (1) year to adults of age greater than 17 years listed in table (3). An age-weighted mean annual dose of $13\mu\text{Sv}$ was obtained as a result of water consumption which is approximately 5% of the total annual ingested dose of 0.29mSv . WHO guidelines for drinking water quality integrate the recommendations of the International Commission on Radiological Protection and agreed on 0.1mSv/year as the reference committed effective dose for water consumption. Accurate calculation of the committed effective dose depends on two factors such as the assumed annual water consumption and the available data obtained from the activity concentration of the radionuclides with the highest dose for water consumption. WHO guidelines and USEPA regulation agreed on assumed intake of two litres per day (2 l day^{-1}) which would be 730 litres per year (730 l year^{-1}) for every age categories (WHO, 2008; WHO, 2011; UNSCEAR, 2000, 2008; Dinh et al., 2011).

2.8 Overview of work done in other countries, some parts of Ghana and Ketu South Municipality Volta Region, Ghana.

Previous studies done in the past years in the determination of naturally occurring radioactive materials (NORMs) in drinking water specified that individual radioactive decay has different physical and chemical characteristics, solubility, mobility and half-life compared to those of the parent radionuclides (Zapeczka and Szabo., 1986; Dinh et al.,

2011; Gilkeson et al., 1983). A study of the radioactivity in ground water from Tanke-Ilorin, Nigeria, has been carried out. Ten water samples were analyzed by gamma-ray spectroscopy to determine the ^{226}Ra and ^{228}Ra concentrations. The activity concentration values ranged from 0.81 ± 0.08 to 7.4 ± 2.2 Bq/l for ^{226}Ra and from 1.8 ± 0.3 to 5.6 ± 2.6 Bq/l for ^{228}Ra . The derived Annual Effective Dose received by the population as a result of the ingestion of ^{226}Ra was estimated to range from 0.08 ± 0.01 to 0.12 ± 0.07 mSv/y with an average of 0.39 ± 0.11 mSv/y; and ^{228}Ra range from 0.50 ± 0.32 to 1.42 ± 0.70 mSv/y with an average of 0.91 ± 0.31 mSv/y. Consequently, the Annual Effective Dose received, as a result of the combined ingestion of ^{226}Ra and ^{228}Ra , was found to range from 0.81 to 1.74 mSv/y with an average of 1.3 mSv/y in other countries. The mean contribution of both ^{226}Ra and ^{228}Ra activities to the committed effective dose from a year's consumption of drinking water in the study area is, therefore, higher than the allowable level of 1 mSv/y to the general public for prolonged exposure as recommended by ICRP; and much more than the new WHO recommended level of 0.1 mSv/y for drinking water (Nwankwo, 2013).

In Ghana, A study of the possible radiological impact of drinking water in two critical mining communities of Dumasi and Chujah at Bogoso in the Western Region of Ghana was carried out and infants less than 1 year old in Chujah using treated water were found to be exposed to 10 % more than the WHO limit of 0.1 mSv. Water samples collected from boreholes and treated water supplied by a gold mining company were analyzed for important radionuclides such as ^{238}U , ^{234}U , ^{226}Ra , ^{210}Po , ^{230}Th , ^{232}Th and ^{224}Ra , using extractive techniques in the Radio Analytical Laboratory of the South African Nuclear Energy Corporation. None of the radionuclide concentrations found exceeded the world

averages in drinking water. The $^{238}\text{U}/^{235}\text{U}$ ratios were also found to fall within those for natural environmental materials. The dose contributions of the radionuclides for different age groups were evaluated using the IAEA recommended dose conversion factors. The lifetime average dose for all the communities are lower than 0.1 mSv as recommended by WHO; however, if age group classification is considered, infants less than 1 year old in Chujah are exposed to 0.11 mSv when the treated water is used (Gbadago et al., 2011).

A study has been conducted in Aflao in the Ketu south municipality which is located in the Volta Region on the impact of naturally occurring radioactive materials (NORMs) in the environments and the public from the operational activities of Diamond Cement factory in Ghana. Both water and soil sample were collected and their activity concentrations measured using gamma spectrometry system high purity germanium detector. The annual effective dose was found to vary from 0.022 to 0.186 mSv with an average of 0.094 ± 0.041 mSv for soil samples. That of the water samples varied from 0.094 to 0.287 mSv with an average of 0.179 ± 0.080 mSv. The average value of the equivalent dose of the soil samples was found to be lower than the world average soil annual equivalent dose of 0.7 mSv (Adukpo et al., 2011). However, that work was limited to the factory area in Aflao within the Ketu South Municipality. This study covers other areas in Aflao in addition to Denu and Agbozume also in the same municipality. This study has been extended to the other towns in Aflao in addition to Denu and Agbozume. In this study, assessment of naturally occurring radionuclide contents in water in a large coverage area of the Ketu South Municipality could help in the identification of major point sources for radionuclides. The activity concentration of the water samples are measured using gamma spectrometry (high purity germanium x-ray

detector). These potential point source(s) are better understood through the various concentrations of radionuclides determined from the water sources located across large span of the Municipality.

2.9 Gamma- ray measurement

Gamma-ray spectrometry is one of the powerful non-destructive analytical tools for the measurement of the gamma emitters both qualitatively and quantitatively. Its outstanding benefit is that it allows the concurrent measurement of many radioisotopes in a bulk sample, without unnecessary time consuming radiochemical sample separation and preparation (Bochud et al., 2008; IAEA, 1989).

In terms of solid materials comprising soils and sediments the sample can often be placed into the sample holder or container after very minimal sample preparation (e.g. drying, ashing, sieving etc.) In order to ensure sample uniformity it is advisable to use the larger sample portions [IAEA, 2010]. The purpose of gamma spectrometric monitoring of environmental samples according to IAEA (2004) is to quantify the activity concentration of gamma ray emitting radioisotopes and the accompanied error analysis of the results. The technique is mostly applied to non-destructive analysis of environmental samples but it can also be conducted in destructive analysis (IAEA, 2004).

Gamma spectrometry is one of the techniques often used in the determination of several environmental radioisotopes. Simultaneous analysis of the absolute activity of

different gamma peaks in a wide energy range can be obtained and in order to compute the absolute activity, the detector full-energy peak efficiency has to be determined.

The resolution is the determining component in the ability of the gamma spectrometry system to distinguish between photons of γ -rays of the same energy.

Gamma-ray spectra are measured with modular equipment consisting of a detector, an amplifier, a pulse-height analyzer, memory, and a permanent data storage apparatus. Germanium drifted in Lithium, Ge (Li), or most recommended High Purity Germanium detectors (p-type or n-type) are used for the determination of complex gamma (γ)-ray spectra due to their excellent energy resolutions. These Ge detectors, however, are very durable and need to be cooled by liquid nitrogen which is also costly. Thallium activated Sodium-Iodide crystals, can be functional at ambient temperatures. On the other hand, their energy resolutions limit their use (HASL-300, 1997).

2.9.1 Germanium detector operational characteristics

Room-temperature operation of germanium detectors of any type is impossible in contrast to sodium iodide detectors because of the large thermally-induced leakage current that would result due to the small band gap (0.7 eV). Thus it is necessary to supply liquid nitrogen to germanium detectors to lessen the leakage current to the point that the associated noise does not spoil their excellent energy resolution. Under normal circumstances, the temperature is decreased to 77 K by means of an insulated Dewar flask where a supply of liquid nitrogen is stored in thermal contact with the detector (Knoll, 2000).

However for Germanium Lithium [Ge (Li)] detectors, the low temperature must be maintained unceasingly to control unnecessary redistribution of the drifted lithium that will rapidly take place at ambient temperature. Lithium drifting is eliminated in HPGe detectors, and they can be allowed to warm to room temperature between uses. Fabrication techniques have been designed to the point that modern detectors will withstand indefinite cycling of the temperature. This operational benefit is the major reason that HPGe detectors have supplanted Ge (Li) configurations (Knoll, 2000).

2.9.2 Calibration of Germanium Detector Systems

The calibration of the Ge system is critical to achieving credible results (ANSI, 1999). Proper calibration safeguards that gamma ray spectra are correctly clarified by means of activity concentration and the energy. Before the samples are measured the analyst has to do the following tasks (Gilmore and Hemingway, 1995):

- (i) Energy calibration which is for the identification of radionuclide;
- (ii) Peak width calibration used as a function of energy;
- (iii) Efficiency calibration which links decay rate against count rate applicable for quantification purposes. It is essential that calibration of gamma spectrometer is conducted properly before the sample can be measured. Standards are often obtained from various manufacturers (or prepared in the laboratory).

2.9.3 Energy Calibration

Energy calibration is achieved by determining energies of corresponding peaks using a standard, which may contain Co-57, Sn-113, Hg-203, Cd-109, Ce-144, Cs-137, Co-60, and Y-88. Usually the sources comprises well known peak energies of particular radioisotopes of interest which include the whole energy region showing a wide spectral range from 50 to 2000 keV over which the spectrometer is to be used. The energy calibration can either be performed manually or automatically (Gilmore and Hemingway, 1995; Luca et al., 2012). The statistics of subsequent measurements demand that adequate counts be obtained in each energy peak so that sufficient uncertainty levels are attained (ANSI, 1999).

The “energy calibration consists in the experimental determination of a function under normal conditions a first or second degree polynomial, depicting the energy dependence of the channel number in the spectrum (Luca et al., 2012).

$$E_{\gamma} = A + B * Ch + Ch^2 \dots\dots\dots (2.1)$$

Where E_{γ} is the gamma-ray energy,

Ch is the spectral channel number for the center of the peak corresponding to E_{γ} (usually the channel with the maximum number of counts),

A, B and C are constants to be determined for calibration.

2.9.4 Peak width calibration-Energy Resolution

One of the vital terms in gamma ray spectrometry is the energy resolution which is associated with the detector response. The resolution is referred to as the ability of the detector to differentiate between two radiations whose energies lie close to each other.

It is usually represented by means of the full width at the half of the maximum pulse height distribution (Bochud et al., 2008).

The resolution calibration is also called Full-Width at Half-Maximum (FWHM) Calibration which sets up a function to portray the peak width versus the spectral energy. It is an important parameter featuring the system performance in separating several photon emissions in a narrow energy range (Luca et al., 2012). Energy resolution ordinarily defined as the quotient of FWHM and the location of the peak centroid (H_o) is given by (Bochud et al., 2008; Knoll, 2000).

$$R = \frac{FWHM}{H_o} \dots\dots\dots (2.2)$$

Where:

R, H_0 Corresponds to energy resolution, peak energy respectively

$$\frac{dN}{dH}$$

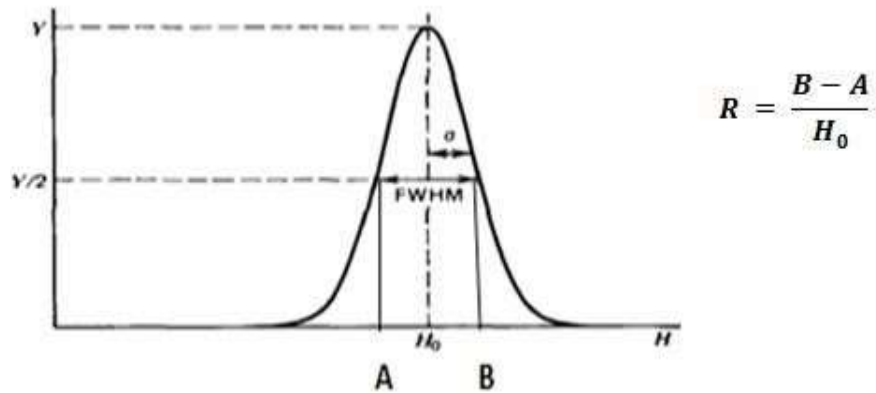


Figure 2.1: Definition of detector resolution (Knoll, 2000)

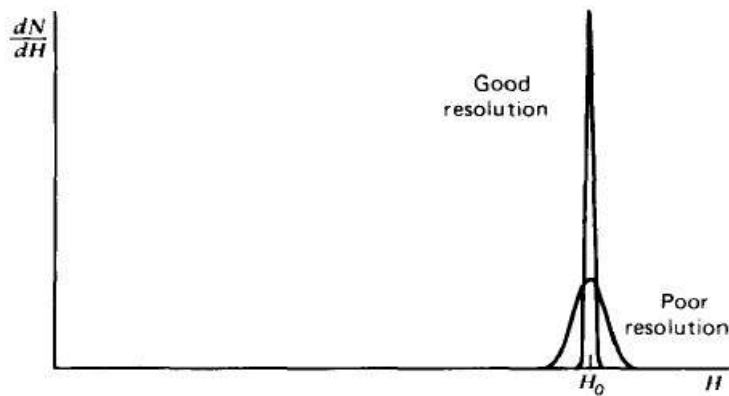


Figure 2.2 the difference between good and bad resolution.

2.9.5 Efficiency calibration

It is frequently used practice, when determining the activity of gamma emitters with HPGe detectors, to compare measurements of an unknown source with those of a calibrated source of equivalent geometry and density. The total efficiency is termed as the ratio of the number of pulses counted in the spectrum to the number of photons emitted by the source (Daraban et al., 2013). The efficiency of gamma spectrometry is not absolute, so the objective behind efficiency calibration of the system is the determination of a factor corresponding to each gamma line that normalizes their activity concentration to its absolute value (Bakr and Ebaid, 2011).

The efficiency calibration involves the calculation of the efficiency of the semiconductor detector system as a function of energy. This comprises effects from the intrinsic detector crystal, the detector-source geometry, the materials surrounding the detector and the absorption in the source matrix. The efficiency calibration is needed for each source detector combination such as disc source, Marinelli container etc. (IAEA, 2004).

The efficiency calibration using standard sources of known initial activity is a procedure intermittently performed for the HPGe detector, as in Vukanac et al., (2008); where the connection between the energy of the gamma radiation and the number of the channel is established. Upon the identification of the energy by standard sources, the efficiency value is computed taking into account the chance of disintegration for each energy. This data is required for the calibration of the detector efficiency, according to the following formula (IAEA, 2004; Daraban et al., 2013).

$$\epsilon = \frac{N}{A\gamma t_s MK} \dots\dots\dots (2.3)$$

Where:

ϵ is the efficiency at photo peak energy,

N is the number of counts;

A is the absolute/ specific activity of the standard;

γ is the emission probability of the gamma line corresponding to the peak energy;

t_s is the sample live counting time;

M is the mass [kg] of the measured standard;

K is the correction factor

$$K = \frac{1}{e^{-\lambda T_d}}$$

Where

λ is the decay constant of individual radionuclides;

and, T_d is the time between sampling and time of counting

CHAPTER THREE

METHODOLOGY

This Chapter describes the location of the study area, the sampling methods, samples preparation, the method of analysis and the calculation of naturally occurring radionuclide materials (NORMs) concentrations. The geochemical analyses were also carried out on some selected boreholes and private wells in the Ketu South Municipality.

3.1 Description of the Study Area

Ketu South is a municipality in the Volta Region situated at the south-eastern part of Ghana and its capital is Denu. The Municipality is known to be the eastern gateway to Ghana and the only district that has a frontier with Lome, the capital of the Republic of Togo (Nyarko et al., 2010). But a second major frontier has been opened at Akanu in the Ketu North District.

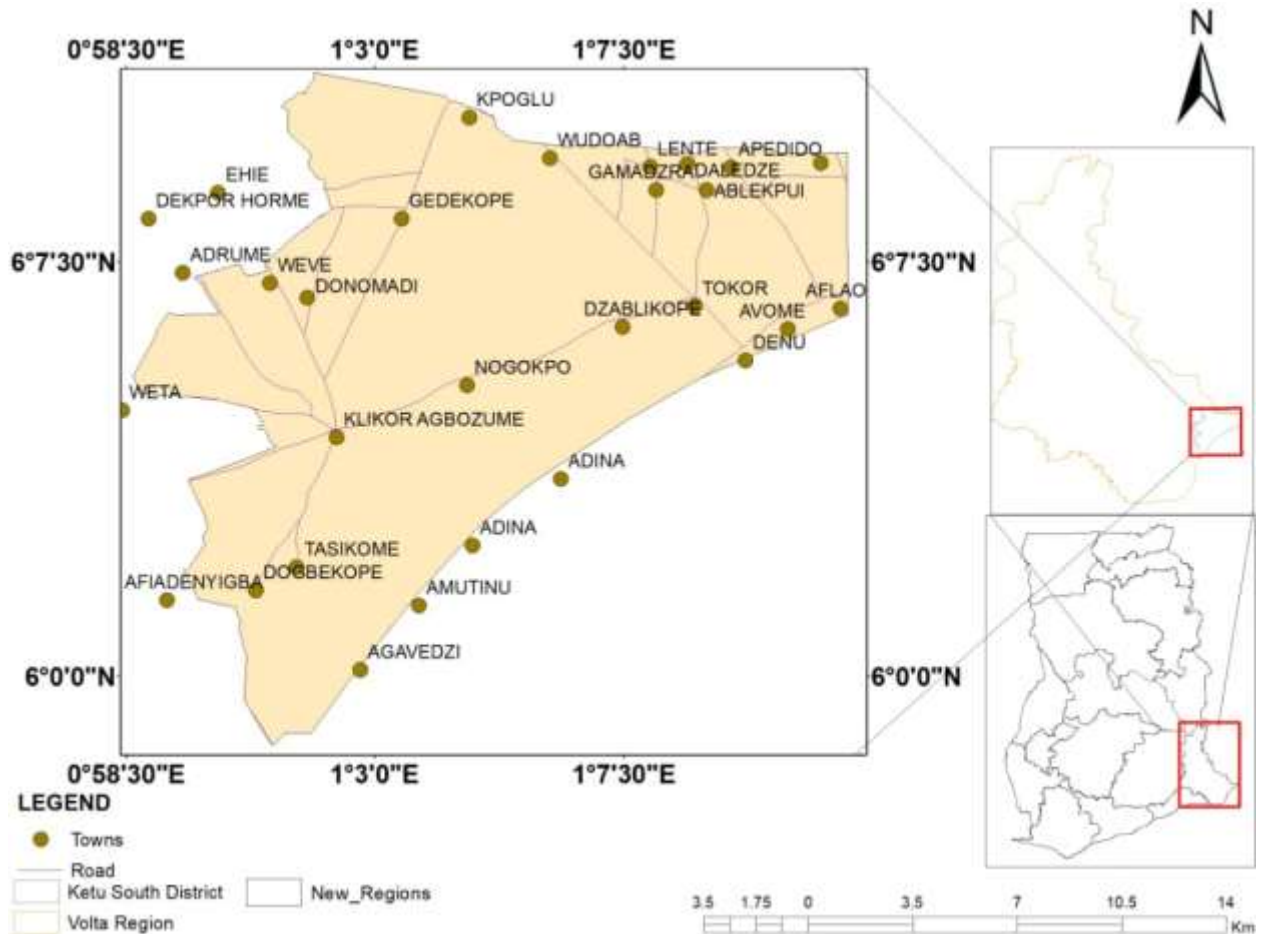


Figure 3.1: Location Map of the Ketu South Municipality

3.1.1 Location and Size of Ketu South

The study areas in the Ketu South Municipality falls within latitudes $6^{\circ} 03' \text{N}$ and $6^{\circ} 10' \text{N}$ and longitudes $1^{\circ} 6' \text{E}$ and $1^{\circ} 11' \text{E}$; and situated at the southeastern corner of Ghana with Denu as the capital town. The Municipality forms boundaries with Ketu North Municipality to the North, Republic of Togo at the east, Keta Municipality at the west and the Gulf of Guinea in the south, with a total land area (size) of approximately 779 square kilometres (km^2) signifying 3.8 percent of the regional land area. (Adukpo et al.,

2011; Nyarko et al., 2010) The population of the municipality stands at 160,756 with 75,648 males and 85,108 females according to 2010 population and housing census.

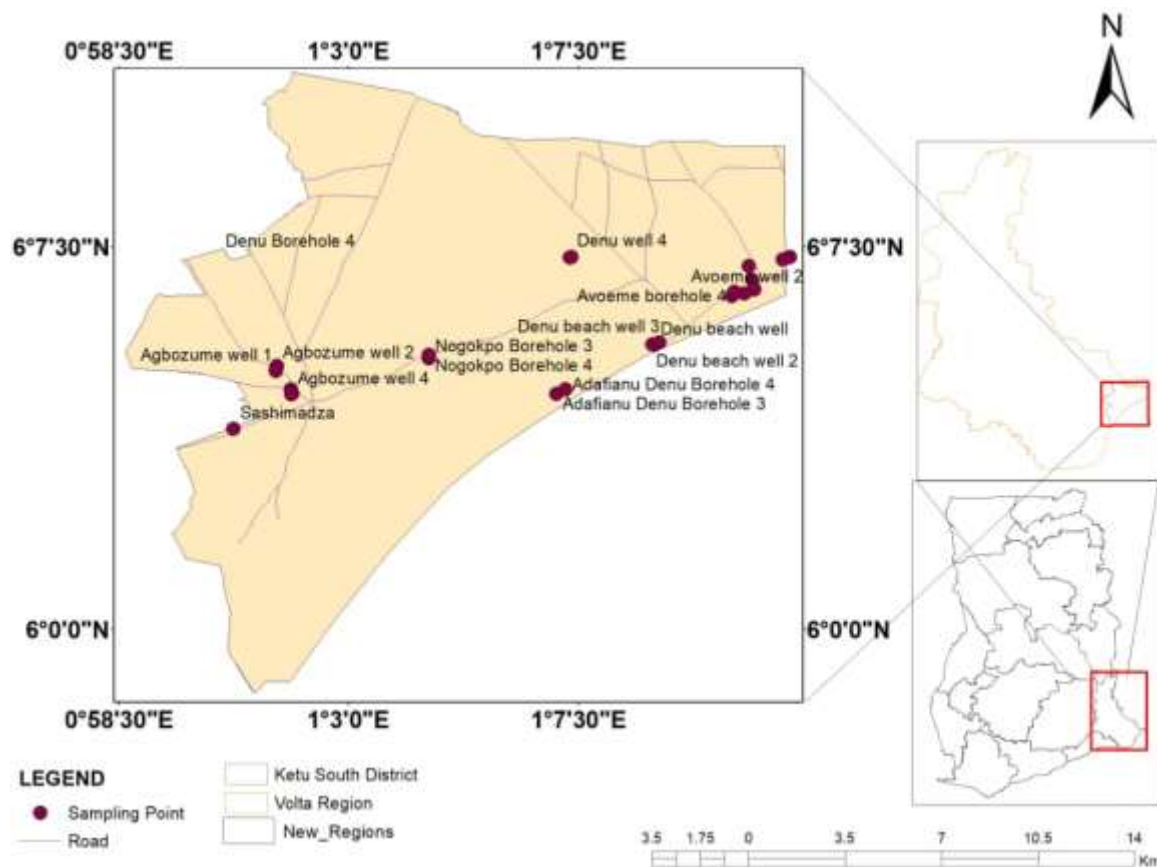


Figure 3.2: Sampling Map of Ketu South Municipality

3.1.2 Climate & Vegetation

The municipality lies within the dry coastal savanna climatic zone of the region. Its rainfall pattern is greatly influenced by the climatic zone which is low and erratic along the coastal belt of Agbozume and Aflao. The temperatures of the municipality range from 24 °C to 30 °C. The municipality has two rainfall maxima which occur from April to July and September to October with its mean annual rainfall between 850 mm along the coast

and 1,000 mm inland and its dry season is mainly the dry harmattan winds which start from December to February (Nyarko et al., 2010). The vegetation consists mainly of coastal Savannah woodland comprising of short grasses with small clumps of bushes found at the northern parts, coastal scrubs, and grassland and mangrove forests in the marshlands in the south. The low rainfall coupled with the soil type and the low rainfall causes low yields in agriculture. The soil type consist of lateritic sandy soils, tropical black clays, tropical grey earths, sodium vleisols and coastal sandy soils (Adukpo et al., 2011).

3.1.3 Geology and Soil

Ketu South Municipality consist of three main geological formations which are the Dahomenyan formation at the North consisting of Tropical Grey and Black Earths soils, the Regosolic groundwater laterites, the littoral deposit comprising of marine sands and the tertiary formation of Savannah Ochrosols for the soil type consisting of lateritic sandy soils, tropical black clays, tropical grey earths, sodium vleisols and coastal sandy soils (Adukpo et al., 2011). The deep black clay is found in and around the lagoons and also around the Denu to Agbozume stretches. The grey calcareous and acid clay are the main soil types in the central and northern belt of the Municipality. Cassava, maize and vegetables are the main crops produced due to the soil type in the area. The area under study is low-lying coastal flat and plain with highest elevation of 70 m above the mean sea level along the coast with lagoons along the southern coastal belt which are saline (Adam et al., 2016)

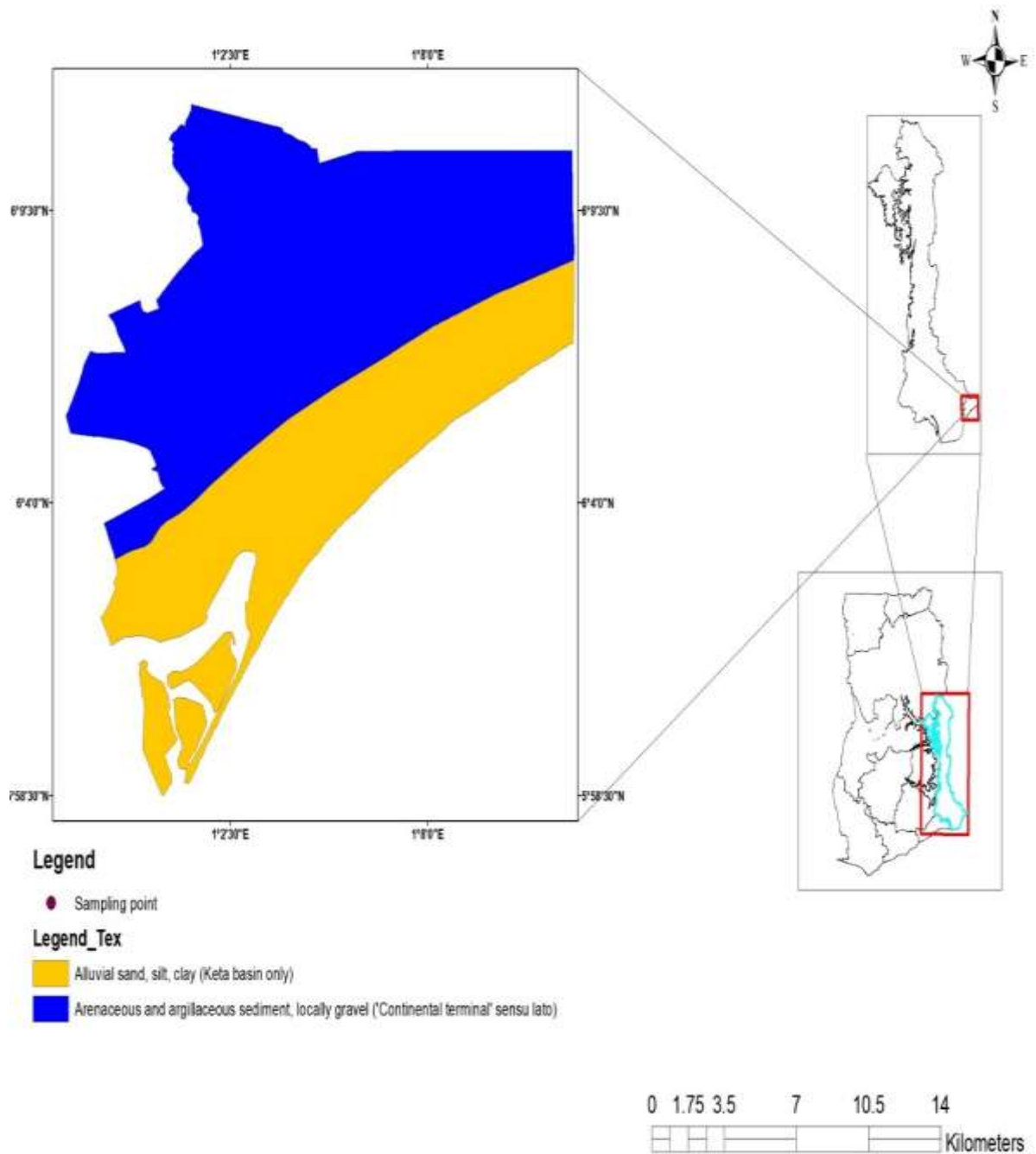


Figure 3.3: Geology Map of Ketu South Municipality

3.1.4 Hydrography & Drainage

Ketu South municipality is a low-lying area with altitudes less than 15 metres at the coast and 66 metres inland. The coastline is flat and distinct by sandbars. The drainage system is in the South direction which is controlled by several seasonal streams with 30 kilometres of lagoons and some of these lagoons join the Keta lagoon at Blekusu to the localities of Aflao which helps in aquaculture and salt mining (Nyarko et al., 2010). The municipality is made up of two major rivers which are Kplikpa and Tsiyia with one fresh water dam at Wudoba .

3.1.5 The hydrogeology of the Municipality

The Municipality under study consists of the recent and tertiary formations which comprise of the weathered Dahomeyan gneiss, the shallow unconsolidated sands and clays of lagoon, delta and littoral area to semi consolidated red continental deposits of sandy clay and gravel. It also consists of shale and sandstones which lie beneath the sediments in the coastal area. The recent deposits are located along the northern banks of the Keta lagoon and marine sands are located along the coastal littoral stretch from Aflao to Anyanui .

Aflao and Denu are situated along the coast consisting of coastal sedimentary basin in the extreme South East (SE) within the Keta basin. The Keta basin is one of the coastal sedimentary basins found at the extreme SE of Ghana adjoining Togo. The Keta basin consists of sands, shales, siltstones, clays and fossiliferous, limestones. The rocks closer to the surface have a gentle dip which is 2^0 towards SE. The rocks at the basement are referred to as the Dahomeyan formation (Kesse, 1985; Leube et al., 1986)

Groundwater occurrence in the study area is controlled by matrix flow. Borehole yields for standard size well (125 mm diameter) reaching a mean depth of 52 m is generally in the range $0.7\text{--}27.5\text{ m}^3\text{ h}^{-1}$ with a mean value of $2.7\text{ m}^3\text{ h}^{-1}$. The measured transmissivity values are generally low due to high clay content of the regolith with variation of 0.23 m^2 in the clayed regolith to $4.0\text{ m}^2\text{ h}^{-1}$ in the fissured zones (Adukpo et al., 2011). The unconsolidated sands and gravels are the main source of high groundwater recharge and the main source of drinking water in the central and south-east of Ketu South Municipality (Adams, 2016).

3.1.6 The coastal sedimentary basin

The felsic gneisses and the composite group of rocks are made up of quartz, feldspar, epidote, mica, hornblende, garnet. The mafic gneisses consist of thick series of rocks rich in ferro-magnesian minerals which are made up of dominant garnet hornblende gneiss, garnet-pyroxene gneiss, garnet-hornblende-pyroxene gneiss and few layers of hornblende and biotite schist and gneiss found at the base. Other geological formations are the Togo series, the Accraian series consisting of sandstones, grits and shales, the tertiary and recent sediments found in the southeastern part of the plain close to the estuary of the river Volta.

The Togo series is made up of quartzites, phyllites, sandstones, schists and silicified limestones (Glover et al., 2012; Kesse 1985). The felsic rocks consist of mica granites highly fractionated and rich in B, Li, F and U (Simov, 1989). Under oxidized atmospheric condition, rain enters through the fractures and pores felsic rocks transforming Uranium into its hexavalent state. Uranium dissolves as an anionic complex as $\text{UO}_2(\text{CO}_3)_n^{2-2n}$ or

$\text{UO}_2(\text{SO}_4)_n^{2-2n}$. The dissolved water containing the uranium migrates into the groundwater which may contain reducing materials such as inorganic (pyrite) or organic (humic) matters. Uranium is then reduced to insoluble U (IV).

Thorium occurs as oxide and its mineral mostly occurs as monazite (ThO_2) which is a golden brown rare earth also found in granite and gneiss. The ground water found in these basement aquifers are of good quality with pH >6.5, low salinity and total hardness but slightly higher salinity occurs in some areas. The recharges of these aquifers are mainly from rainfall (Kesse, 1986 and Leube et al., 1986).

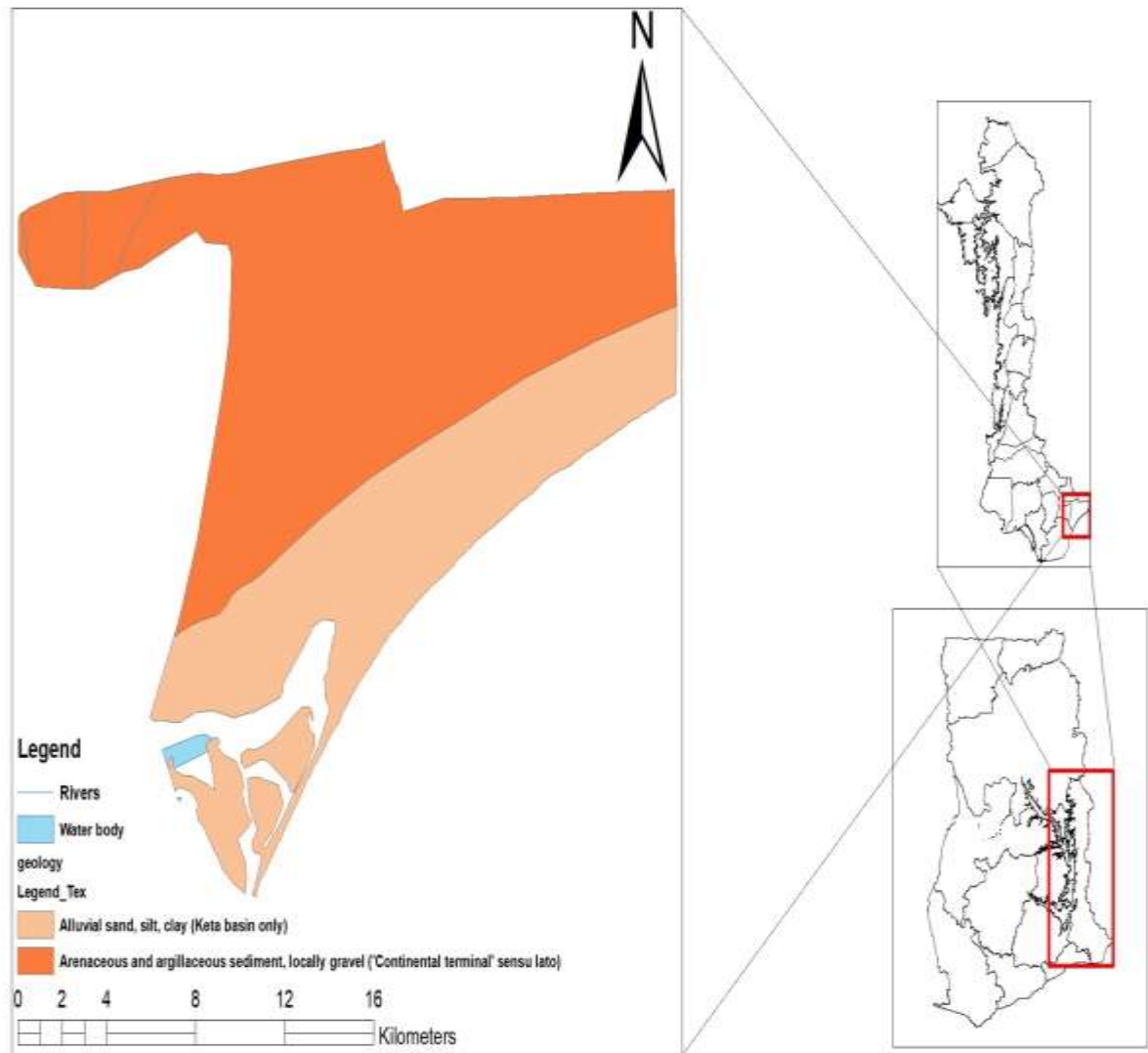


Figure 3.4: Hydrogeological Map of Ketu South Municipality

3.1.7 Socio Economic Activities in the Study Area

Cross boarder trading, farming and fishing are the major occupations in the municipality under study. The farmers produce vegetables such as shallot, leafy vegetables such as (including *ademe* and *gboma*), onion (May-September), cabbage, lettuce, tomatoes (June-September), okro, chilies (green and red peppers) and carrot along the coastal areas. They also cultivate cassava and maize at every part of the municipality in large quantities for both domestic consumption and commercial purposes. The cassava is sometimes processed into gari, cassava dough and starch biscuit locally known as Agbozume biscuit. Coconut is the largest plantation crop grown along the coast in the municipality and some coconuts are also planted on individual compounds in the hinterland. The easy accessibility of the shallow unconfined aquifer in the area makes it possible for farming activities to continue in all season's especially vegetable cultivation which takes place throughout the year through irrigation. The main types of livestock reared in the area are goats, pigs, sheep, cattle and birds such as ducks guinea fowls, domestic and poultry fowls are also produced in the area. The stretches between the sea and the extended lagoon from Blekusu to Keta make it possible for aquaculture activities and salt mining during dry season (Adams, 2016).

3.2 Sampling and Measurement

3.2.1 Collection of Samples

The sampling positions were recorded by Global Positioning System (GPS) reading. The sampling polyethylene gallons were washed and dried. Each of the 2-litre polyethylene gallons used for the random sampling of the water was washed three (3) times with some

of the water to be sampled. Each gallon was filled with the sampling water to the brim. In order to characterize the quality of water, the following parameters were measured; temperature, pH, conductivity and total dissolve solids (TDS) using portable water-analysis kit on the sampling site. After these measurements, 2 drops of 65% nitric acid was added to bring the pH to an appreciable level of 2 in order to prevent the adherence of the radionuclides to the walls of the container. The gallons were tightly covered with their lids and were labeled appropriately.

A total of 21 water samples were collected. These included, 3 boreholes and 4 well each were randomly collected from Aflao, Denu and Agbozume and placed in a thermally-insulated container (ice chest) and transported to the Ghana Atomic Energy Commission (GAEC) laboratories at Kwabenya-Accra. Some of the water samples collected were taken to the National Nuclear Research Institute laboratories for chemical analysis such as calcium magnesium and chlorides and alkalinity. The rest of the water samples were sent to the Radiation Protection Institute(RPI) laboratory for the measurement of ^{226}Ra , ^{228}Ra , ^{232}Th and ^{40}K .



Fig.3.5 sampling point; Denu Well 2



Fig 3.6 sampling point; Denu borehole1

3.2.2 Field measurement

The physical parameters such as temperature, pH, conductivity and total dissolved solids (TDS) were measured on the sampling site.

(i) Temperature and pH

A portable electronic meter consisting of pH and conductivity was calibrated using a buffer solution of pH 4.0, 7.0 and 9.0 obtained from BDH pH buffer standard tablets. Both the temperature and the pH were measured at the sampling site as soon as the sampled water was brought to the surface. The temperature was measured to prevent the water sample from gradually taking the temperature of the surrounding air.

The probe of the calibrated electronic meter consisting of both temperature and pH meter was rinsed with the sampled water and the rinsed water was discarded. The probe was immersed into the water sample and held until a constant reading was obtained. The pH

readings were recorded and the temperature was recorded in degrees Celsius (°C). This procedure was repeated for each water sample (Bartram et al., 1996).

(ii) Conductivity

The conductivity (EC) was measured at the sampling site as soon as the sampled water was brought to the surface by using a portable conductivity meter. The conductivity meter was calibrated using a standard solution of $1413\mu\text{Scm}^{-1}$

The cell containing the electrodes of the calibrated conductivity was rinsed three times with the water sample and immersed into a beaker containing the water sample. The conductivity meter was turned on and held until a constant reading was obtained. The procedure was repeated for each water sample. The conductivity value obtained was recorded.

(iii) Total dissolved solids (TDS)

The total dissolved solids were also measured on the sampling site as soon as the sampled water was brought to the surface using a portable electronic TDS meter.

The electrode of the calibrated TDS meter was rinsed with the water sample and immersed in a beaker containing the water sample. The TDS meter was turned on and held until a constant reading was obtained. The procedure was repeated for each water sample. The TDS values obtained were recorded.

3.2.3 Chemical Analysis

Chemical analysis of water samples was undertaken at the National Nuclear Research Institute laboratories. The analysis comprises of the determination of alkalinity, chlorides, calcium and magnesium.

(i) Alkalinity

Alkalinity was determined using potentiometric titration at pH range of 4.3 to 4.7. The burette was rinsed and filled with 0.02 M H₂SO₄. About 50mL of the water sample was measured into a plain conical flask followed by the addition of 3 drops of methyl orange indicator. The solution was well mixed and titrated against the titrant (0.02 M H₂SO₄). At the end point, the colour changed from yellow to orange colour (APHA, 1998).

$$\text{Alkalinity, CaCO}_3 \text{ mg/l} = \frac{A \times N \times 50,000}{V(\text{ml of sample})} \dots\dots\dots (3.1)$$

Where,

A = volume of acid used (mL)

V = volume of water sample (mL)

N = normality of standard acid used.

(ii) Chlorides (Cl⁻)

Chlorides (Cl⁻) was determined using Argentometric method. The burette was rinsed and filled with silver nitrate (AgNO₃). About 25 mL of water sample was measured into a conical flask. About 2 to 3 drops of potassium dichromate indicator was added to the

water sample. The content was titrated against the titrant (standardized silver nitrate solution).

The end point color changes from yellowish to reddish brown precipitate. The end point values were recorded. A blank titration was done by using 25 mL of distilled water with the same colour changes. The titre value of the blank is subtracted from the titre value of the water sample. A blank of 0.2 to 0.3 ml was used (APHA, 1998).

The value obtained was used in Eqn. 3.9 to obtain Cl^- in mg/L

$$(\text{Cl}^-) \text{ mg/l} = \frac{(A-B) \times N \times 35450}{V(\text{ml of sample})} \dots\dots\dots (3.2)$$

Where,

A= titre value of sample,

B = blank titre value

N= normality of AgNO_3 .

(iii) Calcium

The burette was rinsed and filled with EDTA. About 25 mL of water sample was transferred into a conical flask. 2.0 mL of 1.0 M NaOH was added followed by a few grains of Murexide indicator. The content was titrated against the titrant. The color changes from salmon to orchid purple. The average titre value is calculated and the value obtained was used in Eqn. 3.11;

$$\text{Calcium}(\text{Ca}^{2+}) \text{ mg/l} = \frac{A \times B \times 400.8}{V(\text{ml of sample})} \dots\dots\dots (3.3)$$

Where,

A = ml of EDTA titrant used

B = mg CaCO₃ which is equivalent to 1.00 ml EDTA titrant. The calcium indicator end point result was expressed as mg/L (APHA, 1998).

(iv) Total Hardness (EDTA Titrimetric Method)

The burette was rinsed and filled with EDTA. About 25mL of the water sample was measured into a conical flask. About 2.5 ml ammonia buffer solution of pH 10 was added to the water sample with 2 to 3 drops of Erichrome Black T; the mixture was titrated against the titrant (standard EDTA solution of 0.01 M). The end point colour changes from wine red to blue.

$$\text{Total Hardness (TH), CaCO}_3 \text{ mg/L} = \frac{A \times B \times 1000}{V(\text{mL of sample})} \dots\dots\dots(3.4)$$

Where,

A = Volume of EDTA titrant used

B = mg CaCO₃ which is equivalent to 1.00ml EDTA titrant at the calcium indicator end point results is expressed as mg/L (APHA,1998).

(v) Magnesium

The magnesium was calculated by subtracting the calcium value obtained from the total hardness since total hardness is equal to the sum of calcium and magnesium hardness (APHA, 1998).

$$\text{magnesium}(Mg^{2+})\text{mg/L} = \left(\frac{A \times B \times 1000}{V(\text{mL of sample})} \right) - \left(\frac{A \times B \times 400.8}{V(\text{mL of sample})} \right) \dots\dots\dots(3.5)$$

3.3 Measurement of NORMs

3.3.1 Preparation of Samples

In the Radiation Protection Institute laboratory, each of the water samples was transferred into one liter Marinelli beaker and tightly sealed with a masking tape to eliminate the background radiation and labeled prior to counting using gamma spectrometer.

3.3.2 Gamma-ray Spectrometric Measurement

The purpose of gamma spectrometry measurement of environmental samples is to determine the activity of gamma emitting radionuclides. In gamma-ray spectrometry with germanium detectors, the pulse height scale is calibrated with respect to absolute gamma-ray energy in order for the various peaks in the spectrum to be properly identified. In various normal applications, the gamma rays anticipated to appear in the spectrum are well known in advance and the corresponding peaks are readily identified by inspection. However, in other applications, where unknown gamma ray spectra may be encountered which do not provide a clear calibration of the energy scale; a separate calibration gamma-ray source is ordinarily used to supply peaks of known energy in the spectrum [Knoll, 2000]. To precisely quantify activity concentrations, correct and reliable determination of the efficiency curve is very essential. Detection efficiency is a rigorous function of the energy, spectrometer characteristics, measurement, geometry, volume and density of the sample, etc. In order to calibrate the spectrometer in a proper manner, calibration standards are prepared with matrices with identical chemical composition and density,

(i) Calibration of the Gamma Spectrometry

Prior to the measurement of the radionuclides, standard reference materials having the same geometry like the sample container donated by IAEA were utilized to calibrate to ascertain the quantification and identification of radionuclides. To achieve accurate results, Genie-2000 software was used to acquire quantitative result of the radionuclides. Gamma ray energies were used to identify individual radionuclides. To achieve a good gamma spectrum, which best describes the actual activity in Becquerel per unit litre, (Bq/L), a correct calibration was needed.

(ii) Energy calibration

Standard reference sources with known full-peak energies were used to measure the spectrum in the calibration process to show the relationship between radionuclides and channel number in the spectrometer. The standard sources were counted for a long period to detect the peak energies in the spectrum. The energy calibration was done for the 1.0L Marinelli beaker using a standard reference source provided by the International Atomic Energy Agency. The standard reference source contained different radionuclides with their corresponding energies (Gilmore & Hemingway, 1995).

The equation in relation to energy and channel number is given by the expression:

$$E_{\gamma} = B_0 + B_1 CN \quad \dots\dots\dots (3.6)$$

Where, B_0 and B_1 are calibration constants,

E_γ is the energy and

CN is the number of channels for a given radionuclide.

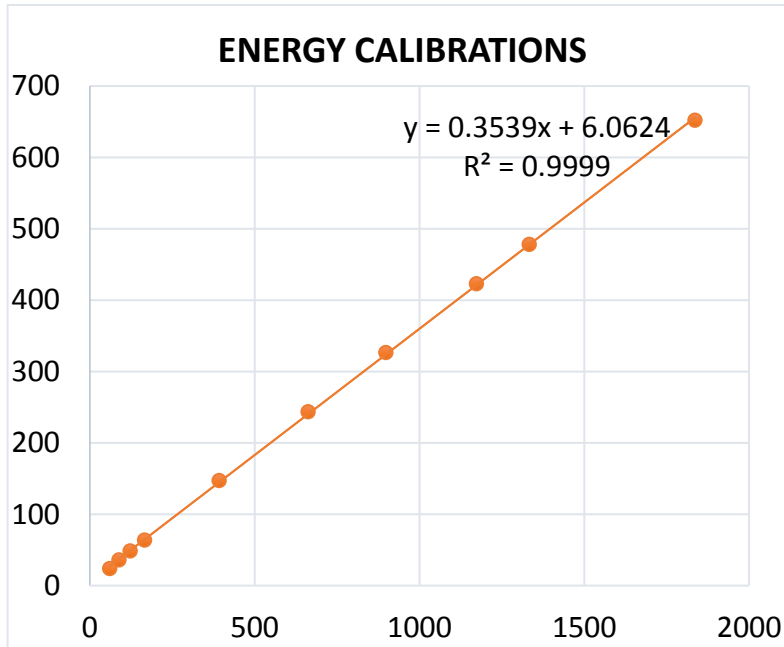


Figure 3.7: Energy Calibration Curve.

The expression for the energy calibration is represented by the relationship below:

$$E_\gamma = 0.3539CN + 6.0624$$

Where 0.3539 and 6.0624 are the calibration constants

(iii) Efficiency calibration

The efficiency calibrations were performed by counting a standard reference solution of known activities with well-defined energies in the energy range of 60-2000KeV. The net count rates were investigated for all the energies. The efficiency was matched to the activity of the standard and count rate by the expression:

$$\mathcal{E}(E_{\gamma}) = \frac{N}{A \cdot P \cdot t_c} \dots\dots\dots (3.7)$$

Where,

P is the gamma emission probability,

t_c is the counting time, A is the activity and

N represents full energy peak net count which maps up to the various gamma photons and having their energy E_γ and gamma emission probability P which is constant for all.

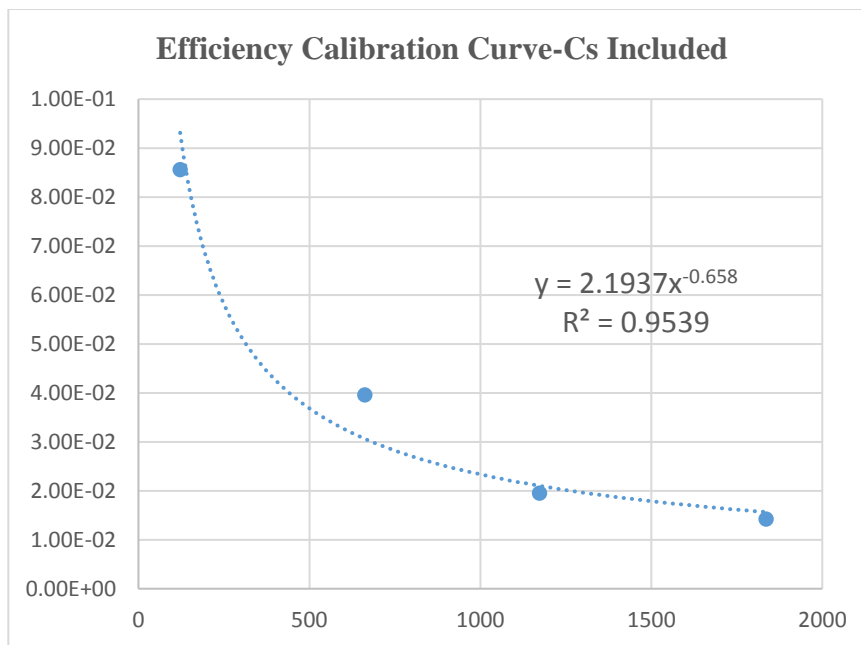
The efficiency matches energy by the expression:

$$\ln \mathcal{E}(E_{\gamma}) = a_0 + a_1(\ln E_{\gamma})^1 + a_2(\ln E_{\gamma})^2 \dots\dots\dots 3.8)$$

Where,

a₀, a₁, a₂, are calibration constants for a given geometry and the other symbols have the usual meaning given earlier in the passage. The following expression was obtained from efficiency calibration curve.

$$\ln \mathcal{E} = 0.4853 - 0.66161 \ln E_{\gamma} \dots\dots\dots (3.9)$$



$$L_{NE} = -2.34 - 2.14L_N$$

For $E_\gamma > 100$ keV

Figure 3.8: Efficiency Calibration

Nuclides	Energy (kev)	Net Area	P_γ	T_c	A_{std} (Bq)	E_f
Am-241	60	3250442	0.359	36000	3414.412	0.07366
Cd-109	88	471958	0.0361	36000	8701.768	0.041734
Ce-139	166	90995	0.8	36000	92.79025	0.03405
Co-57	122	532170	0.856	36000	201.6356	0.085646
	136.4743	36643.95	0.1068	36000	212.6916	0.04481
Co-60	1173	1999427	0.999736	36000	2842.388	0.019545
	1333	1814652	0.999856	36000	2842.388	0.017737
Cs-137	662	3353355	0.851	36000	2764.502	0.039594
Sn-113	392	192278	0.64	36000	213.61	0.039068
Y-88	898	440832	0.937	36000	383.0651	0.034116
	1836	194485	0.992	36000	383.0651	0.014217

Table 3.1: Peak Position for Energy and Efficiency Calibration

(iv) Sample Measurement

After the energy and efficiency calibrations were carried out, then the samples were counted and spectrum analyzed. Following the general principles of quantitative analysis in chemistry, each sample was moved to the specimen container and put in the same way as was done in the course of system calibration. Each sample was counted for 36,000 seconds to obtain a γ -ray spectrum which would meet the minimum admissible counting uncertainty [HASL-300, 1997].

(v) Background Measurement

Six clean Marinelli beakers were filled with distilled water and counted for 36,000 secs in the same geometry as the samples. The spectral background was used to investigate the measured isotopes and minimum detectable activities of ^{226}Ra , ^{228}Ra , ^{232}Th , and ^{40}K .

3.3.3 Evaluation of Gamma Spectrum

(i) Determination of activity concentration of NORMs in water

The activity concentration of ^{226}Ra , ^{228}Ra , ^{232}Th and ^{40}K were calculated using the following equation [Darko et al., 2010]

Thus,

$$A_{sp} = \frac{N_{sam} \exp(\lambda T_d)}{P_E * \epsilon(E) * T_c * V} \dots\dots\dots (3. 10)$$

Where,

N_{sam}	=	net counts of the radionuclide in the sample,
P_E	=	gamma ray emission probability (gamma yield),
ϵ	=	total counting efficiency of the detector system,
T_d	=	Delay time between sampling and counting,
$\exp(\lambda T_d)$	=	Correction factor between sampling and counting,
T_c	=	sample counting time.
M_{sam}	=	mass of sample (kg) or volume (L)

(ii) The Annual Committed Effective Dose of Individual Due to Drinking Water Injection

The Annual Committed Effective Dose was determined from the activity concentration of the radionuclides by using the Annual Water Consumption Rate of Adults of 730 in L/year which would be estimated by multiplying the number of water consumption per day (2L/day) by 365 days. (IAEA, 1996; ICRP 1995; Dinh et al., 2011; Gbadago et al., 2011).

The dose conversion factors of the radionuclides from the BSS and IAEA as shown in table 3.2 and table 3.3 (IAEA, 1996; Gbadago et al., 2011).

Table3.2: Water Consumption (Wc) in litres per annum for different age groups (IAEA, 1996)

Age group	< 1year	1-2years	2-7years	7-12years	12-17years	>17years
Wc	200	260	300	350	600	730

Table 3.3: Dose Conversion Factors, E (g), for ingestion by various age groups of the public, in Sv/Bq (IAEA, 1996)

Radionuclide	< 1year	1-2years	2-7years	7-12years	12-17years	>17years
	E (g)	E (g)	E (g)	E (g)	E (g)	E (g)
²³⁸ U	3.4E-07	1.2E-07	8.0E-08	6.8E-08	6.7E-08	4.5E-08
²³⁴ Th	4.0E-08	2.5E-08	1.3E-08	7.4E-09	4.2E-09	3.4E-09
²³⁴ U	3.7E-07	1.3E-07	8.8E-08	7.4E-08	7.4E-08	4.9E-08
²³⁰ Th	4.1E-06	4.1E-07	3.1E-07	2.4E-07	2.2E-07	2.1E-07
²²⁶ Ra	4.7E-06	9.6E-07	6.2E-07	8.0E-07	1.5E-06	2.8E-07
²²⁸ Ra	3.0E-05	5.7E-06	3.4E-06	3.9E-07	5.3E-06	6.9E-07
²³² Th	4.6E-06	4.5E-07	3.5E-07	2.9E-07	2.5E-07	2.3E-07
⁴⁰ K	6.2E-08	4.2E-08	2.1E-08	1.3E-08	7.6E-09	6.2E-09

The total dose (Annual Committed Effective Dose) D in $mSv\ y^{-1}$ to an individual was estimated from the equation (IAEA, 1996; Gbadago et al., 2011):

$$D = W_c C E_{(g)} \dots\dots\dots (3.11)$$

D is the annual dose in $mSv\ y^{-1}$,

W_c being the water consumption per annum for each age group,

C is the specific radionuclide concentration of the decay chain in mBq/l and

$E(g)$ is the specific radionuclide ingestion dose convention factor.

(iii) Calculation of cancer Risk from Water Injection

The risk of exposure to the inhabitants was calculated by establishing a linear correlation between dose and risk; and therefore double dose would lead to double risk for several years. It is assumed by the international bodies that the relationship is linear for low doses which reduce to zero referred to as linear–no threshold or LNT hypothesis (Nguele et al., 2013). The fatal risk factor for cancer is estimated to be $0.05\ Sv^{-1}$ as per ICRP 60. For the risk factor, the possibility of an individual dying of cancer rises by 5% for a total dose of 1 Sv absorbed during one's lifetime. The estimated Average annual committed effective dose D (Sv/y) of the water samples were used to calculate the cancer risk for an adult using the equation (Qureshi et al., 2014; AL-Alawy et al., 2018 and ICRP 2012)

$$\text{Cancer Risk} = D(\text{Sv/y}) \times \text{LE} \times \text{RF} (\text{Sv}^{-1}) \dots \dots \dots (3. 12)$$

Where,

D (Sv/y) = mean annual committed effective dose

LE = Life expectancy(66years)

RF = Fatal Risk factor per sievert (0.05) as per ICRP 60,

CHAPTER FOUR

RESULTS AND DISCUSSIONS

The main objective of this research work are to assess the concentration of naturally occurring radionuclides in domestic water used by the people of Aflao, Denu and Agbozume-Klikor Communities of Ketu South Municipality in order to estimate the annual effective doses as a result of water consumption. The physico-chemical parameters were also measured to study their influence on the radionuclide concentrations. In section 4.1, the activity concentrations of ^{226}Ra , ^{228}Ra , ^{232}Th and ^{40}K and the corresponding physical parameters (temperature, pH, conductivity and total dissolved solids) are presented in Tables 4.1.1 to 4.1.3. Figures 4.1.4 to 4.1.6 compare the radionuclide activity concentrations with the chemical parameters (magnesium, calcium chloride and alkalinity) in the domestic water collected from the various locations in the three communities. The annual committed effective dose for various age groups was estimated in Section 4.2. The risk associated with the exposure was also evaluated in Section 4.3.

4.1 Radionuclides, Physical and Chemical Parameters

Generally, the results obtained for the physical parameters (Tables 4.1.1, 4.1.2 and 4.1.3) showed that the electrical conductivity and TDS recorded relatively high values for Aflao and Denu compared to Agbozume-Klikor. According to Vengosh (2003), salinity increases with conductivity and total dissolved solids. This might be the reason for the high salinity of the domestic water in these localities. pH values recorded are generally within the alkaline zone. There are no significant temperature variations in the sampling

locations. Generally, no significant variations of radionuclide concentrations with the physical parameters.

^{238}U -series, ^{232}Th -series and ^{40}K are part of the matrix of the underlying rock formations of the area. In all the localities (Tables 4.1.1 to 4.1.3), the mean concentration of these radionuclides varies in this order, $^{40}\text{K} > ^{226}\text{Ra} > ^{228}\text{Ra} > ^{232}\text{Th}$. The concentrations were found in the following ranges in Bq/ℓ, Aflao: ^{40}K (3.4 - 17.5) $> ^{226}\text{Ra}$ (1.6 - 8) $> ^{228}\text{Ra}$ (0.001 - 5.5) $> ^{232}\text{Th}$ (0.3 - 0.95); Denu: ^{40}K (4.5 - 7.5) $> ^{226}\text{Ra}$ (0.4 - 9.3) $> ^{228}\text{Ra}$ ($> 0.001 - 5.5$) $> ^{232}\text{Th}$ (0.3 - 0.95); and Agbozume-Klikor: ^{40}K (4.5 - 7.5) $> ^{226}\text{Ra}$ (4 - 9.3) $> ^{228}\text{Ra} > ^{232}\text{Th}$ (0.3 - 0.95). However, ^{40}K is generally not considered in the standards (IAEA-BSS, 1996), therefore, the radionuclides of much concern in the domestic water of the municipality are: $^{226}\text{Ra} > ^{228}\text{Ra} > ^{232}\text{Th}$. Thorium isotopes were detected in all the measurements however, their contribution to the radioactivity in water is negligible due to their high insolubility (Gbadago, 2011). The ^{232}Th radionuclides are essentially insoluble in the reservoir fluids, and therefore immobile. This might have contributed to the low concentrations of ^{232}Th recorded. However, the radium isotopes ^{226}Ra , and ^{228}Ra which are daughters of ^{238}U and ^{232}Th respectively, are somehow soluble in water and are therefore mobile.

High exposure to radium -226 could cause anaemia, eye cataracts, broken teeth, and reduced bone growth. Radium -226 can also affect the respiratory tract. This is because, ^{218}Po which is progeny of radon-222 and when ingested can affect the respiratory track and other tissues and organ in the body (Kpeglo et al., 2011; Aslam et al., 2012 and Özdiş et al.2017)

According to the World Health Organization (WHO, 2004) standards for drinking water, the concentration of these radionuclides should not exceed a specified limit of $^{226}\text{Ra}/^{228}\text{Ra} = 1 \text{ Bq/l}$, $^{232}\text{Th} = 1 \text{ Bq/l}$ and $^{238}\text{U} = 10 \text{ Bq/l}$. From the results obtained, Aflao, Table 4.1.1 (Aflao Second Lowcost Well 1, Water Works BH 3, and Lowcost BH 1 and Well 5) recorded significant values above that of the WHO (WHO, 2004). Clearly, this calls for the examination of the human activities and geology that might be responsible. The Aflao Second Lowcost Well 1, Water Works BH 3, Lowcost BH 1 and BH 2 are within 2 km radius from a cement producing factory (The Diamond cement) and the Gulf of Guinea. Other human activities are vegetable farming in which phosphate fertilizers are applied. The Wells are generally opened, and this may receive airborne particulates emanating from the cement production. The geology of the municipality is generally sedimentary, which are known to contain lower levels of radionuclides (Gbadago, 2010). Similarly, significant values were recorded at Denu – Tokor BH 2 and Adafienu – Denu BH 3, Table 4.1.3. These locations are within 5 – 7 km radius from the cement factory; however farming practices such as vegetable production are very prominent.

Table 4.1.1 Physical parameters and Radionuclides in Bq/l, Aflao

Sampling Points	Radionuclides(Bq/l)				Physical Parameters			
	²²⁶ Ra	²²⁸ Ra	²³² Th	⁴⁰ K	pH	Elec. Cond. μS/cm	Temp. °C	TDS mg/L
A SL W 1	5.85±1.9	2.76 ±1.07	2.88±0.2	17.98±2.27	7.4	1090	28.1	547
B9 - AW 2	0.46 ± 0.10	0.01 ±0.001	0.41 ± 0.05	3.80 ±0.40	7.5	1530	28	765
A W3	5.24±1.9	0.81± 0.08	0.14 ± 0.02	12.23± 2.56	7.8	702	27.8	352
A S L BH I	5.85 ±1.5	2.76 ± 0.14	0.28 ± 0.03	18.00 ±0.34	7.7	1357	27.8	679
ASL BH2	0.37 ± 0.11	0.52 ±0.60	0.52±0.04	5.83 ±1.5	7.7	931	27.8	466
AWW BH3	2.86 ± 0.92	2.69 ±1.18	2.81± 0.30	17.90 ± 3.58	8.0	1009	28	502
MEAN	3.44±1.07	1.59±0.51	1.17±0.11	17.98±1.78	7.4-8.0	702-1530	27.8-28.1	352-765

Table 4.1.2 Physical parameters and Radionuclides in Bq/l, Denu

Sampling Points	Radionuclides				Physical Parameters			
	²²⁶ Ra Bq/l	²²⁸ Ra Bq/l	²³² Th Bq/l	⁴⁰ K Bq/l	pH	Elec. Cond. μS/cm	Temp. °C	TDS mg/L
DW1	1.12±0.25	0.52±1.05	0.80±0.09	6.04±1.33	7.8	1935	27.8	971
D W 2	0.05±0.01	0.02 ±0.003	0.04± 0.008	3.65 ±0.80	6.0	842	28.2	423
D BH 1	0.69 ±0.09	0.24 ±0.03	0.67 ±0.08	4.86±0.97	8.7	3643	28	1322
DETBH2	5.80 ±1.34	3.69 ±0.85	2.19±0.31	5.82± 1.22	6.5	635	28/0	319
ADBH3	2.69±1.55	1.38±0.30	7.68±1.50	8.98± 1.79	8.0	897	28.0	450
T -D BH4	0.50±0.04	0.54±0.07	1.56±0.20	8.98± 1.08	8.0	5050	28.3	252
MEAN	1.97±0.60	1.06±0.38	2.16±0.36	6.38±1.20	6.0-8.7	635-5050	27.8-28.3	252-1322

Table 4.1.3 Physical parameters and Radionuclides in Bq/ℓ, Agbozume-Klikor

Sampling Points	Radionuclides(Bq/ℓ)				Physical Parameters			
	²²⁶ Ra	²²⁸ Ra	²³² Th	⁴⁰ K	pH	Elec.Cond. μS/cm	Temp. °C	TDS mg/L
AKW1	0.62±0.15	0.07±0.01	0.54±0.06	1.21±0.20	8.0	1270	27.8	635
A KW2	0.30±0.05	0.06±0.07	0.27±0.06	1.40±0.10	6.5	954	27.9	478
AK W 3	0.57±0.15	0.39±0.05	0.02±0.01	2.42±0.40	6.5	604	28.0	304
A K W 4	0.56±0.08	0.02±0.003	0.45±0.09	4.52±0.46	6.6	2679	28.0	1840
A K BH1	0.45 ±0.11	0.11±0.02	0.11±0.02	2.54±0.41	6.3	663	27.8	332
SBH5	0.69±0.17	0.06±0.009	0.07±0.01	1.09±0.13	8.13	919	25.0	460
MEAN	0.70±0.12	0.12±0.03	0.65±0.10	2.20±0.28	6.3-8.13	604-2679	25-28	304-1840

The concentrations of free SO_4^{2-} and CO_3^{2-}/HCO_3^- in water can serve to indicate a more or less appropriate environment for the local retention of radium and uranium isotopes on sediments. For instance, a higher concentration of free sulphate in the water means a lower concentration of Ra and thus greater immobilization on the sediments, probably by co-precipitation of Ra with $CaSO_4$. Similarly, higher concentrations of CO_3^{2-}/HCO_3^- can also enhance the retention of Ra, on the sediments, but at the same time improve markedly the mobilization of uranium via the formation of stable complexes that keep the uranium isotopes dissolved (Gbadago, 2010).

The result obtained for the Chemical parameters (figure 4.1.4, 4.1.5 and 4.1.6) showed that for Aflao; Wells ASLW1, AW3 and Boreholes ASLBH1, AWWBH3 seemed to contain more $^{226}\text{Ra}/^{228}\text{Ra}$ than Ca^{2+}/Mg^{2+} , a possible indication of higher concentrations

of CO_3^{2-}/HCO_3^- which seemed to have improved markedly the dissolution of radium in the water. However, in Well B9-AW2 and Borehole ASLBH2 of Aflao, Ca^{2+}/Mg^{2+} contents recorded higher values than the $^{226}Ra/^{228}Ra$, a possible indication that there was relatively greater immobilization of Ra on the sediments by co-precipitation with the sulphates. Similar trends were repeated in the Denu and Agbozume-Klikor Wells and Boreholes. The higher values of Cl^- might be attributed to the proximity of the municipality to the sea and the Keta lagoon.

Generally, the radionuclide values recorded for Agbozume – Klikor are significantly lower than that obtained for Aflao and Denu. Similarly, the Cl^- , Ca^{2+} and Mg^{2+} values obtained though significant are lower than that for Aflao and Denu. Agbozume – Klikor is about 20 km away from Aflao and 15 km away from Denu. The influence of the Cement factory, the sea and lagoon may not be pronounced. Also, vegetable farming activities are also on the lower side. However, the geology of the three localities (Aflao, Denu and Agbozume) is the same. Thus, the factors responsible for the relatively high values of ^{226}Ra obtained for Aflao and part of Denu might be attributed largely to human activities such as the cement factory operation and farming activities in these locations.

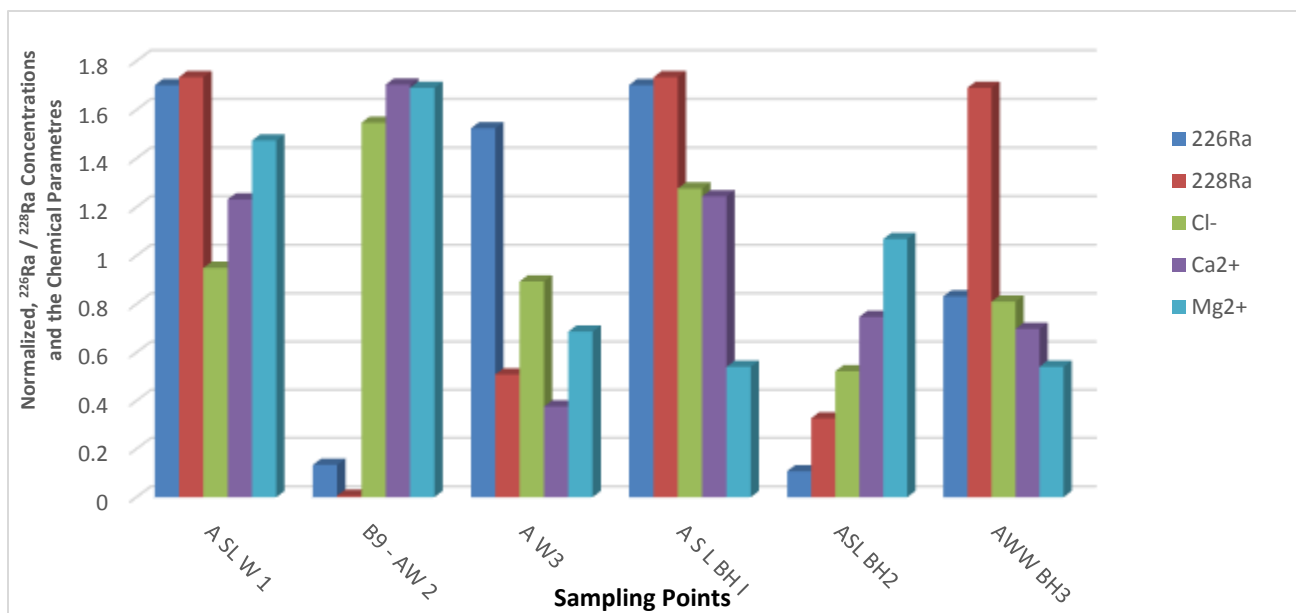


Figure 4.1.4 Comparison of the Normalized values of ^{226}Ra / ^{228}Ra activity concentrations and the chemical parameters (Cl⁻, Ca²⁺ and Mg²⁺), Aflao

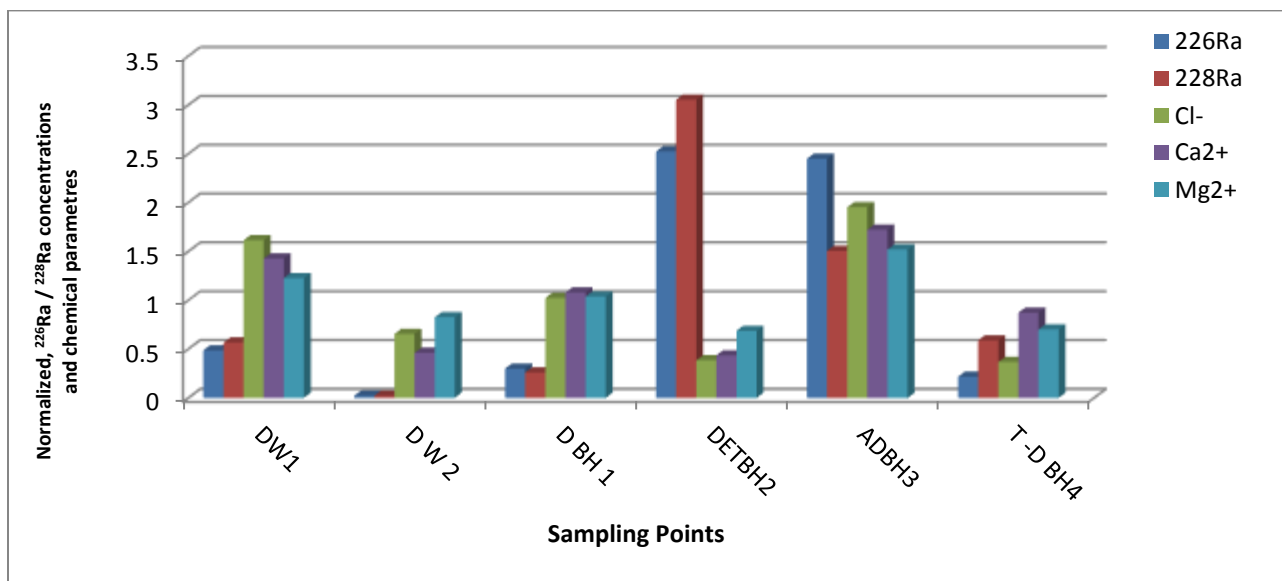


Figure 4.1.5 Comparison of the Normalized values of ^{226}Ra / ^{228}Ra activity concentrations and the chemical parameters (Cl⁻, Ca²⁺ and Mg²⁺), Denu

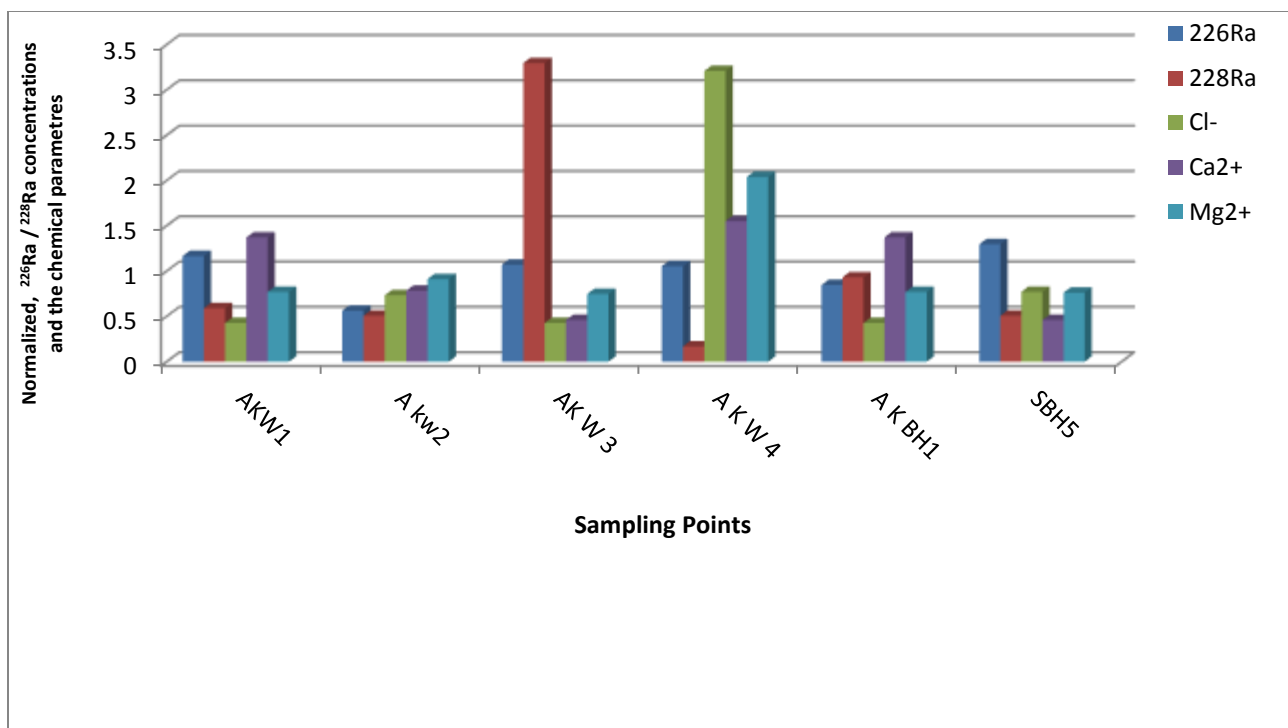


Figure 4.1.6 Comparison of the Normalized values of ^{226}Ra / ^{228}Ra activity concentrations and the chemical parameters (Cl^- , Ca^{2+} and Mg^{2+}), Agbozume-Klikor

4.2 The Annual Committed Effective Dose for Various Age Groups

As stated, the contribution of Thorium to the radioactivity of water is negligible due to their high insolubility and also, that of ^{40}K is excluded from the standards. Clearly, any possible radiological impact as a result of usage of water in these localities might likely come from ^{226}Ra , which has recorded relatively significant concentrations. (Figure 4.2.1 to 4.2.3) show the mean annual dose for the individual age groups in the Ketu South localities as a result of water consumption. The estimated total equivalent doses for the various age groups of the Municipality (Aflao, Denu and Agbozume) as a result of water consumption from Wells and Boreholes are shown in (figure 4.2.1 to 4.2.3). For the Aflao Community, the highest doses range from 1.64 to 5.50 mSv/a. The highest doses

for Denu also range from 1.62 to 5.45 mSv/a and that of Agbozume ranges from 0.01 to 0.58 mSv/a. The WHO (2004) recommended limit for quality water is 0.1 mSv/a. This suggests that the water quality in the Wells of Aflao Second Low-cost, and Aflao Well 5 do not meet the WHO reference limit, however, Aflao Beat-9, (figure 4.2.1) generally seemed to be nearer to the reference limit but, not good for infants < 1a. Similarly, the Aflao Boreholes, (figure 4.2.1) do not generally meet the WHO standards. In Denu, (figure 4.2.2), Well 1 does not meet the WHO standards but Well 2 was found to be largely within the limit, whilst the Boreholes generally do not meet the WHO reference limit.

Agbozume Klikor Wells, (figure 4.2.3), on the average recorded slightly higher doses than the allowable limits especially for infants at age <1a. Similarly for Agbozume Boreholes (figure 4.2.3), the doses recorded were above the world allowable limits (0.1 mSv/a). Thus the trends are similar for the Wells and Boreholes respectively in the Municipality. The Wells in the Municipality (figure 4.2.1, 4.2.2 and 4.2.3) have generally recorded doses lower than Boreholes. This difference may be due to the varying depths. The Wells are generally shallow with depths ranging from 15 m to 30 m compared to the Boreholes which are deeper with a mean depth of 52 m in the range 0.7-27.5 m³ h⁻¹ with a mean value of 2.7 m³ h⁻¹.

The Boreholes are possibly closer to the geological rocks than the Wells. Thus water from the Boreholes have higher chances of interaction with the rocks than the Wells. Interaction with these geological materials increases the possibility of leaching the radionuclides into the water.

The annual effective dose of ^{226}Ra , for the age groups (<1a,1-2a,2-7a,7-12a,12-17a and >17a and the sampling points are plotted in figure 4.2.1,4.2.2 and 4.2.3.

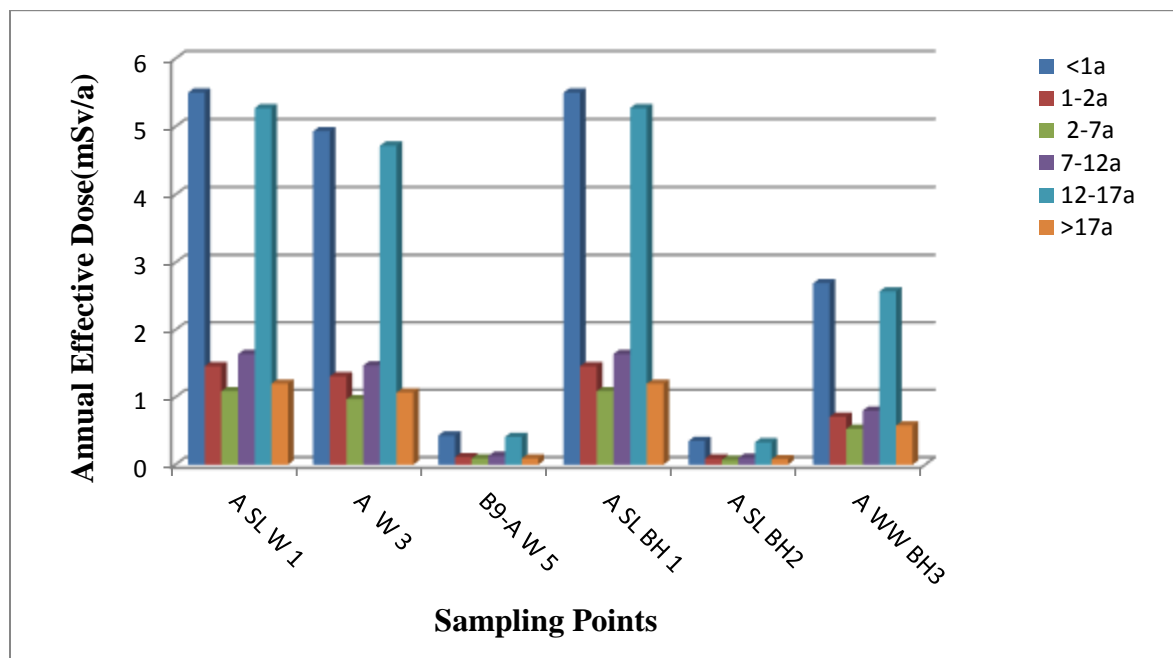


Figure 4.2.1 A graph of Annual Effective Dose of ^{226}Ra for different age groups, Aflao

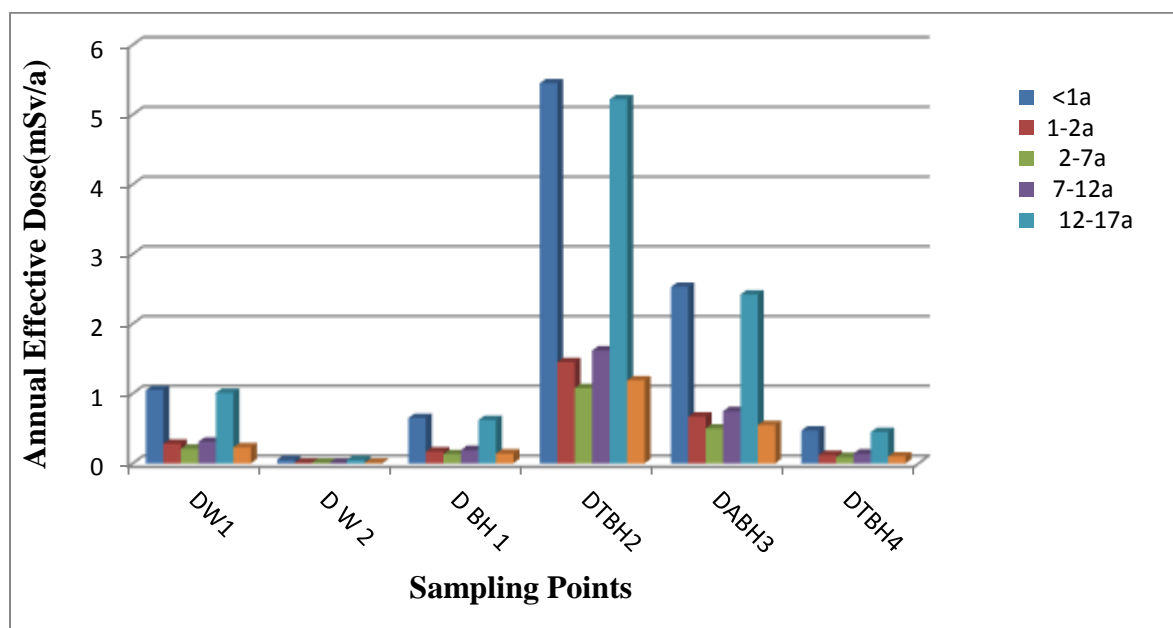


Figure 4.2.2 A graph of Annual Effective Dose of ^{226}Ra for different age groups, Denu

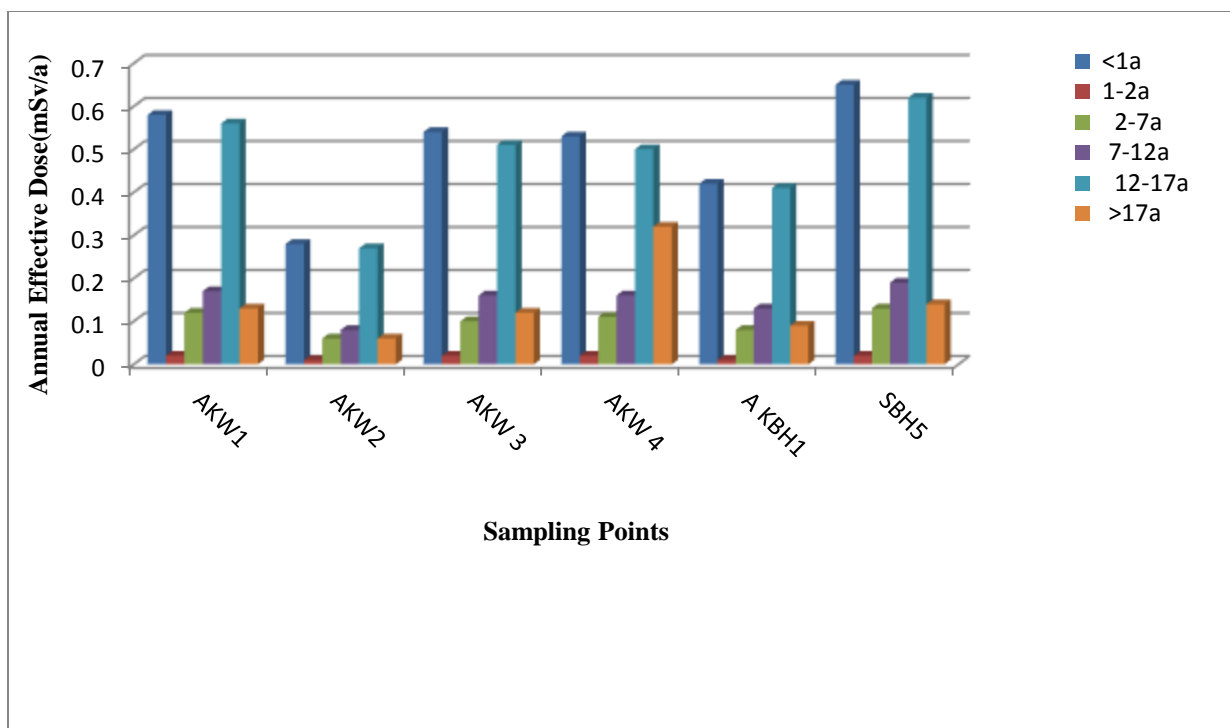


Figure 4.2.3 A graph of Annual Effective Dose of ^{226}Ra for different age groups, Agbozume-Klikor

4.3 Excess Lifetime Risk (*ELCR*) assessment

The mean Annual Committed Effective Dose(D) due to adults'water ingestion was estimated to be 0.70, 0.37 and 0.14 mSv for Aflao, Denu and Agbozume-Klikor respectively. Base on these values, a life expectancy of 66 years (LE) in the three communities and a fatal risk factor of 0.05 Sv^{-1} (RF) as per ICRP-60. The excess lifetime risk were estimated to be 2.31×10^{-3} , 1.22×10^{-3} and 0.46×10^{-3} respectively. The values obtained for Aflao is slightly higher than the world's average value of 1.45×10^{-3} while values obtained for Denu and Agbozume are within the range (Qureshi et al., 2014; AL-Alawy et al., 2018 and ICRP 2012)

CHAPTER FIVE

CONCLUSION

Naturally occurring radionuclides (^{226}Ra , ^{228}Ra , ^{232}Th and ^{40}K) in the domestic water from hand dug wells and few mechanized boreholes used by the people of Aflao, Denu and Agbozume -Klikor communities of Ketu South Municipality was measured using gamma spectrometry. The annual effective dose resulting from the consumption of water was also estimated. The physico-chemical parameters such as pH, temperature, TDS, conductivity, Ca^{2+} , Mg^{2+} , alkalinity and Cl^- were measured using portable water kits analyser and titrimetric method.

Generally, the concentrations of the radionuclides measured in the Wells and Boreholes exceeded the maximum allowable World limits of 1 Bq/l for $^{226}\text{Ra}/^{228}\text{Ra}$ and ^{232}Th . However, due to the high insolubility of thorium isotopes, their contribution to radioactivity in water is negligible. Also, ^{40}K is generally not considered in the standards. The radium isotopes ^{226}Ra and ^{228}Ra which are daughters of ^{238}U and ^{232}Th respectively are somehow soluble in water and are therefore mobile and of radiological concern. Thus any possible radiological impact as a result of usage of water in these localities might likely come from ^{226}Ra , which has recorded relatively significant concentrations. The Wells in the Municipality have generally recorded doses lower than the Boreholes, this difference might be due to the varying depths. The Wells are generally shallow with depths ranging from 15 m to 30 m compared to the Boreholes which are deeper with a mean depth of 52 m and 70 m in the range $0.7\text{--}27.5\text{ m}^3\text{ h}^{-1}$ with a mean value of $2.7\text{ m}^3\text{ h}^{-1}$ and possibly closer to the geological rocks than the Wells. Thus water from the Boreholes have higher chances of interaction with the rocks than the Wells. Interaction with these

geological materials increases the possibility of leaching of the radionuclides into the water. Human activities such as vegetable farming in which phosphate fertilizers are applied and cement production in the municipality have also been identified as possible contributory factors. The Wells are generally opened, and may receive airborne particulates emanating from the cement production. The relatively high doses suggest that consumption of groundwater in these communities may pose threats of radiological health hazards such as anemia, eye cataracts, broken teeth, reduced bone growth and lung cancer to the public. The total lifetime fatality cancer risk estimated for adults of 66 years in the three communities showed that Aflao recorded slightly high value while Denu and Agbozume recorded values within the world's average value.

Generally, the results obtained for the physical parameters showed that the electrical conductivity and TDS recorded relatively high values for Aflao and Denu compared to Agbozume-Klikor. This might be the reason for the high salinity of the domestic water in these localities. pH values recorded are generally slightly acid to neutral to slightly alkaline. There are no significant temperature variations in the sampling locations. The high salinity might have contributed to relatively enhancing the concentration of the radionuclides.

The Cl^- , Ca^{2+} and Mg^{2+} values obtained for Agbozume-Klikor though significant are lower than that for Aflao and Denu. Agbozume – Klikor is about 20 km away from Aflao and 15 km away from Denu, therefore, the influence of the Cement factory, the sea and lagoon might not be pronounced. Also, vegetable farming activities are also on the lower side but the geology of the three localities (Aflao, Denu and Agbozume) is the

same. Thus, the factors responsible for the relatively high values of ^{226}Ra obtained for Aflao and part of Denu might be attributed largely to human activities such as the cement factory operation and farming activities in these locations.

5.2 RECOMMENDATIONS

1. Further studies should be carried out by the Department of Nuclear Sciences and Applications on sediments from Wells in the Ketu District Municipality, to determine possible accumulation of radionuclides as a result of immobilization.
2. Further studies should be conducted by the Department of Nuclear Sciences and Applications on Farm soil evaluation, to determine the amount of radionuclides deposited as a result of the usage of artificial fertilizers in the three communities.
3. The Environmental Protection Agency should come out with a programme to monitor the ambient air at the various Wells which recorded high level of radionuclides
4. Ministry of Health should carry out survey on prevailing health hazards in the three communities to determine any related radiation sickness.
5. There is the need for a sustained medium to long term studies to establish the general dose levels in these water sources. The Environmental Protection Agency and Nuclear Regulatory Authority (NRA) could take up this responsibility for regulatory reasons.

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APPENDIX A

TableA₁: Radionuclides in Bq/ℓ and Chemical Parameters (mg/L), Aflao

Water Sources	Radionuclides (Bq/ℓ)				Chemical Parameters (mg/L)			
	²²⁶ Ra	²²⁸ Ra	²³² Th	⁴⁰ K	ALK	Cl ⁻	Ca ²⁺	Mg ²⁺
A SL W 1	5.85	2.76	2.88	17.98	96	204	295	687
B9 - AW 2	0.46	0.01	0.41	3.8	398	332	408	788
A W3	5.24	0.81	0.14	12.23	364	192	90	320
A S L BH I	5.85	2.76	0.28	18.00	328	274	298	252
ASL BH2	0.37	0.52	0.52	5.83	228	112	179	498
AWW BH3	2.86	2.69	2.81	17.9	90	174	167	252

Table A₂: Radionuclides in Bq/ℓ and Chemical Parameters (mg/L), Denu

Water Sources	Radionuclides (Bq/ℓ)				Chemical Parameters (mg/L)			
	²²⁶ Ra	²²⁸ Ra	²³² Th	⁴⁰ K	ALK	Cl ⁻	Ca ²⁺	Mg ²⁺
DW1	1.12	0.52	0.8	6.04	358	448	324	545
D W 2	0.05	0.02	0.04	3.65	208	182	105	367
D BH 1	0.69	0.24	0.67	4.86	556	284	245	461
DETBH2	5.8	2.8	2.19	5.82	26	107	99	305
ADBH3	5.63	1.38	7.68	8.98	332	542	391	675
T -D BH4	0.5	0.54	1.56	8.98	192	102	198	311.7

Table A3: Radionuclides in Bq/l and Chemical Parameters (mg/L), Agbozume-Klikor

Water Sources	Radionuclides (Bq/l)				Chemical Parameters (mg/L)			
	²²⁶ Ra	²²⁸ Ra	²³² Th	40K	ALK	Cl ⁻	Ca ²⁺	Mg ²⁺
AK W 1	0.62	0.07	0.54	1.21	2.6	70	191	108
AKW 2	0.30	0.06	0.27	1.40	60	120	109	128
AKW3	0.57	0.39	0.02	2.42	90	70	64	105
AKW4	0.56	0.02	0.45	4.52	734	524	216	286
AKBH1	0.45	0.11	0.11	2.54	26	70	191	108
SBH5	0.69	0.06	0.07	1.09	714	126	64	107

APPENDIX B**Table B₁: Annual Committed Effective Dose (mSv/a) for Aflao**

SAMPLING POINTS	Wc (< 1a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	<1a
AFLAO SECOND LUCOS WELL 1	200	5850	4.70E-06	5.50
AFLAO WELL 3	200	5240	4.70E-06	4.93
BEAT 9 - AFLAO WELL 5	200	460	4.70E-06	0.43
AFLAO SECOND LOCOST BH I	200	5850	4.70E-06	5.50
AFLAO SECOND LOCOST BH 2	200	370	4.70E-06	0.35
AFLAO WATER WORKS BH3	200	2860	4.70E-06	2.69

Table B₂: Annual Committed Effective Dose (mSv/a) for Denu

SAMPLING POINTS	Wc (< 1a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	<1a
DENU BH 1	200	690	4.7E-06	0.65
DENU WELL 2	200	50	4.7E-06	0.05
DENU-WELL 1	200	1120	4.7E-06	1.05
DENU -TOKOR BH2	200	5800	4.7E-06	5.5
TETEKOPÉ -DENU BH4	200	500	4.7E-06	0.47
ADAFIENU-DENU BH3	200	2690	4.7E-06	2.53

Table B₃: Annual Committed Effective Dose (mSv/a) for Agbozume

SAMPLING POINTS	Wc (< 1a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	<1a
AGBOZUME KLIKOR WELL 1	200	620	4.70E-06	0.58
AGBOZUME KLIKOR WELL 2	200	300	4.70E-06	0.28
AGBOZUME KLIKOR WELL 3	200	570	4.70E-06	0.54
AGBOZUME KLIKOR WELL 4	200	560	4.70E-06	0.53
AGBOZUME KLIKOR BH1	200	450	4.70E-06	0.42
SASHIMADZA BH5	200	690	4.70E-06	0.65

Table B4: Annual Committed Effective Dose (mSv/a) for Aflao

SAMPLING POINTS	Wc (1-2a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	1-2a
AFLAO SECOND LUCOS WELL 1	260	5850	9.6E-07	1.46
AFLAO WELL 3	260	5240	9.6E-07	1.31
BEAT 9 - AFLAO WELL 5	260	460	9.6E-07	0.11
AFLAO SECOND LOWCOST BH I	260	5850	9.6E-07	1.46
AFLAO SECOND LOWCOST BH 2	260	370	9.6E-07	0.09
AFLAO WATER WORKS BH3	260	2860	9.6E-07	0.71

Table B5: Annual Committed Effective Dose (mSv/a) for Denu

SAMPLING POINTS	Wc (1-2a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	1-2a
DENU-WELL 1	260	1120	9.6E-07	0.28
DENU WELL 2	260	50	9.6E-07	0.01
DENU BH 1	260	690	9.6E-07	0.17
DENU -TOKOR BH2	260	5800	9.6E-07	1.45
ADAFIENU-DENU BH3	260	2690	9.6E-07	0.67
TETEKOPPE -DENU BH4	260	500	9.6E-07	0.12

Table B6: Annual Committed Effective Dose (mSv/a) for Agbozume

SAMPLING POINTS	Wc (1-2a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	1-2a
AGBOZUME KLIKOR WELL 1	260	620	9.6E-07	0.02
AGBOZUME KLIKOR WELL 2	260	300	9.6E-07	0.01
AGBOZUME KLIKORWELL 3	260	570	9.6E-07	0.02
AGBOZUME KLIKOR WELL 4	260	560	9.6E-07	0.02
AGBOZUME KLIKOR BH1	260	450	9.6E-07	0.01
SASHIMADZA BH5	260	690	9.6E-07	0.02

Table B7: Annual Committed Effective Dose (mSv/a) for Aflao

SAMPLING POINTS	Wc (2-7a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	2-7a
AFLAO SECOND LUCOS WELL 1	300	5850	6.20E-07	1.09
AFLAO WELL 3	300	5240	6.20E-07	9.75
BEAT 9 - AFLAO WELL 5	300	460	6.20E-07	8.56
AFLAO SECOND LOCOST BH I	300	5850	6.20E-07	1.09
AFLAO SECOND LOCOST BH 2	300	370	6.20E-07	6.88
AFLAO WATER WORKS BH3	300	2860	6.20E-07	5.32

Table B8: Annual Committed Effective Dose (mSv/a) for Denu

SAMPLING POINTS	Wc (2-7a)	Concentration(C) mBq/ ℓ	Dose Convention Factor [E]	2-7a
DENU-WELL 1	300	1120	6.20E-07	0.21
DENU WELL 2	300	50	6.20E-07	0.01
DENU BH 1	300	690	6.20E-07	0.13
DENU -TOKOR BH2	300	5800	6.20E-07	1.08
ADAFIENU-DENU BH3	300	2690	6.20E-07	0.50
TETEKOPPE -DENU BH4	300	500	6.20E-07	0.09

Table B9: Annual Committed Effective Dose (mSv/a) for Agbozume

SAMPLING POINTS	Wc (2-7a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	2-7a
AGBOZUME KLIKOR WELL 1	300	620	6.20E-07	0.12
AGBOZUME KLIKOR WELL 2	300	300	6.20E-07	0.06
AGBOZUME KLIKOR WELL 3	300	560	6.20E-07	0.10
AGBOZUME KLIKOR WELL 4	300	570	6.20E-07	0.11
AGBOZUME KLIKOR BH1	300	450	6.20E-07	0.08
SASHIMADZA BH5	300	690	6.20E-07	0.13

Table B₁₀: Annual Committed Effective Dose (mSv/a) for Aflao

SAMPLING POINTS	Wc (7-12a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	7-12a
AFLAO SECOND LUCOS WELL 1	350	5850	8.00E-07	1.64
AFLAO WELL 3	350	5240	8.00E-07	1.47
BEAT 9 - AFLAO WELL 5	350	460	8.00E-07	0.13
AFLAO SECOND LOCOST BH I	350	5850	8.00E-07	1.64
AFLAO SECOND LOCOST BH 2	350	370	8.00E-07	0.10
AFLAO WATER WORKS BH3	350	2860	8.00E-07	0.80

Table B₁₁: Annual Committed Effective Dose (mSv/a) for Denu

SAMPLING POINTS	Wc (7-12a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	7-12a
DENU-WELL 1	350	1120	8.00E-07	0.31
DENU WELL 2	350	50	8.00E-07	0.01
DENU BH 1	350	690	8.00E-07	0.19
DENU -TOKOR BH2	350	5800	8.00E-07	1.62
ADAFIENU-DENU BH3	350	2690	8.00E-07	0.75
TETEKOPPE -DENU BH4	350	500	8.00E-07	0.14

Table B₁₂: Annual Committed Effective Dose (mSv/a) for Agbozume

SAMPLING POINTS	Wc (7-12a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	7-12a
AGBOZUME KLIKOR WELL 1	350	620	8.00E-07	0.17
AGBOZUME KLIKOR WELL 2	350	300	8.00E-07	0.08
AGBOZUME KLIKOR WELL 3	350	570	8.00E-07	0.16
AGBOZUME KLIKOR WELL 4	350	560	8.00E-07	0.16
AGBOZUME KLIKOR BH1	350	450	8.00E-07	0.13
SASHIMADZA BH5	350	690	8.00E-07	0.19

Table B13: Annual Committed Effective Dose (mSv/a) for Aflao

SAMPLING POINTS	Wc (12-17a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	12-17a
AFLAO SECOND LUCOS WELL 1	600	5850	1.50E-06	5.27
AFLAO WELL 3	600	5240	1.50E-06	4.72
AT 9 - AFLAO WELL 5	600	460	1.50E-06	0.4
AFLAO SECOND LOCOST BH I	600	5850	1.50E-06	5.27
AFLAO SECOND LOCOST BH 2	600	370	1.50E-06	0.33
AFLAO WATER WORKS BH3	600	2860	1.50E-06	2.57

Table B14: Annual Committed Effective Dose (mSv/a) for Denu

SAMPLING POINTS	Wc (12-17a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	12-17a
DENU-WELL 1	600	1120	1.50E-06	1.10
DENU WELL 2	600	50	1.50E-06	0.05
DENU BH 1	600	690	1.50E-06	0.62
DENU -TOKOR BH2	600	5800	1.50E-06	5.22
ADAFIENU-DENU BH3	600	2690	1.50E-06	2.42
TETEKOPÉ -DENU BH4	600	500	1.50E-06	0.45

Table B₁₅: Annual Committed Effective Dose (mSv/a) for Agbozume

SAMPLING POINTS	Wc (12-17a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	12-17a
AGBOZUME KLIKOR WELL 1	600	620	1.50E-06	0.56
AGBOZUME KLIKOR WELL 2	600	300	1.50E-06	0.27
AGBOZUME KLIKOR WELL 3	600	570	1.50E-06	0.51
AGBOZUME KLIKOR WELL 4	600	560	1.50E-06	0.50
AGBOZUME KLIKOR BH1	600	450	1.50E-06	0.41
SASHIMADZA BH5	600	690	1.50E-06	0.62

Table B₁₆: Annual Committed Effective Dose (mSv/a) of Aflao

SAMPLING POINTS	Wc (>17a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	>17a
AFLAO SECOND LUCOS WELL 1	730	5850	2.80E-07	1.20
AFLAO WELL 3	730	5240	2.80E-07	1.07
BEAT 9 - AFLAO WELL 5	730	460	2.80E-07	0.09
AFLAO SECOND LOCOST BH I	730	5850	2.80E-07	1.20
AFLAO SECOND LOCOST BH 2	730	370	2.80E-07	0.07
AFLAO WATER WORKS BH3	730	2860	2.80E-07	0.59

Table B17: Annual Committed Effective Dose (mSv/a) for Denu

SAMPLING POINTS	Wc (>17a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	>17a
DENU-WELL 1	730	1120	2.80E-07	0.23
DENU WELL 2	730	50	2.80E-07	0.01
DENU BH 1	730	690	2.80E-07	0.14
DENU -TOKOR BH2	730	5800	2.80E-07	1.19
ADAFIENU-DENU BH3	730	2690	2.80E-07	0.55
TETEKOPÉ -DENU BH4	730	500	2.80E-07	0.10

Table B18: Annual Committed Effective Dose (mSv/a) for Agbozume

SAMPLING POINTS	Wc (>17a)	Concentration(C) mBq/ ℓ	Dose convention Factor [E]	>17a
AGBOZUME KLIKOR WELL 1	730	620	2.80E-07	0.13
AGBOZUME KLIKOR WELL 2	730	300	2.80E-07	0.06
AGBOZUME KLIKOR WELL 3	730	570	2.80E-07	0.12
AGBOZUME KLIKOR WELL 4	730	1580	2.80E-07	0.32
AGBOZUME KLIKOR BH1	730	450	2.80E-07	0.09
SASHIMADZA BH5	730	690	2.80E-07	0.14

APPENDIX C

Table C₁ Normalized Values of ^{226}Ra / ^{228}Ra , Cl^- , Ca^{2+} and Mg^{2+} , Aflao

	A SL W 1	B9 - AW 2	A W3	A S L BH I	ASL BH2	AWW BH3
^{226}Ra	1.701406	0.133786	1.523994	1.701406	0.10761	0.831798
^{228}Ra	1.734031	0.006283	0.508901	1.734031	0.326702	1.690052
Cl^-	0.950311	1.546584	0.89441	1.276398	0.521739	0.810559
Ca^{2+}	1.231733	1.703549	0.375783	1.244259	0.74739	0.697286
Mg^{2+}	1.473722	1.690383	0.68645	0.540579	1.068287	0.540579

Table C₁ Normalized Values of ^{226}Ra / ^{228}Ra , Cl^- , Ca^{2+} and Mg^{2+} , Denu

	DW1	D W 2	D BH 1	DTBH2	DABH3	DTBH4
^{226}Ra	0.48731	0.021755	0.300218	2.523568	2.449601	0.217549
^{228}Ra	0.567273	0.021818	0.261818	3.054545	1.505455	0.589091
Cl^-	1.614414	0.655856	1.023423	0.385586	1.953153	0.367568
Ca^{2+}	1.427313	0.462555	1.079295	0.436123	1.722467	0.872247
Mg^{2+}	1.227155	0.826359	1.038016	0.686756	1.519871	0.701843

Table C₃ Normalized Values of ^{226}Ra / ^{228}Ra , Cl^- , Ca^{2+} and Mg^{2+} , Agbozume-Klikor

	AKW1	A kw2	AK W 3	A K W 4	A K BH1	SBH5
^{226}Ra	1.166144	0.564263	1.0721	1.053292	0.846395	1.297806
^{228}Ra	0.591549	0.507042	3.295775	0.169014	0.929577	0.507042
Cl^-	0.428571	0.734694	0.428571	3.208163	0.428571	0.771429
Ca^{2+}	1.372455	0.783234	0.45988	1.552096	1.372455	0.45988
Mg^{2+}	0.769596	0.912114	0.748219	2.038005	0.769596	0.76247

APPENDIX D

Table D₁ Radiation Exposure (²²⁶Ra) for Wells and Boreholes Water Consumption in mSv/a, Aflao

Sampling Points	Radiation Exposure (mSv/a) for Age Groups					
	<1a	1-2a	2-7a	7-12a	12-17a	>17a
Aflao Second Low-Cost Well 1	5.50	1.46	1.09	1.64	5.27	1.20
Aflao Well 3	4.93	1.31	0.97	1.47	4.72	1.07
Beat 9 - Aflao Well 5	0.43	0.11	0.09	0.13	0.41	0.09
Aflao Second Low-Cost BH 1	5.50	1.46	1.09	1.64	5.27	1.20
Aflao Second Low-Cost BH 2	0.35	0.09	0.07	0.10	0.33	0.08
Aflao Water Works BH3	2.69	0.71	0.53	0.80	2.57	0.58

Table D₂ Radiation Exposure (²²⁶Ra) for Wells and Boreholes Water Consumption in mSv/a, Denu,

Sampling Points	Radiation Exposure (mSv/a) Age Groups					
	<1a	1-2a	2-7a	7-12a	12-17a	>17a
Denu-Well 1	1.05	0.28	0.21	0.31	1.01	0.23
Denu Well 2	0.05	0.01	0.01	0.01	0.05	0.01
Denu BH 1	0.65	0.17	0.13	0.19	0.62	0.14
Denu -Tokor BH 2	5.45	1.45	1.08	1.62	5.22	1.19
Denu - Adafienu BH 3	2.53	0.67	0.50	0.75	2.42	0.55
Denu - Tetekope Denu BH 4	0.47	0.12	0.09	0.14	0.45	0.10

Table D₃ Radiation Exposure (²²⁶Ra) for Wells and Boreholes Water Consumption in mSv/a, Agbozume

Sampling Pointns	Radiation Exposure (mSv/a) Age Groups					
	<1a	1-2a	2-7a	7-12a	12-17a	>17a
Agbozume - Klikor Well 1	0.58	0.02	0.12	0.17	0.56	0.13
Agbozume - Klikor Well 2	0.28	0.01	0.06	0.08	0.27	0.06
Agbozume - Klikor Well 3	0.54	0.02	0.10	0.16	0.51	0.12
Agbozume -Klikor Well 4	0.53	0.02	0.11	0.16	0.50	0.32
Agbozume Klikor BH 1	0.42	0.01	0.08	0.13	0.41	0.09
Sashimadza BH 5	0.65	0.02	0.13	0.19	0.62	0.14