RISK ASSESSMENT FROM INTAKE OF NATURALLY OCCURING RADIOACTIVE MATERIALS IN SOME BOTTLED DRINKING WATER ON THE GHANAIAN MARKET

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DECLARATION

I hereby declare that with the exception of references to other people work which have duly been acknowledged, this compilation is the result of my own research work and no part of it has been presented for another degree in this university or elsewhere.

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ABSTRACT

Activity concentrations of the Naturally Ocurring Radioactive Materials (NORMs) in some bottled water brands were analyzed using gamma spectrometry. ^{40}K activity concentrations were in the range of 3.57-5.47Bq/L, the highest occurring in brand L9. Similarly ^{232} Th activity concentrations were in the range of 0.30-0.56 Bq/L with the highest occurring in brand L8. ^{226}Ra was identified in eleven brands with the remaining five below detection limit. The highest value (0.53Bq/L) occurred in brand L9. Comparison of the mean concentrations showed significant differences at (α=0.05) between the various brands of bottled water. Estimated committed effective doses were generally below 0.1mSv/a for all age groups with the exception of children <1yr. Estimated lifetime cancer and hereditary risk was done using the ICRP risk assessment methodology. Relationship between Activity concentrations and some physicochemical parameters were established using scatter graphs. The significant one was the conductivity parameter and how estimated activity concentrations tend to correlate (Jobbàgy et al, 2013). Trace elements and heavy metals were analysed using titrimetry, UV-VIS spectroscopy and atomic absorption spectroscopy. Their levels were below recommended and conventional levels. Conclusively bottled water brands analyzed were therefore radiologically safe.

ACKNOWLEDGEMENT

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ABBREVIATIONS AND SYMBOLS

ADC-	Analogue-To-Digital Converter
ALARA-	As Low As Reasonably Achievable
ANOVA-	Analysis Of Variance
Bq-	Becquerel
BW-	Bottled Water
BWC-	Bottled Water Company
DNA –	Deoxyribonucleic Acid
EC -	Electron Capture
EDTA-	Ethylenediaminetetraacetic Acid
EPA-	Environmental Protection Agency
FDA-	Food and Drugs Authority
GSA-	Ghana Standards Authority
HPGe-	High Purity Germanium Detector
IAEA-	International Atomic Energy Agency
ICBWA-	International Council of Bottled Water Associations
ICRP-	International Commission on Radiological Protection
IDC-	Individual Dose Criterion
keV-	Kilo Electron-Volt
LSD –	Least Square Difference
MCA-	Multi-Channel Analyser
NCSWP-	National Community Water Supply and Sanitation Policy
NMW-	Natural Mineral Water
NPP-	Nuclear Power Plant
NW-	Nuclear Waste
PET-	Polyethylene Terephthalate
PW-	Prepared Water
R^2-	Correlation Coefficient
SPI-	Society of the Plastics Industry
TDS-	Total Dissolved Solids
UN-	United Nation
UV-	Ultra Violet
WHO-	World Health Organization
WRC-	Water Resource Commission

CHAPTER ONE

INTRODUCTION

1.1 Background

Natural radiation accounts for 98% of radiation exposure to the public due to its random occurrence and apparent lack of control over it. Natural radiation comes from cosmic rays, naturally-occurring radioactive elements in the earth's crust, and radioactive decay products. Since these radionuclides are present in soil and rock, they can also be found in groundwater and surface water. Natural radionuclides commonly found in waters include ^{238}U, ^{234}U, ^{232}Th, ^{226}Ra, ^{238}Ra, ^{222}Rn, ^{210}Pb and ^{40}K (Gbadago et al, 2011). The existence of these radionuclides normally occurs in wells dug deep into aquifers containing radionuclides variable oxidation states. The mineralized radionuclides dissolve slowly; however, for water that has high contact time with these rocks, there is a higher probability of significant radionuclide concentration. The concentration is however not necessarily restricted to the surface geological characteristics. It is also dependent on the physical and chemical factors prevailing in the aquifers for which reason radionuclide concentrations may vary for aquifers that are few meters apart. Even variable ground flow patterns may result in seasonal variations in radionuclide concentrations (Lieser et al, 1990).

Water is a basic necessity for biological survival and continuity, hence the need for it to be accessible, adequate and safe. The issue of safe drinking water has been a major topic for stakeholders and policy makers due to the apparent lack of commitment on successive national governments to prioritise it. In sub-Saharan Africa, a high percentage relies on running surface waters which are unimproved water sources (Table 1). However, the population relying on improved water sources has increased from 49% to 63% from 1990 to

2011 respectively (UN, 2013). In 2004, 75% of the rural population in Ghana had access to safe water, an increase of 92% on 1990 levels.

The quality and safety of drinking water should therefore be of prime importance which should be reflected in national health and security policies. This is accomplished through developing a systemic framework on water drinking quality including;

1. Health targets on safe drinking water by using a public health protection criteria
2. Developing detailed water safety plans to include;
    - Assessment of water quality systems
    - Monitoring and surveillance using standardized methodologies
    - Insightful management and effective communication
3. Setting of guidelines based on national circumstances.

All these require coordinated efforts from research institutions and policy stakeholders to develop criteria. Fortunately, extensive work has been done internationally on water quality and safety for which reason a clear monitoring criteria is founded (WHO, 2011).

Ghana has climbed the pedestal into becoming a middle income country with a high consumist middle income class. Over the years a number of bottled water companies have emerged to meet the demands of the middle class due to its perceived quality and safety. About twenty bottled water companies (BWC) are registered and approved to provide such services. However, most of the bottled water companies limit their water quality assessment to microbial, chemical and acceptability requirements with no further studies to quantify the radionuclide contents. Water from aquifers and surface water areas are ideal sources for the BWC's due to their rich mineral contents like calcium, magnesium, nitrates and sulphates.

However, the possible presence of significant amounts of radionuclides as explained earlier, the uncontrolled anthropogenic exploits that occur at aquifer locations and the

weakness of the regulatory agencies to enforce standards gives enough reason to assess the radiological components of some bottled drinking water on the Ghanaian market.

1.1.1 Global need for improved water

The increasing world population and its consequential effect on nature led to an adoption of the United Nation (UN) Millennium Declaration in 2000. The so called Millennium Development Goals (MDG‟s) were adopted by 189 nations which seek generally to promote health, gender equality, environmental preservation and worldwide prosperity. Prior to this declaration, reports from the world health organization (WHO) indicated high death rate associated with unsafe water, hygiene and sanitation as shown in Figure 1.1.

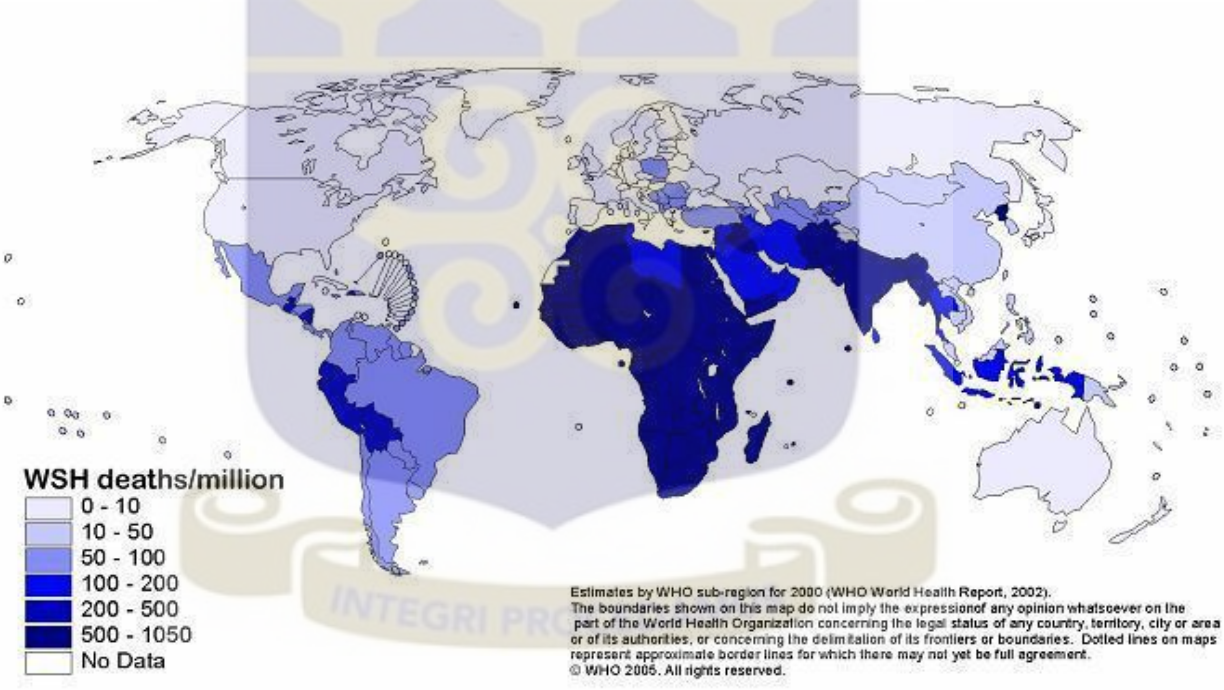

Figure 1.1: Deaths caused by unsafe water, sanitation, and hygiene for the year 2000, by country (WHO, 2002)

More than 2.1 billion people gained access to improved drinking water sources. The proportion of the global population using such sources reached 89 % in 2010, up from 76 % in 1990. Despite such progress, 768 million people still drew water from an

unimproved source (WHO, 2011). 83 % of the population without access to an improved drinking water source live in rural areas. Furthermore, concerns about the quality and safety of many improved drinking water sources persist. As a result, the number of people without access to safe drinking water may be two to three times higher than official estimates (UN, 2013).

According to WHO, an improved water source is defined as one that by the nature of its construction and design adequately protects the source from outside contamination, in particular by faecal matter (WHO, 2011). Table 1.1 outlines the improved and unimproved drinking water sources.

Table 1.1: Water supply technologies considered "improved" and "not improved" (WHO, 2011)

IMPROVED DRINKING WATER SOURCES	UNIMPROVED DRINKING WATER SOURCES
- piped water into dwelling, yard or plot -public tap or standpipe - tubewell or borehole - protected dug well -protected spring -rainwater collection	- unprotected dug well - unprotected spring - cart with small tank or drum provided by water vendor -tanker truck provision of water -surface water (river, dam, lake, pond, stream, canal, irrigation channel) - bottled water*

*Bottled water is considered to be improved only when the household uses drinking water from an improved source for cooking and personal hygiene.

1.1.2 The status of Ghana's water sanitation and delivery

Water sanitation is a huge problem in the nation's quest for safe drinking water. This led to the adoption of a National Community Water Supply and Sanitation Policy (NCWSP) to rationalize the rural water and sanitation sector to promote and improve the delivery of water and sanitation services in terms of economy, efficiency, effectiveness and satisfaction. Water Sector Restructuring programme was also instituted to rehabilitate major urban supply

systems by providing logistics, funding and technical support to players in the national supply chain. The specific aims were to extend distribution networks to the low and average income consumers and to assist the sector to maintain a financial anchor.

Water sanitation is to a large extent linked to the supply system which is also a function of the source of water. In urban communities with piped water systems, middle to high income earners are connected. Those without piped systems rely on boreholes, rainwater, bottled water and water tankers as water sources for domestic use. In the rural communities, surface waters (rivers, lakes) and hand dug wells are heavily relied on. Though Ghana has vast water resources, accessibility is the reason for inadequacy and its safety. A national demographic and household survey report by the Water Resource Commission (WRC, 2008) found that only 40% of urban residents had piped water in their homes. The report cites only 25% of urban dwellers enjoy this commodity for 24 hours. This underlie the inconsistent supply and rationing which is dependent on high population growth, diversified use of water and technical failures on the part of the suppliers.

It is, however, interesting to note that many urban households would not drink piped-water or waters from improved sources other than sachet or bottled water. There is an increased perception that packaged water is hygienic and safer than piped water (Doria, 2006). Consumers are justified due to the negative organoleptic experience with piped water and also, the often "exaggerated" adverts on bottled water products. Private water vendors are the least trusted due to the clandestine nature of their business and the apparent lack of regulatory oversight.

Since pipe water is generally not drunk in the urban centres, drinking water vending has become a unique business venture with packaged water the dominant product. They are sachet and bottled drinking water with both appealing to the general economic classes. They are, however, different based on the price and event at which they are used. It must be

emphasized that they go through the same treatment procedures; the difference comes only during packaging. Sachet water normally comes in 500 ml machine sealed polythene bags whiles bottled drinking water come in plastic hermetically sealed bottles of varying volumes ranging from 500 ml to 2500 ml.

1.2 Statement of the problem

Water from aquifers and some surface waters are ideal sources for bottled water companies because of their natural mineral content. However, depending on contact time between water and rocks in aquifers as well as retention time in surface waters, radionuclides concentrations may be significant and will warrant investigation. Recent survey to ascertain the consumption pattern, suggests a higher rate of consumption of bottle water especially among the middle income class (Duenas et al, 1997; Doria, 2006; Jobbàgy et al, 2013). In view of this, if higher levels of radioactivity are associated with bottled water, it could result in ingestion of higher doses by the consuming public and consequently increase health risk. As a result of the above reasons, a study to establish the activity concentrations of these radionuclides and also assess the water quality will be useful to various stakeholders including the water producing companies and regulatory bodies.

1.3 Objectives

The general aim of this study is to assess the radiation risk to the general public through the continuous consumption of bottled water produced locally. The study focused on determination of levels and distribution of naturally occurring radionuclides of the U/Th decay series and ^{40}K, as well as investigates the geochemical factors existing in the aquifer and surface water sources from which the bottled water is produced.

The study has the following specific objectives to;

- Determine the activity concentrations of Naturally Occurring Radioactive Materials (NORMs) in bottled water samples across the country

- Estimate annual effective doses and compare with recommended limits.
- Assess the radiation risk to the public based on dose values obtained.
- Determine the physical and chemical parameters in order to establish relationships between activity concentrations.
- Suggest a suitable radiation protection guideline for the BWC's if necessary.

At the end of the study, data on natural radioactivity levels in the selected bottled water will be disseminated to the public and as a result the knowledge and awareness on the issue of NORM in the study area will be increased.

1.4 Relevance & Justification

Globally, there is general concern about NORM in drinking water and very recently on bottled water. It is for this reason why national regulatory bodies have established guidelines for public protection. However the public to whom this is targeted has little or no appreciation of the health risks radiations poses to them. Consumption of bottled water is on ascendency as evidenced by recent findings. Its relatively moderate price makes it an easy commodity to acquire hence a higher possibility of its future consumption. Knowing the limitation of bottling companies in assessing the radiological aspects, assessment of this requirement would position consumers to take informed decisions. This would fit into the public health status of Ghana and justify its role in ensuring improved source of drinking water to consumers.

1.5 Scope and Limitation

The study is limited to bottled water produced locally for the Ghanaian market. The estimated risks were due to determined NORMs only. However, none of the results can be considered typical of any specific company or brand. For each analyte measured, two bottles (1.5 L each) of water were analyzed. Variations may be due to the water source, water treatment option and analytical variability.

CHAPTER TWO

LITERATURE REVIEW

2.1 Naturally Occurring Radiation

Radioactive substances are widely distributed in the earth's atmosphere and lithosphere. Major proportions are ores of U, Th and K salts as well as progenies of U and Th. Their concentrations in granitic rocks and seawater are estimated to be 4-13 mg/kg and 3 μg/L respectively (Leiser, 2001). Radionuclides are found in almost all natural materials such as soil, rocks and water though in low concentrations. Thus, to be able to quantify the activity concentrations requires the use of sensitive instruments. Naturally occurring radioactive substances are generally classified based on their origin and they include primordial radiation, cosmic radiation, cosmogenic radiation and anthropogenic radiation (Cember, 2009).

2.1.1 Primordial Radiation

These radionuclides have lifetimes comparable to the age of the earth and also form part of natural decay chain beginning with U and Th in the so-called uranium and thorium series (Cember, 2009).

2.1.1.1 Uranium Series

Uranium has three isotopes: about 99.3% of naturally occurring uranium is ^{238}U, 0.7% is ^{235}U, and about 5×10^{-3}% is ^{234}U. The uranium series consist of ^{238}U and ^{234}U (the uranium-radium decay series), whiles ^{235}U is the first member of another series called the actinium series. High concentrations of uranium in phosphate rich soils is due to formation of stable compounds with elemental phosphorus and are usually located downstream from mountain ranges. Uranium predominantly exists in its hexavalent state thereby dissolving in

the anionic complex forms (usually as carbonate $UO_2(CO_3)_n^{2-2n}$ or sulphate forms $UO_2(SO_4)_n^{2-2n}$ at high temperatures (Choppin et al, 2002).

When dissolved, uranium migrates downstream. It interacts with areas of reducing material, either inorganic or organic matter, which causes reduction to U^{4+}. Since most tetravalent uranium compounds are insoluble, the uranium precipitates, possibly as sulphides or, more likely, as hydroxides. Many of these original uranium precipitates are later covered by sedimentary material. The decay of uranium usually results in about ten different products which are migrated via groundwater with varying concentrations due to different physical and chemical characteristics of surrounding soil or rock (Loveland et al, 2006).

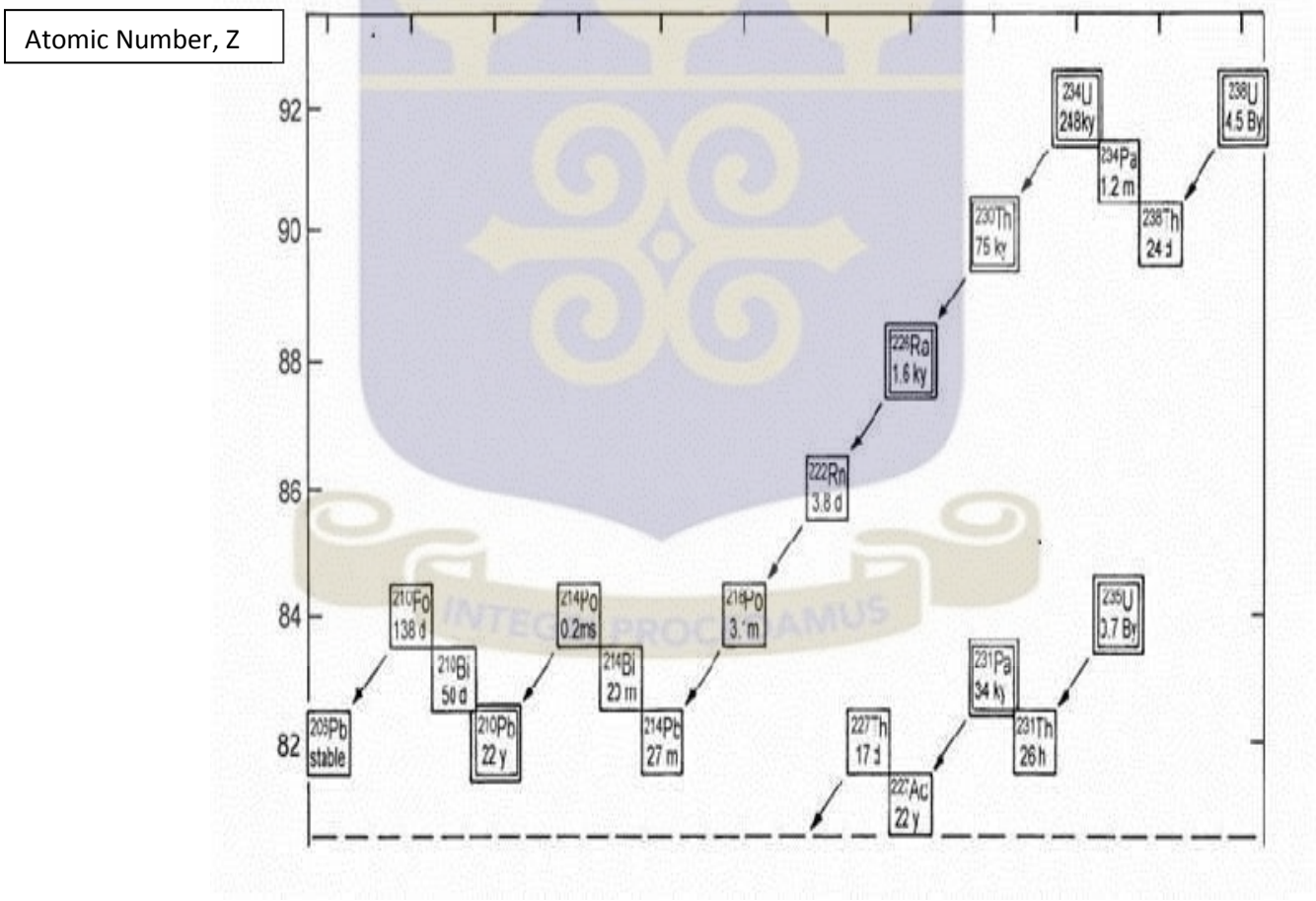

Figure 2.1: The Uranium Series (Lieser, 2001)

2.1.1.2 Thorium Series

Natural thorium (^{232}Th) starts this series with abundance of almost 100%. It is four times more abundant than uranium in nature though its specific radioactivity is less than that of uranium. It mainly exists as oxides in the minerals with a lower concentration ($<5\times10^{-3}$ g/m^3) in sea water due to its low solubility. Monazite, a rare earth phosphate is the most common thorium mineral containing about 15 % ThO_2 and usually 0.1 - 1% U_3O_8. Granite and gneiss rocks also contain a little amount of this element (Durance, 1986).

Both decay series have lead as their terminal stable element with the uranium series ending in ^{206}Pb and that of the thorium series ending in ^{208}Pb.

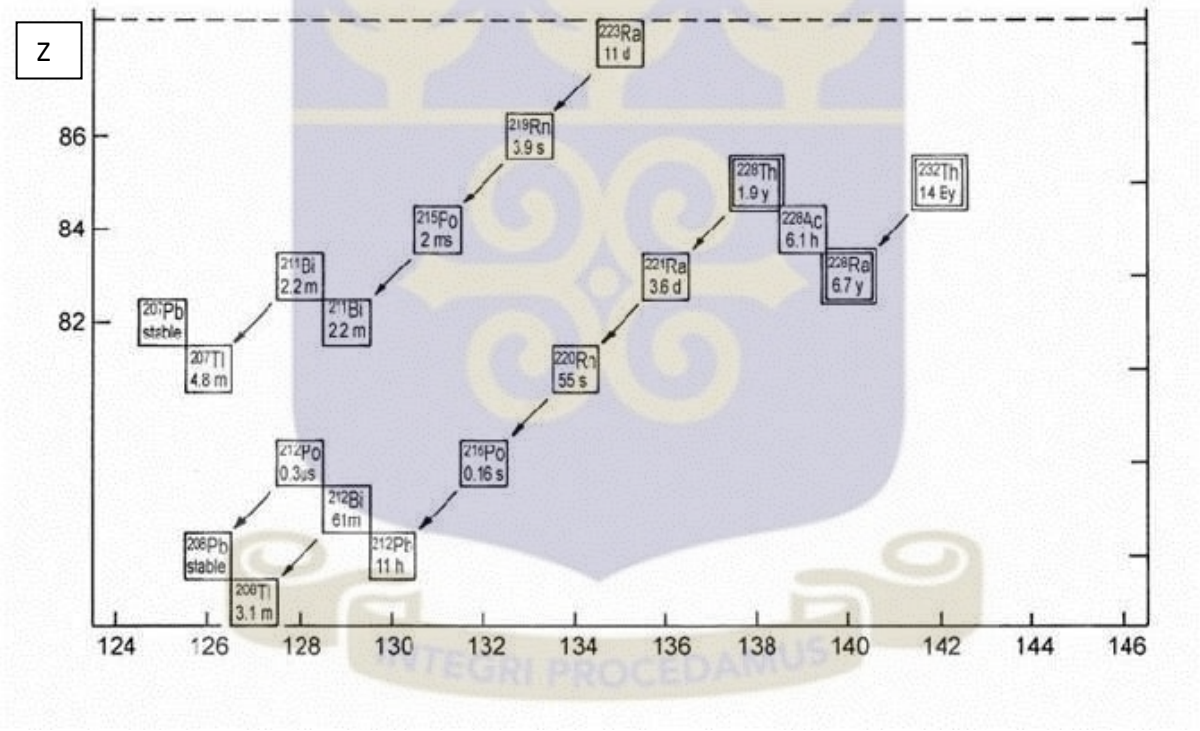

Figure 2.2: The Thorium Series (Lieser, 2001)

2.1.1.3 Potassium-40 (^{40}K)

There are 24 known isotopes of potassium of which three occur naturally: ^{39}K (93.3%), ^{40}K which is the radioactive isotope of terrestrial importance (0.0117%) and ^{41}K (6.7%). Naturally occurring ^{40}K decays to stable ^{40}Ar (11.2%) and ^{40} Ca (88.8%) by the mechanisms of electron capture and positron emission respectively. This implies for every 100 disintegrations of ^{40}K, 89% leads to beta particle emission whiles 11% leads to emission of gamma photons. Potassium-40 decay results in two daughter nuclides: ^{40}Ar by electron capture and ^{40}Ca by positron emission.

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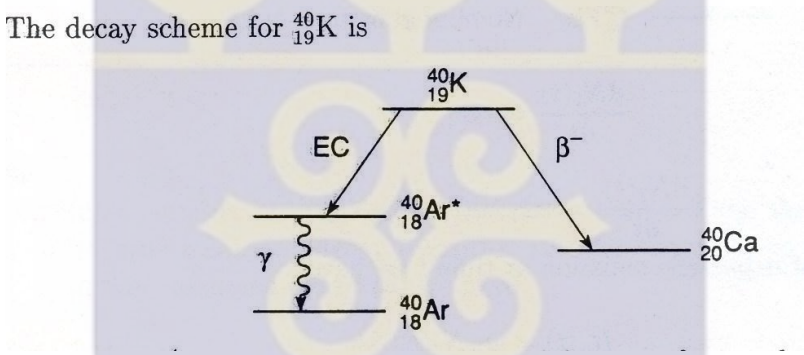


Figure 2.3: ^{40}K decay scheme

$$^{40}_{19}K \longrightarrow {}^{40}_{20}Ca + \beta^- + E \quad \ldots\ldots\ldots\ldots\ldots \text{(eqn. 2.1)}$$

$$^{40}_{19}K + e^- \longrightarrow {}^{40}_{18}Ar^* + E \quad \ldots\ldots\ldots\ldots\ldots \text{(eqn. 2.2)}$$

$$^{40}_{18}Ar^* \longrightarrow {}^{40}_{18}Ar + \gamma \quad \ldots\ldots\ldots\ldots\ldots \text{(eqn. 2.3)}$$

The ^{40}K-^{40}Ar parent-daughter radionuclide relationship is specially used in dating especially in the mineral industry (Maddock & Willis, 1961). ^{40}K has a half-life of 1.250×10^9yrs and it is generally classified as of low radiotoxicity. ^{40}K is easily measurable due to the emission of relatively high-energy β^-, β^+ and γ radiation (1460.93keV).

2.2 Cosmic Radiation

These are very high-energy particles from extra-terrestrial sources that bombard the earth. Radiation that enters the earth's atmosphere from space can come from as close as the earth's radiation belts and the sun or as far away as beyond the boundaries of the solar system and even beyond the galaxy (galactic radiation). Radiation from beyond the solar system has enough energy to generate additional radiation as it passes through Earth"s atmosphere, creating either radionuclides in the air or secondary particles (Cember, 2009).

2.2.1 Cosmogenic Radiation

These are due to interactions of cosmic radiation with the atmosphere. Cosmic radiation reacts with atmospheric elements like nitrogen, oxygen and argon to produce radionuclides like tritium and radiocarbon. Cosmogenic radiation is a continuing process with nuclides being produced at constant rate and brought to the earth's surface by rainwater (Draganic et al, 1990).

2.2.2 Tritium, $^{3}_{1}H$

This peculiar hydrogen isotope is produced directly by the process of spallation or in the atmosphere via a nuclear reaction between fast neutrons (from cosmic radiation) and nitrogen as shown in Equation 2.4.

$$^{1}_{0}n\ (fast) + {}^{14}_{7}N \longrightarrow {}^{12}_{6}C + {}^{3}_{1}H \quad \text{.....(eqn. 2.4)}$$

Tritium has a half-life of 12.33y decaying by a weak β emission to form ^{3}He. Tritium is rapidly transferred into water thereby displacing the lighter ^{1}H to form heavy tritiated water $^{3}H_2O$ (Norman, 1994).

2.2.3 Radiocarbon, ^{14}C

This isotope is formed when thermalized neutrons from cosmic radiation interacts with atmospheric nitrogen

$$^{1}_{0}n \text{ (slow)} + ^{14}_{7}N \rightarrow ^{14}_{6}C + ^{1}_{1}H \quad \text{(eqn. 2.5)}$$

Radiocarbon production in nuclear reactors proceeds by the same reaction mechanism. Most of the carbon produced stays in the atmosphere as $^{14}CO_2$ which is incorporated into plant tissues via photosynthesis and consequently through the food chain. However, there is significant dilution of ^{14}C due to burning of fossil fuel which is mainly composed of ^{12}C.

2.3 Anthropogenic Radiation in Nature

This form of radiation is human related and deliberate which adds to the natural radiation background. Nuclear weapons test, nuclear power plant, mining and underground drilling, and nuclear satellite burnt-up in the atmosphere can release major radionuclides into the atmosphere. Though this is a highly regulated industry, significant amounts of radionuclides find their way into the atmosphere via accidents at nuclear power plants (NPPs), leakages at nuclear waste (NW) repositories, etc. Some radionuclides of concern include ^{90}Sr, ^{137}Cs, ^{131}I, ^{3}H, and ^{14}C.

Table 2.1: Events leading to large scale emissions (Lieser, 2001)

Source	Country	Year	Conc. (Bq)	Important nuclides
Hiroshima & Nagasaki	Japan	1945	$4*10^{16}$	Fission products. Actinides
Atmospheric weapons test	USA USSR	1963	$2*10^{20}$	Fission products. Actinides
Chelyabinsk	USSR	1957	$8*10^{16}$	Fission products ^{90}Sr, ^{137}Cs
Harrisburg	USA	1979	$1*10^{12}$	Noble gases, ^{131}I
Chernobyl	USSR	1986	$2*10^{18}$	^{137}Cs

2.4 Overview of NORMs Found In Rock, Soil and Water in Ghana.

Several studies have been conducted by research institutions and graduate students on the radionuclide content of some natural systems in Ghana. Gbadago et al (2011), reported on the presence of natural isotopes of U, Po, Th and Ra in domestic water below significant health risk levels. Faanu et al (2011), reported on low risk ^{40}K, ^{232}Th and ^{238}U concentrations in soil and rock samples in some mining areas around the Tarkwa concession in Ghana. A brief summary of some publications indicate a general presence of natural radionuclides in soil, rock and water (surface and underground). However, that on underground water is inadequate (Faanu et al, 2011; Awudu et al, 2011). By mining of ores and minerals, appreciable amounts of natural radionuclides, in particular ^{40}K, ^{232}Th, ^{235}U, ^{238}U and the members of the thorium, uranium and actinium decay series, are brought up to the surface of the earth and contribute to the radioactivity in the environment. Generally, low concentrations have been reported and seldom exceed recommended values especially when dose results are extrapolated to children (Gbadago et al, 2010).

2.5 Water Systems in Ghana

Ghana is well endowed with water resources. The Volta river system basin, consisting of the Oti, Daka, Pru, Sene and Afram rivers as well as the white and black Volta rivers, covers 70% of the country water area (UNSCEAR, 2009). Another 22% of Ghana's water area is covered by the south-western river system watershed comprising the Bia, Tano, Ankobra and Pra rivers. The coastal river system watershed, comprising the Ochi-Nawuka, Ochi Amissah, Ayensu, Densu and Tordzie rivers, covers the remaining 8% of the country water area. Groundwater is available in mesozoic and cenozoic sedimentary rocks and in

sedimentary formations underlying the Volta basin. The total actual renewable water resources in Ghana are estimated to be 53.2 billion m^3 per year (UNSCEAR, 2009).

Even though surface water abounds in the country, groundwater remains the major and reliable source of water supply for the rural communities, some urban towns and commercial entities. This is due to the huge financial commitment required to develop the surface water resources to supply the numerous rural communities; and also due to the seasonal flow of most of the rivers in the country (TISDA, 2011). Furthermore, surface waters are often polluted and are the source of water-related diseases. Most rural communities depend on wells constructed using local tools. Unfortunately, some of these wells are polluted by the sipping of polluted surface waters into these wells.

The unreliability of flow in urban pipe–borne water and the perception of unsafe water treatment by the state water agency has led to the increase in consumption of sachet and bottled mineral water. Mineral water often originate from very deep aquifers and usually show higher loads of natural radionuclides leached from the surrounding bedrock. Anthropogenic radionuclides are however not found in these very old waters. Agyekum et al (2002), explored the groundwater resources and aquifers of Ghana and found a higher exploitation of this resource in the domestic life of Ghanaians.

Figure 2.4: Surface water systems in Ghana (WRC, 2008)

2.6 Hydrogeological Settings in Ghana

The geology of Ghana may be grouped into three broad hydrogeological units. These are:

- Precambrian Crystalline Basement Complex rocks,
- Palaeozoic consolidated sedimentary rocks, and
- Tertiary to Recent unconsolidated sediments and Cretaceous limestone beds.

Apart from these major geological units, minor geological provinces consisting Cenozoic/Mesozoic sedimentary strata and Quaternary alluvia occur at the coast and along narrow belts of major rivers.

2.6.1 The Pre-Cambrian Crystalline Basement Complex Rocks

This basement complex underlies about 55% of the country and shares common boundaries with the southern part of Burkina-Faso, as well as the eastern block of Côte d"Ivoire. On the basis of lithological differences, geology and groundwater conditions, the crystalline basement complex rocks are sub-divided into five different geohydrologic units namely;

- Birimian System and the associated granitic intrusive,
- Dahomeyan System,

- Tarkwaian system,
- Togo Series and the
- Buem formation.

The distribution of these rock units is shown in Figure 2.5. The Birimian system consists of thick isoclinally folded, metamorphosed sediments with metamorphosed tuff and lava inserted. The rocks are generally strongly-foliated and fractured, and are also intruded by batholitic masses of granites. They have been made porous as a result of weathering and fracturing. The rocks consist mainly of schists, phyllites, gneisses, quartzites, migmatites and granitic-gneiss. The Birimian system covers most of the densely populated areas in Ghana hence an important source of water supply (Boakye & Siakwan, 2000).

The Dahomeyan formation consists mainly of crystalline gneiss and migmatite, with minor quartz and biotite schists. The gneiss is generally massive and has few fractures. Silicic and mafic gneisses undergo change processes to develop into impermeable calcareous clay. The generally impervious nature of the weathered zone and the massive crystalline structure of the Dahomeyan rocks limit their groundwater yielding capacity (Kortatsi, 1994).

Even though the rocks of the Tarkwaian System, Togo Series and Buem formation are different in ages, they have similar lithologic sequence. Tarkwaian rocks consist of slightly metamorphosed, shallow-water sedimentary strata, comprising mainly sandstone, quartzite, shale and conglomerate. The Togo Series consists of metamorphosed and folded arenaceous and argillaceous sedimentary strata, comprising rocks such as indurated sandstone, quartzite, schist, phyllite and shale. The Buem formation consists of a thick sequence of shale, sandstone, and some minor volcanic rocks with subordinate limestone, conglomerate and grit. When fracture openings in the Togo Series, Tarkwaian and Buem rock formations are extensive and are not filled with impervious material, substantial amount of groundwater can be obtained.

2.6.2 Palaeozoic Consolidated Sedimentary Rocks

These rocks form the Voltaian formation and underlie about 42% of the country. The Voltaian is made up of well-consolidated and gently folded rocks consisting predominantly of sandstone, shale, arkose, mudstone, sand and limestone. Junner and Hirst (1946) subdivided the Voltaian formation into three groups based on lithology and field relationships comprising: Upper Sandstone, consisting of massive sandstones and thin-bedded sandstones; Middle Voltaian or Obosum/Oti beds; comprising arkose, mudstone, shale, sandstone, limestone and conglomerate, and Lower or basal sandstones; consisting mainly of quartz-sandstones and pebbly-grit beds.

2.6.3 Recent To Tertiary Unconsolidated Sediments and Cretaceous Limestone Beds

These formations constitute the two separate coastal aquifers of great international importance since they are located at the south-western and south-eastern borders of Ghana. The Cretaceous to Lower Tertiary sedimentary rocks are located at the south-western corner of Ghana and share a common boundary with Côte d"Ivoire. This area is locally referred to as the Tano Basin. The geology of the basin consists of thick sections of alternating sand and clay with occasional thin beds of gravel and fossiliferous limestone. The limestone is known to have oil and gas potential (Boakye and Siakwan, 2000). The Tertiary to Eocene and Cretaceous unconsolidated alluvial sediments, which consist of alternating limonitic sand, sandy-clay, gravel, and limestones, are located to the south-eastern corner of the country. This area shares a common boundary with the Republic of Togo, and is locally referred to as the Keta Basin. The geology is exposed, being covered extensively by lagoons, marshes and thick under-growths. The surficial sediments of this formation are very permeable due to their sandy and unconsolidated nature, and the high water percolation rate. Rainwater therefore finds its way down to the gravel bed where large quantity of water is stored.

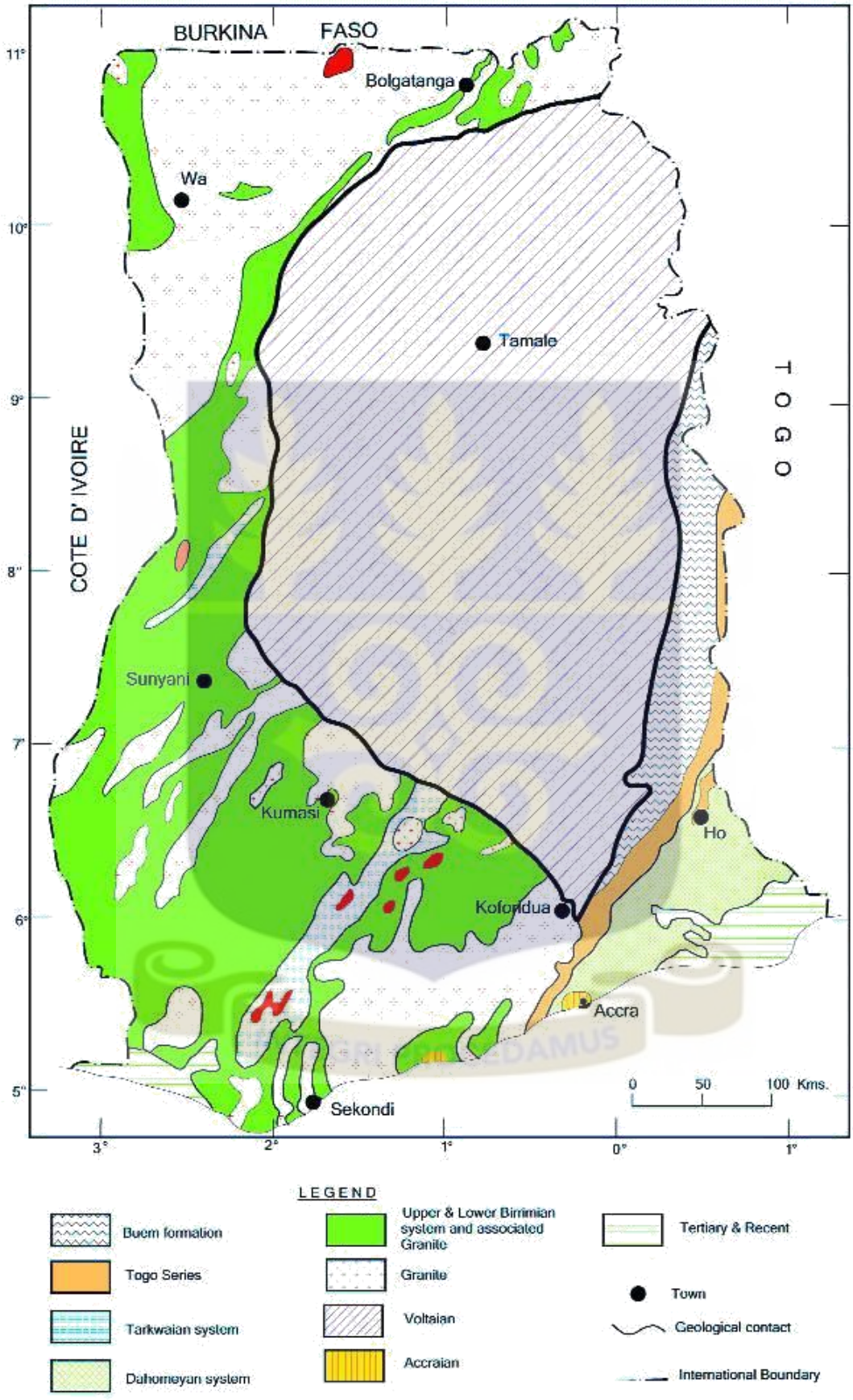


Figure 2.5: Geological map of Ghana (geological survey of Ghana)

2.7 Radiation Exposure through Ingestion of Drinking Water

Radionuclides if present in significant quantities in drinking water could be a source of radiation dose to the consuming public and could pose health risk. Under normal conditions, the risks could be small. However under accidental conditions, significant amount of radiation could be released and could lead to pollution of water particularly surface water bodies. Radionuclides of concern are usually those of natural origin since there is little or no control applied as compared to those used in practices. However, there are situations when their levels could be quite significant to cause significant exposure of humans. This is because anthropogenic radionuclides are often amenable to control at the point of entry into the water supply. However, naturally occurring radionuclides are less amenable to control due to the fact that they can enter the water supply at any point or multiple entry points, prior to consumption hence the need to screen randomly (WHO, 2011).

2.8 Reactions of Radionuclides with Natural Water Components

In aqueous media, most of the radionuclides are in their cationic forms hence they undergo hydration, hydrolysis, condensation, and radiocolloid formation and complexation reactions. Inorganic anions such as $C1^-$, CO_3^{2-}, SO_4^{2-}, NO_3^- and HPO_4^- and some organic compounds compete with the formation of aqua and hydroxo complexes, depending on their chemical properties and their concentrations. Relatively strong covalent bonds are formed between transition element cations and ligands containing donor atoms (Lieser, 2001).

Ground and surface waters contain a great variety of substances that may interact with radionuclides. Besides the main component (water), other inorganic compounds of interest include dissolved gases, such as oxygen and carbon dioxide, which influence the redox potential and the pH. Salts such as NaCl, $NaHCO_3$ and others, which affect pH and complexation and are responsible for the ionic strength. Organic components in natural water comprise compounds of low molecular mass, e.g. organic acids, amino acids and other

metabolites; suspended coarse particles of organic matter.

Inorganic salts affect the behaviour of radionuclides in natural waters in various ways. Dissolved salts influence pH, hydrolysis and complexation (Lieser, 2001). Anions in natural waters form ion pairs and complexes with cationic radionuclides and affect solubility, colloid formation and sorption behaviour (Dozol & Hagemann, 1993). Mobility may be enhanced by complexation; chloride ions, for example, are relatively weak complexing agents, but they are able to substitute OH^- ions in hydroxo complexes and to suppress hydrolysis, if they are present in relatively high concentrations.

2.9 Biological Effects of Ionizing Radiation

Radiation interaction with human body may lead to cell modification or death which might lead to deterministic or stochastic effect. This occurs via DNA damage (double strand break), hence the initiation of immediate effects or long term harm (UN, 2010). The mechanism of the biological effect arising from exposure to ionizing radiation is a result of direct and indirect actions:

2.9.1 Direct Action

Overexposure of the body to ionizing radiation initiates a series of biological events which is a direct function of the body molecule affected (Cember, 2009). The dissociation, due to ionization or excitation of an atom on the deoxyribonucleic acid (DNA) molecule prevents the information originally contained in the gene from being transmitted to the next generation. Such anomaly may occur in germinal or somatic cells and may be passed on to next generations or affect daughter cells. Since these point mutations are thereafter transmitted to succeeding generations of cells, it is clear that, for those biological effects of radiation that depend on point mutations, the radiation dose is cumulative, every little dose may result in a change in the gene burden, which is continuously transmitted (Cember, 2009).

2.9.2 Indirect Action

The average human body is composed of about 75% water; therefore most direct action by radiation is on this molecule. Water reacts with ionising radiation consequently producing highly reactive free radicals that are chemically toxic- the so called radiolysis of water (Cember, 2009: Lieser, 2001) as shown below.

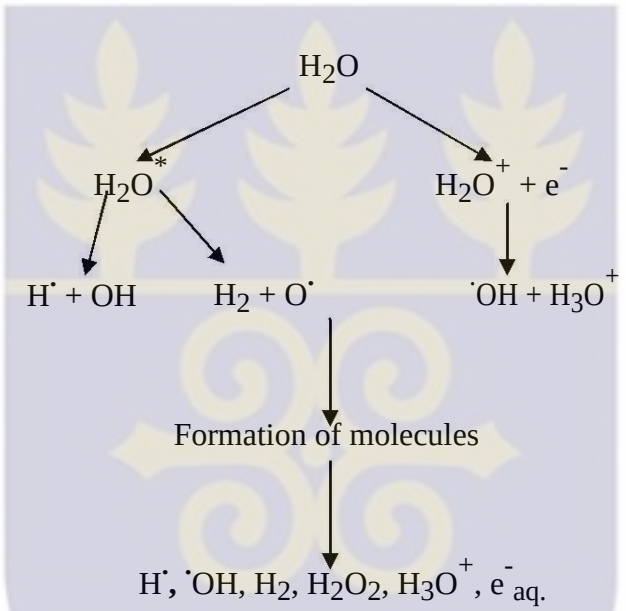


Figure 2.6 : Water radiolysis scheme (Choppin, 2002)

The H_2O_2 formed in the above equation is a very stable and potent oxidising agent and can affect molecules or cells that did not suffer radiation damage directly.

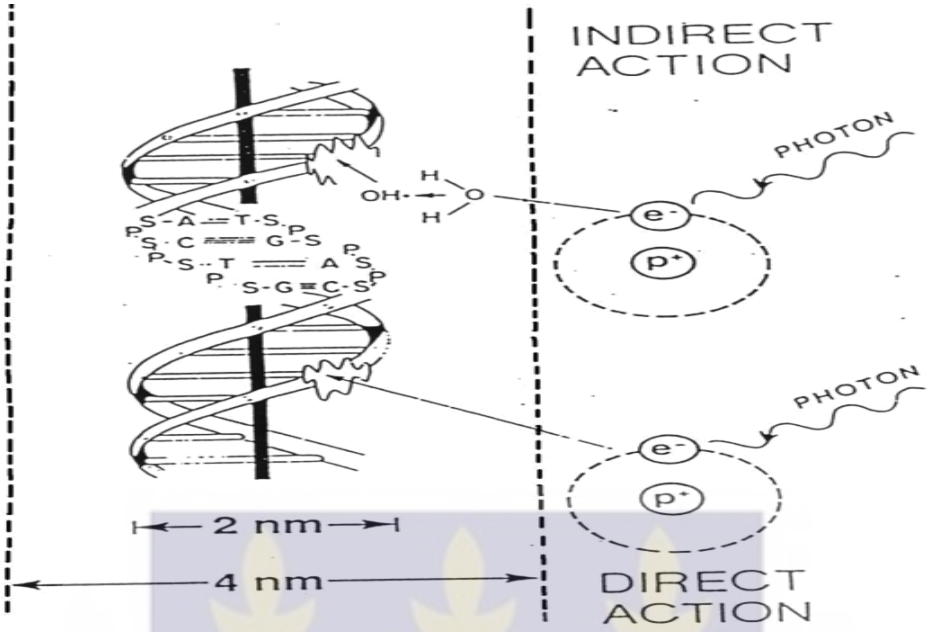


Figure 2.7: Mechanism of direct and indirect action by ionizing radiation. (Cember 2009)

2.10 Physical and Chemical Parameters of Water and Significance to Human Health

The physicochemical parameters of water and the importance to human health include: pH, turbidity, total dissolved solids (TDS) and other dissolved chemical elements affecting the quality of water.

- **pH**

Although no health-based guideline has been given on pH values, it is very important parameter since it goes to affect the organoleptics of water. pH is important in water treatment schemes as it has impact on water distribution routes and appliances. Low pH also increase the release of metals, some toxic, from soils and sediments. Alkalinity is an important parameter because it measures the water ability to resist acidification, for instance, to acid rain. The significant environmental impact of pH involves synergistic effects. That is, the pH value of the water may influence levels at which certain chemical substances become toxic.

- **Turbidity**

Turbidity in water is caused by suspended particles or colloidal matter that obstructs light transmission through the water. Solids particles suspended in water absorb or reflect light and cause the water to appear "cloudy". These particles are suspended inorganic minerals or organic matter picked up over or under the ground. Since the earth acts as an excellent the water from deep well is usually clear without significant amounts of turbidity. Turbidity is, however, profound in surface water supplies due to periodic interference from anthropogenic and animal activities. Although turbidity is not necessarily a threat to health, it is an important indicator of the possible presence of contaminants that would be of concern for health, especially from inadequately treated or unfiltered surface water.

- **Total dissolved solids (TDS)**

TDS is correlated fairly well to the total mineral content of the water. The palatability of water with a total dissolved solids (TDS) level of less than about 600 mg/L is generally considered to be good; drinking water becomes significantly and increasingly unpalatable at TDS levels greater than about 1000 mg/L (Oyelude & Ahenkorah, 2012). Prior knowledge about TDS is also important in gross alpha spectrometry due to the fact that alpha particles are easily stopped by solids.

- **Nitrates & sulphates**

Nitrate levels exceeding 1mg/l may cause significant health risk within six months of continuous exposure. The nitrate anion (NO_3^-) is not adsorbed by soil and moves with infiltrating water. Nitrates are present in water particularly in regions where agriculture fertilization is intense. Nitrates in infants are converted by the body to nitrites that oxidize blood haemoglobin to methaemoglobin (WHO, 2011). The altered bloods cells can no longer carry oxygen, which can result in brain damage or suffocation. Water with nitrite levels

exceeding 1.0 mg/l should not be used for feeding babies. Epidemiological studies show a correlation between high nitrate levels and gastric and stomach cancers.

Sulphates are associated with gypsum formations in the granitic region of Ghana. Sulphates of Calcium and Magnesium can cause hardness in water. They are discharged into water in industrial wastes and through atmospheric deposition; however, the highest levels usually occur in groundwater and are from natural sources. In general, the average daily intake of sulphate from drinking water, air and food is approximately 500 mg, food being the major source. High sulphate levels can also have a corrosive effect on plumbing.

- **Potassium**

Potassium is an essential element in humans and is seldom found in drinking water at levels that could be a concern for healthy humans. The recommended daily requirement is greater than 3000 mg. Potassium occurs widely in the environment, including all natural waters. Potassium chloride is used in ion exchange for household water softening in place of, or mixed with, sodium chloride, so potassium ions would exchange with calcium and magnesium ions. Health concerns would be related to the consumption of drinking- water treated by potassium-based water treatment, affecting only individuals in high-risk groups.

2.11 Some Drinking Water Treatment Modalities

Various water treatment options have emerged over the years with a common goal to providing safe and reliable water. The treatment option used is dependent on the quality of the source, the nature of impurities and the volume of treated water required. Removal certain of radionuclides as well as chemical and physical parameters requires options like reverse osmosis, multi layered filtration (ultra-, nano-, micron –filtration) and granular activated carbon treatment. For biological treatment (algae, bacteria etc.), options normally used are ultra-violet (UV) treatment, ozonation and chlorination (Manahan, 2000; Patnaik, 2004).

2.12 The Advent of Bottled Drinking Water

Earliest literature on bottled water was on the holy wells of medieval United Kingdom where water which was believed to be of holy significance were sold in glass bottles. Fast forwarding to 1767, the first commercially distributed water was bottled and sold by Jackson‟s spa in Boston USA (Back et al, 1995). Since then, the popularity of bottled drinking water has risen partly due to public perceptions and also on the rise of a liberal consumist middle income class. People prefer bottled water for reasons including convenience, taste, safety, poor tap-water quality and the marketing spin attached to it.

Globally, approximately 300 billion bottles of water are consumed annually. Bottled water are generally classified as;

- Natural mineral water
- Packaged water (other than natural mineral water)

The classification is based on the water source, chemical composition and purification modality. Below is a flow chart of BW production.

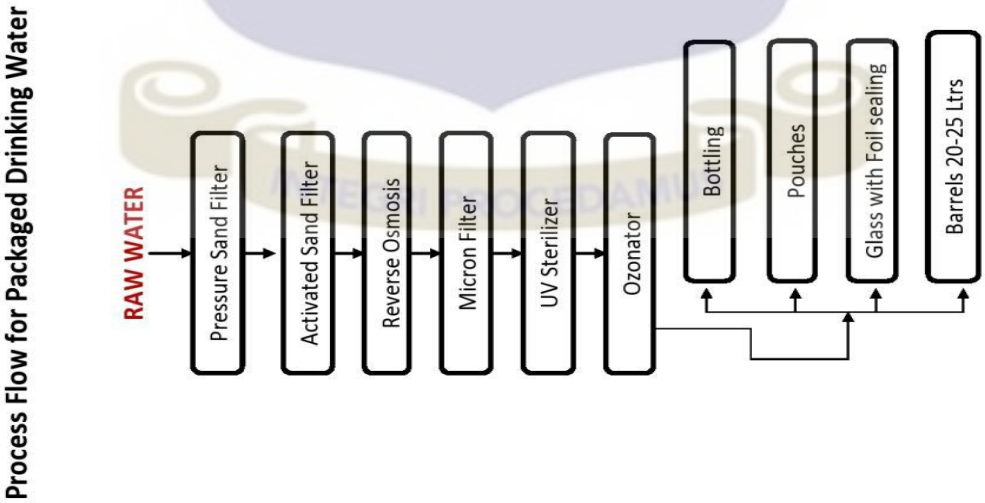


Figure 2.8: Process flow diagram for bottled water

This industry is regulated by the Food and Drugs Authority (FDA), Environmental Protection Agency (EPA) or the bottled water association. In any case, there is an umbrella body, the International Council of Bottled Water Associations (ICBWA) which provides a harmonized code of conduct and hygienic practices in parallelism with the codex alimentarius set by the Food and Agriculture Organization (FAO) and WHO.

In Ghana, the industry is regulated by the FDA and the Ghana Standards Authority (GSA) which ensures consumer protection information is provided on bottles. Labels should include;

- Type of water i.e. natural mineral water, purified water, etc.
- Ingredient labelling
- Name and place of business of the manufacturer
- Net weight
- Distributor
- Nutritional facts.

Concerns, however, have been raised over the quality and integrity of drinking water in Ghana. The general state of little-resourced regulatory agencies and the apparent indifference of drinking water companies to consumer health imply drinking waters might not be what it is claimed to be.

2.13 Drinking Water Quality Guidelines

Generally, the guidelines do not primarily apply to bottled drinking water (BDW). However for purposes of comparison, BDW would be secondarily adapted to the guidelines since it is being consumed anyway. For purposes of this research only three would be viewed namely the radiological, chemical and physical qualities.

2.13.1 WHO Guidelines

2.13.1.1 Radiological Aspect

Naturally occurring radionuclides in drinking water usually give radiation doses higher than those provided by artificially produced radionuclides and are therefore of greater concern. The radiation risks associated with these radionuclides made the WHO come out with screening and guidance levels recommended by the ICRP (2008). The guidance levels are only meant for health risk management and measures for reducing radionuclide concentrations, hence radiation doses. In the third edition of the ICRP recommendations, the individual dose criterion (IDC) was based on screening levels of 0.5 Bq/l for gross alpha activity and 1 Bq/l for gross beta activity. The IDC was set at 0.1mSv/year representing below 5% of the average annual dose due to natural radiation. The guidance levels are not mandatory compliance limits; however they serve the purpose of prompting further investigations and specific radionuclide analysis.

2.13.1.2 Chemical Aspect

Some chemical pollutants have been shown to cause severe health effects in humans as a result of prolonged exposure through drinking water. These pollutants have been assessed for possible health effects, and guideline values have been established only on the basis of health concerns. Chemical pollutants are generally categorized into five main groups as shown in Table 2.2.

Table 2.2: Chemical constituents and their sources (WHO, 2011)

Source of chemical constituents	Sources
Industrial sources and human dwellings	Mining, manufacturing and processing industries, sewage , solid wastes, urban runoff, fuel leakages
Naturally occurring	Rocks, soils and the effects of the geological setting and climate; eutrophic water bodies

Water treatment or materials in contact with drinking water	Coagulants, DBPs, piping materials
Pesticides used in water for public Health	Larvicides used in the control of insect vectors of disease
Agricultural activities	Manures, fertilizers, intensive animal practices and Pesticides

2.13.1.3 Physical Aspect

This area is essentially about acceptability. They are factors that affect people's perception about the quality of drinking water. This comprises the colour, taste and odour. There are no clear guidelines on this aspect due to the fact that these parameters have not been established to have a direct health effect on consumers. However, the occurrence of these factors suggests the presence of contaminants which may be of significant health risk. For example, a very turbid drinking water suggests a high amount of suspended solids which may be chemical or radiological in nature. It also exposes flaws in treatment methods (e. g. chlorination), storage and distribution.

2.13.2 The Food & Drugs Authority and Ghana Standards Authority

The Food and Drugs Authority (FDA) and the Ghana Standards Authority (GSA) were set up in 1992 and 1965 respectively. The GSA basically provides and maintain standards on all items in all fields of life; food materials, electrical appliances, textiles etc. Their standards include general water quality of drinking water (GS 175-1: 2009), physical characteristics of drinking water (GS 175-2: 1998); radiological characteristics of drinking water (GS 175-5:1998), etc. The FDA also regulate all items that have direct impact on human health i.e. food, water, drugs, cosmetics, etc. Their roles are complementary with the FDA assuming a much more specific one.

In Ghana, bottled drinking water is regulated by both institutions, however, it is optional to be certified by a GSA but mandatory to be registered and approved by the FDA. The GSA‟s mark of conformity is purely a reputational issue.

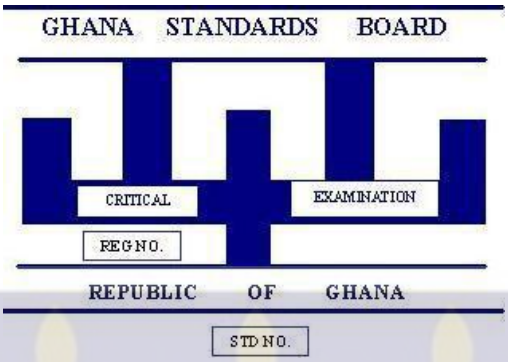


Figure 2.9: The GSA Mark of Conformity

Applications for the establishment of BW factories are submitted with supporting documents which include a site plan of the production premise and an environmental permit from the EPA. Other requirements include;

- Information on personnel- owners, key stakeholders, quality controllers, etc.
- Information on water, safety, health and hygiene- source of water, health status of personnel, protective clothing, safety policy, etc.
- Premises and equipment- sewage systems, emergency assembly and exit points, maintenance policy, etc.
- Record keeping- documentation on water batches produced, quality control records, records on corrective measures if any problem was encountered earlier.
- Minimum treatment modality- the minimum allowed is filtration followed by UV treatment. Filter cartridges are required to be replaced every three months.

2.13.3 The Codex Alimentarius Standard

The international body for standards on packaged water is the Codex Alimentarius Commission formed jointly by the Food and Agriculture Organization (FAO) and the WHO. It has established standards on natural mineral water as well as bottled/packaged mineral water. Natural mineral waters must conform to strict requirements, including collection and bottling without further treatment from a natural source, such as a spring or well. The standard for natural Mineral waters which describes the product and its compositional and quality factors, including prescribed treatments, limits for certain chemicals, hygiene, packaging and labelling. Standards for bottled/packaged water include waters from other sources, in addition to springs and wells, and treatment to improve their safety and quality (Codex Alimentarius, 2008).

2.14 Instrumentation for the Analysis of Water

2.14.1 Gamma Spectrometry

This analytical method allows the identification and quantification of gamma emitting isotopes in a variety of matrices. In one single measurement and with little sample preparation, gamma ray spectrometry allows the detection of several gamma emitting radionuclides in a sample (Gilmore, 2008). A typical analogue High Purity Germanium (HPGe) detector-based gamma spectroscopy system consists of a HPGe detector, high voltage power supply, preamplifier, amplifier, Analogue to Digital Converter (ADC), and Multi-Channel Analyser (MCA).

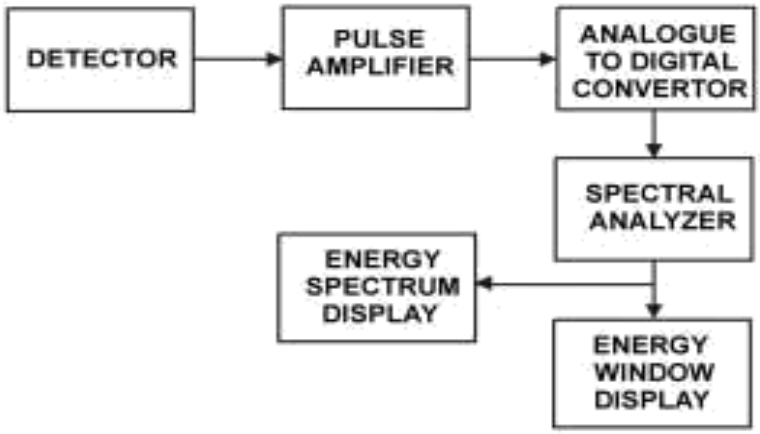


Figure 2.10: Block diagram of a gamma ray spectrometer

Measurement of gamma radiation can also be done using a scintillation detector consisting of Sodium Iodide crystal activated with thallium NaI(Tl) and optically coupled to a photomultiplier tube. Tl serves as an impurity in the detector crystal structure converting absorbed energy to light. Semiconductor detectors are also used in gamma detection. Examples include silicon and germanium detectors. The problem with germanium is that thermal excitation creates electron-hole pairs. For this reason liquid nitrogen is used to cool the electronics of germanium systems. Sodium Iodide (NaI)(Tl) detectors have higher efficiency than high purity germanium (HPGe) detectors which has higher resolution because of the high density of the crystal and high effective atomic number (Cember, 2009).

The multichannel analyser measures the output from the amplifiers by measuring pulse heights and count numbers within small voltage ranges (Gilmore, 2008). Because the height of each pulse is proportional to the amount of energy absorbed in the detector, the resulting lists of numbers of counts become the gamma-ray spectrum.

2.14.2 Atomic Absorption Spectroscopy (AAS)

Atomic spectroscopy refers to the emission of UV-VIS light by atoms and monoatomic ions. In absorption spectroscopy, atoms in gaseous phases absorb UV-VIS light from a light source thereby producing spectra that are characterized by narrow wavelength

absorption bands (Kenkel, 2003). AAS is used for determining metals by analysing samples in aqueous solution. Due to the metals presenting themselves as ionic species, atomization is done to convert all metal ions into free gas ground state atoms using an atomizer. The requirement for high thermal energy in this procedure has given rise in different atomization modalities hence flame spectroscopy. Spectral line sources are preferred to continuum line sources in this technique (Harvey, 2000).

2.15 Estimation of Uncertainty

Every measurement or analytical procedure has a degree of doubt associated which may be random or systematic hence the concept of uncertainty estimation. Uncertainty expresses the range of possible values a measurement or result might be reasonably expected to have (Harvey, 2000). Uncertainty is a random one when errors vary each time a measurement is made and is environment dependent e.g. humidity, temperature, pressure, etc. This uncertainty type is detected by repeating a measurement several times. If results are not identical, then random uncertainties exist. This problem is however solved by obtaining the mean which is normally considered the best value. The concept of random uncertainties is strongly related to the precision concept as it gives a fair idea about the reproducibility of the measurements or the extent to which individual values deviate from the average.

Systematic uncertainty cannot be detected by repeating a measurement. It can only be detected by using a different experimental procedure. If two methods consistently give different results, then at least one must involve a systemic uncertainty. If a true value is known (e.g. $g=9.81ms^{-2}$), then systemic uncertainties can be detected by comparing to the experimental value to the true value. This uncertainty type is also related to the accuracy concept i.e. how close a measure value is to the true value.

CHAPTER THREE

METHODOLOGY

3.1 Sampling

Most bottled drinking water are sourced from aquifers with a few sourced from surface waters. Study was done on their availability across the country and sixteen samples commonly found in shops were selected. Of the sixteen brands, ten are natural mineral waters (NMW), five are prepared water (PW) and one uses sources for which natural NMW or PW are classified. The NMW"s are normally bottled at source with the whole factory set-up located near the source. However, the PW"s are drawn from municipal tap water systems which are drawn from surface waters and consequently into large reservoirs located at manufacturers premises.

Table 3.1. Bottled water samples and their sourcing.

BRANDS	SOURCE
10	Aquifer source
5	Municipal tap system
1	Either aquifer or municipal tap system

Two dominant aquifer sources were highly exploited; the Medie aquifer enclaves and the relatively isolated mountains on the Dodowa-Agormanya low lying plains which form part of the pre-Cambrian crystalline basement complex rocks. Figure 3.1 is a map showing the locations of the source of water to the bottling water companies.

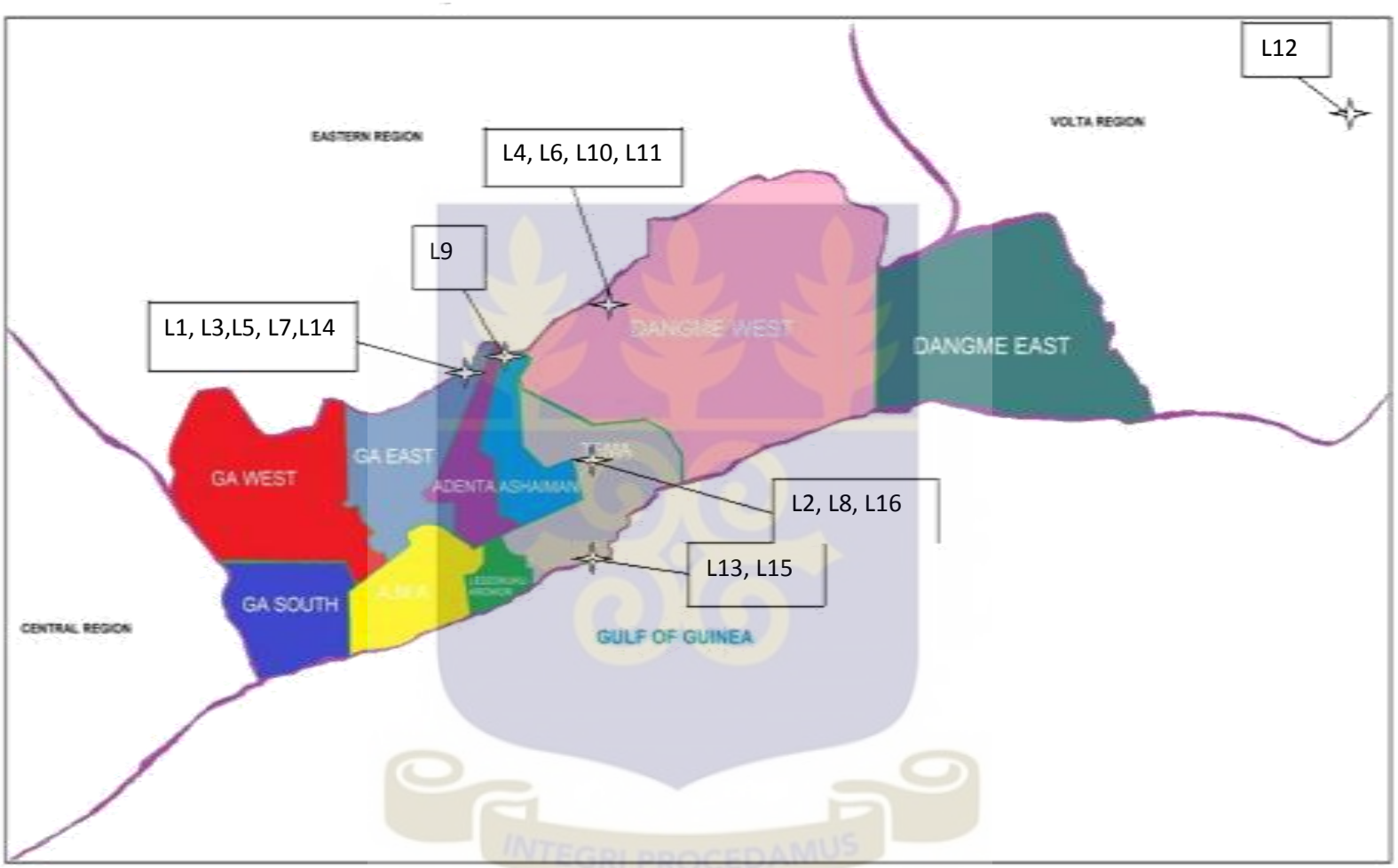


Figure 3.1: Location of different brands of BW samples used for analysis

Grab samples were obtained directly from the shelves of supermarkets and information as provided by the label was recorded. They include nutrient content, pH, FDA number, company details and water category. Accompanying labels were subsequently removed and replaced with different identities from L1 to L16 (see Appendix 1A).

3.1.1 General Sample Information.

All the bottled water (BW) samples had labels indicating brand name, water category and contact information. However, details of nutrient component or FDA registration numbers were not indicated on samples L8, L11, L13 and L15. In general, levels of trace minerals were indicated for Ca, Mg, K, NO_3^-, etc. and as well as the pH and to some extent the purification technique applied. Samples were available in polyethylene terephthalate (PET) bottles with different hermetic shapes to enhance grip and portability. Portable volumes found were 350 mL, 500 mL, 600mL, 750 mL, 1.5 L and as large as 18.9 L (for water dispensers). All BW were sealed with plastic cap and cap lid safety ring with some adding plastic wrapper around the cap. Some have the Society of the Plastics Industry (SPI) resin type symbol for PET bottles at the bottom of the bottle.

Figure 3.2: SPI resin-type symbol for PET

Bottled water are further packaged in boxes or large rubber wrappers for ease of transportation. There are 24 bottles (for 350, 500,600 and 750 mL) or 12 bottles (for 1.5 L) in a box.

3.2 Determination of NORMs

3.2.1 Sample Preparation

The water samples were transferred into 1L Marinelli beakers which are made of a chemical resistant polypropylene. Marinelli beakers are used for gamma-spectral analysis due to their light weight and their ability to eliminate leaks. Prior to filling the beaker, acetone-soaked cotton was used to wipe the inside and allowed to volatize. The beaker was subsequently sealed hermetically with paper tape and adequately labelled.

3.2.2 Energy Calibration

The relationship between peak positions and corresponding gamma ray energies are important for correct spectral analysis of a gamma spectrometer. Energy calibration is accomplished by measuring the spectrum of a source emitting gamma-rays of precisely known energy and comparing the measured peak position with energy (Gilmore, 2008). This was done using a mixed radionuclide source containing ^{241}Am, ^{109}Cd, ^{113}Sn, ^{85}Sr, ^{57}Co, ^{139}Ce, ^{137}Cs, and ^{88}Y. These radionuclides provide a range of energies between 60 keV and 2000 keV. The mixed radionuclide standard was counted long enough (36000s) on the detector (HPGe) to produce well defined photopeaks. Channel numbers generated were a function of the centroid to each full energy event on the Multi Channel Analyser (MCA).

3.2.3 Efficiency Calibration

An accurate efficiency calibration is necessary for radionuclide quantification. The ratio of the events registered by a detector system to the total events emitted by the radiation source is its efficiency. For efficiency calibration, nuclides with known accurate gamma ray emission probabilities and known source activities were used. Certified multi radionuclide standard from the Czech Metrology Institute was used to ensure proper traceability and maximum value of calibration. In general, the efficiency of detection decreases

logarithmically as a function of energy and it is dependent on the detector geometry (IAEA, 1989; Gilmore, 2008).

The standard was counted similarly as in the energy calibration and net areas corresponding to distinct energies were obtained in the spectrum. The efficiencies were determined using the equation 3.1 (Faanu et al, 2011; Darko et al, 2007)

$$\eta\,(E) = \frac{N_T - N_B}{P_E\, A_{STD}\, T_{STD}} \qquad \text{..... (eqn. 3.1)}$$

Where

$\mathbf{P_E}$ is gamma emission probability for energy (E),

$\boldsymbol{\eta(E)}$ is the efficiency of the detector,

$\mathbf{N_T}$ is the total counts under a photopeak

$\mathbf{N_B}$ is the background count

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

$\mathbf{T_{STD}}$ is the counting time of the standard.

3.2.4 Minimum Detectable Activity (MDA)

The MDA is the minimum radioactive nuclide that can be detected with a degree of certainty (Gilmore, 2008). In low level counting where the sample activity is approximately that of the background, the MDA is necessary. Under this condition the background is counted with the blank which could be the sample holder and everything else that may be counted, and the unknown if possible, except for the analyte (Kenkel, 2003). A 1.0 L Marinneli beaker was filled with distilled/deionised water and counted for 36000s. For ^{226}Ra, the minimum detectable activity was determined using average peak areas of the daughter gamma ray lines 351.92 keV of ^{214}Pb and 609.31, 1764.5 keV of ^{214}Bi. That of ^{40}K was determined using the gamma ray line at 1460.83 keV. The daughter gamma ray lines of

238.63 keV of ^{212}Pb, 583.19 and 2614.53 keV of ^{208}TI and 911.21 keV of ^{228}Ac keV were used to determine the MDA of ^{232}Th. Equation 3.2 was used to calculate the MDA,

$$\mathbf{MDA} = \frac{\sigma\sqrt{B}}{\eta PTV} \quad \text{..... (eqn 3.2)}$$

Where

σ is the statistical coverage factor equal to 1.645 (confidence level of 95%),

B is the background for the region of interest of each radionuclide,

T is the counting time in seconds,

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

V is the volume of the Marinneli beaker, and

η is the detector efficiency for the measured gamma ray energy.

3.2.5 Activity Concentration Calculation

Gamma ray spectral analysis was done using the GENIE 2000 gamma analysis software. Activity concentrations for radionuclides of interest (^{40}K, ^{232}Th, ^{226}Ra) were calculated using the equation 3.3

$$\mathbf{A_{sp}} = \frac{N_D}{pT_C\,\eta V} e^{\lambda p T_d} \quad \text{..... (eqn. 3.3)}$$

Where

$\mathbf{N_D}$ is the net counts of the radionuclide in the samples,

$\mathbf{T_d}$ is the delay time between sampling and counting,

P is the gamma emission probability (gamma yield),

η is the absolute counting efficiency of the detector system,

$\mathbf{T_C}$ is the sample counting time (s),

V is the volume (L) of the beaker,

$\mathbf{e^{\lambda pTd}}$ is the decay correction factor for delay between time of sampling and counting, and

λp is the decay constant of the parent radionuclide.

3.2.6 Calculation of Committed Effective Doses

The committed effective doses (E_{ing}) were estimated from the activity concentrations of each individual radionuclide and applying the annual water consumption rate for adults of 730 L/year and the dose conversion factors of ^{232}Th, ^{226}Ra and ^{40}K taken from the safety report 19 and UNSCEAR 2000. Equation 3.4 was used (IAEA, 2001)

$$E_{ing}(w)=A_{sp}(w).I_w.\sum_{j=1}^{3} DCFi(Th, Ra, K) \quad \text{.....(eqn 3.4)}$$

Where

$E_{ing}(w)$ is the committed doses due to ingestion.

$A_{sp}(w)$ is the activity concentration of the radionuclides in a sample in Bq/L,

I_w is the intake of water in litres per year,

DCF*i* is the ingestion dose coefficient in Sv/Bq

3.2.7 Risk Estimation Due To Ingestion

Ideally, fatal cancer and hereditary risk calculations are functions of the total effective doses. These doses are dependent on all exposure pathways i.e. ingestion, inhalation and immersion. For purposes of this study, only the risk due to ingestion of bottled water would be considered and compared to lifetime risk values of 5×10 Sv^{-1} (ICRP, 2007) to the public. The risk of exposure to low doses to members of the public who drinks bottled water were estimated and assumed 70 years lifetime of continuous exposure of the population to low level radiation.

Fatality cancer risk = E_{ing} (Sv) x cancer nominal risk factor……..(eqn 3.5)

Hereditary effect = E_{ing} (Sv) x hereditary nominal effect factor……(eqn 3.6)

Table 3.2: Detriment-adjusted nominal risk coefficients for stochastic effects after exposure to radiation at low dose rate (10^{-2}) [ICRP, 2007]

Exposed Population	Cancer		Heritable effects		Total detriment	
	2007	1990	2007	1990	2007	1990
Whole	5.5	6.0	0.2	1.3	5.7	7.3
Adult	4.1	4.8	0.1	0.8	4.2	5.6

3.2.8 Estimation of Uncertainty

Every measurement should be quoted with its associated uncertainty. This individual values are required in error propagation when calculating parameters of interest, taking into consideration the coverage factor and confidence level. In estimating the uncertainty in the activity concentrations, equation 3.3 was used.

The uncertainty would therefore be a function of the;

- Net count
- Volume
- Count time
- Detection efficiency

The total uncertainty in the activity concentration was estimated using equation 3.7 which is a modification of equation 3.3

$$dA_{sp} = A_{sp}\left[\left(\frac{dN}{N}\right)^2 + \left(\frac{d\eta}{\eta}\right)^2 + \left(\frac{dV}{V}\right)^2\right]^{0.5} \quad \text{..... (eqn. 3.7)}$$

Where

$d\mathbf{N}$ is determined from the uncertainty in the integration of the peak area of each full energy event.

$d\mathbf{V}$ is the standard uncertainty in the volume

$d\boldsymbol{\eta}$ is the uncertainty in the efficiency calibration of the counting system

3.3 Determination of Physical Parameters.

Some physical parameters were determined within 24 hours of sampling. This includes the pH, temperature, colour, total suspended solids (TSS), conductivity and turbidity. The pH of the samples was determined using a calibrated PHYWE pH-meter. A multipurpose colorimeter was also used to measure the TSS, turbidity, and colour. The instrument used was the HACH DR/890 colorimeter which operated at a wavelength of 750nm.

The instrument is codified with specific instructions to operate on number modes and specific sample volumes. For TSS, 25 mL of sample was required and a TSS number mode of 94 entered. Similarly turbidity required 10ml sample in the cell sample cuvette and number code 95 entered. Colour measurement was operated at mode 19 with 25 mL required.

Total hardness was determined by a simple EDTA titration using Erichrome black T as indicator. The EDTA was titrated against 25ml of water sample buffered with 1.5 mL NH_3. Alkalinity measurement was by a simple acid-base titration using 0.02 M HCl against 25 mL of water sample. The indicator used was methyl orange.

3.4 Determination of Some Chemical Parameters

3.4.1 Chloride

An argentometric method was employed here using 0.02 M $AgNO_3$ solution against 25ml of the water sample. The indicator used was the orange potassium dichromate $K_2Cr_2O_4$ (Pradyot, 2004). However reagent blank was first determined and so the titres were corrected values.

3.4.2 Calcium

Calcium was determined via EDTA titration against 2.5 mL of the water sample. The sample aliquot was made alkaline with 2.5 mL of 1M NaOH and swirled to obtain a homogenous mixture. Murexide was the indicator used.

3.4.3 Sulphates

External standard was used and a calibration curve drawn. UV spectroscopy was used to determine the sulphates in the sample. 1mL acidic salt was added to 10 mL aliquots of the water sample. 0.5 mL glycerol solution and 0.5 g $BaCl_2$ was subsequently added and shaken for a minute. The mixture was then allowed to stand for about 5 mins and then transferred into the cuvette of the spectrophotometer. The device was operated at 420 nm and the absorbance recorded.

3.4.4 Nitrates

An external standard was used and a calibration curve drawn. To determine nitrates, 1ml of 30% NaCl was added to 5ml of the water sample. The mixture was then acidified with 5ml of 6.5M of H_2SO_4. Consequently 0.25ml of Brucine reagent was added and warmed. The mixture was then allowed to cool for about 5mins. The device was operated at 410nm and the absorbance recorded.

3.4.5 Phosphate

An external standard was used and calibration curve drawn. 2ml of a mixture of ascorbic acid and antimony molybdate (1:4) was added to 10ml of the water sample. The device was operated at 880nm and the absorbance recorded.

3.5 Determination of Heavy Metals

3.5.1 Digestion of Samples

A mixture of concentrated nitric acid and hydrochloric acid (1:3) also known as aqua regia was added to 40 mL each water sample. It was then warmed on a hot plate for 3hours and subsequently cooled.

3.5.2 Atomic Absorption Spectroscopy (AAS)

Heavy metal determination was done using the VARIAN AA240FS spectrophotometer designed with double beam optics and deuterium lamp. Atomization of the

water samples was achieved using the flame technique. A flame atomization assembly consists of a spray chamber and a burner head. The spray chamber is equipped with an aspirator for sample intake and a nebulizer. The sample is aspirated into a spray compartment by passing a high pressure combustion gas of acetylene and air pass a capillary tube immersed in the sample.

The interaction of the sample with nebulizer set-up produces an aerosol mist which passes to the burner where the flame‟s thermal energy desolvates the aerosol mist to a dry aerosol of small, solid particles. The thermal energy then volatilizes the particles, producing a vapour consisting of molecular species, ionic species, and free atoms. The thermal energy in flame atomization is provided by the combustion of a fuel–oxidant mixture of acetylene-air in the temperature range of 2100-2400 ^{o}C.

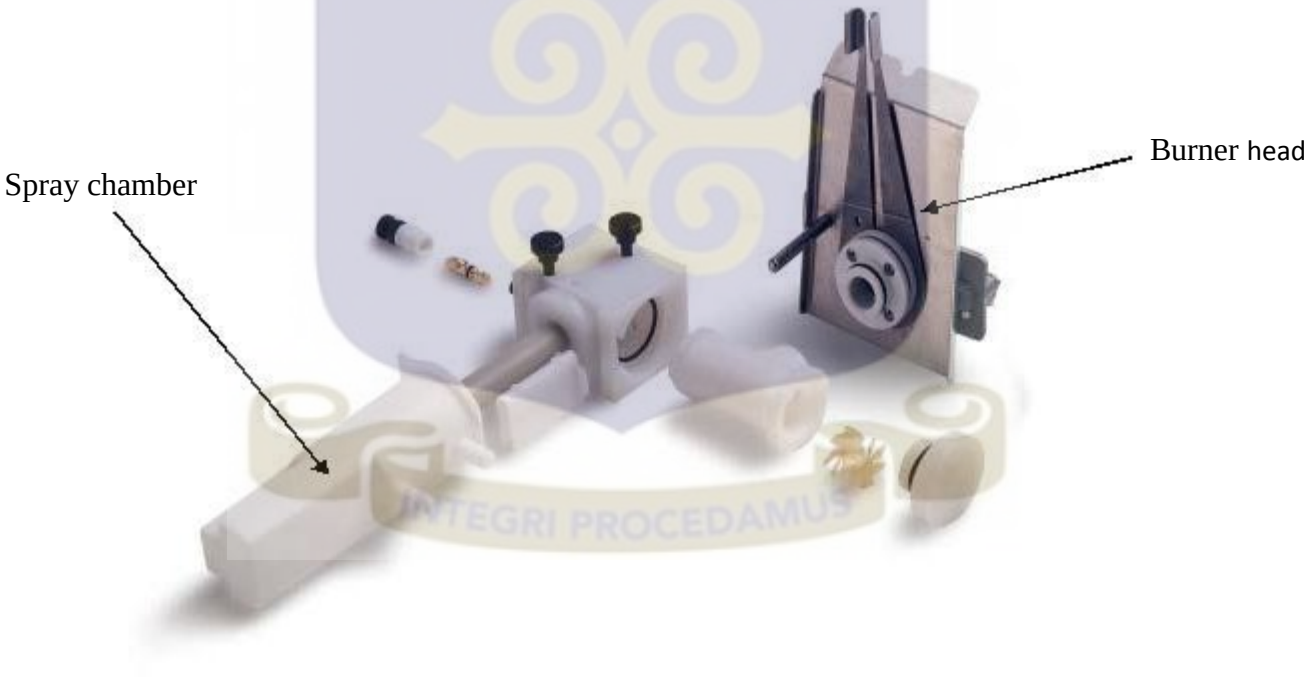


Figure 3.3: A flame atomization assembly by Varian Inc.

Standards of the metals to be determined were analysed for calibration purposes for which calibration curves were plotted (see appendix 1F).

CHAPTER FOUR

RESULTS

Sixteen brands of bottled water were analysed in this work. They were selected randomly and directly from the shelves. In all, ten (10) were of natural origin (NMW) and the remaining from municipal water systems. Labelling identities are presented in appendix 1. The results from the laboratory work are shown in Tables 4.1- 4.7 and in Figures 4.1to 4.13.

The reliability of gamma spectrometry is highly dependent on the efficiency and energy calibrations of the detection system. Mixed radionuclides from the Czech Institute of Metrology (Appendix B) were utilized used in the energy calibration of the HPGe detector. For energy calibration, a plot of energy (keV) the channel numbers was obtained (Figure 4.1). The same radionuclides were used in the efficiency calibration as shown in Figure 4.2. The MDA for the analysed radionuclides are also summarized in Table 4.1.

The estimated activity concentrations of ^{232}Th, ^{226}Ra and ^{40}K as well as the committed effective doses are summarized in Table 4.2 with an associated activity concentration chart shown in Figure 4.3. The percentage contribution of each radionuclide to the total gamma activity is shown in Figure 4.4 as well as a chart on the committed doses associated with each water brand in Figure 4.5.

Physical analysis was done on the water samples to determine pH, TDS, hardness, temperature, and alkalinity. The results for such parameters were elaborated in Table 4.3. The relationship between some physical parameters and the activity concentrations were established. It was specifically done for TDS (Figure 4.6), pH (Figure 4.7), conductivity (Figure 4.8) and temperature (Figure 4.9).

Chemical parameters were in two forms: the nutrients (i.e. Ca^{2+}, Cl^{-}, sulphates, phosphates, nitrates) and the heavy metals. Table 4.4 shows the anion concentrations in the analysed samples. Figure 4.10 shows the nutrient concentrations in water samples as well as

that of total anion concentrations in the samples (Figure 4.11). Heavy metals concentrations are shown in a graphical form in Figure 4.12. Since most of these radionuclides exist in their ionic state, the relationship between the total salt and total gamma activity was established in Figure 4.13.

An estimation of the radiation dose to different age groups was performed using the estimated annual consumption and the appropriate dose conversion coefficients (Table 4.9). Since the objective of this work was on the risk due to continuous ingestion of bottled water, an attempt was made to establish the fatality cancer risk and the hereditary risk associated (Table 4.8).

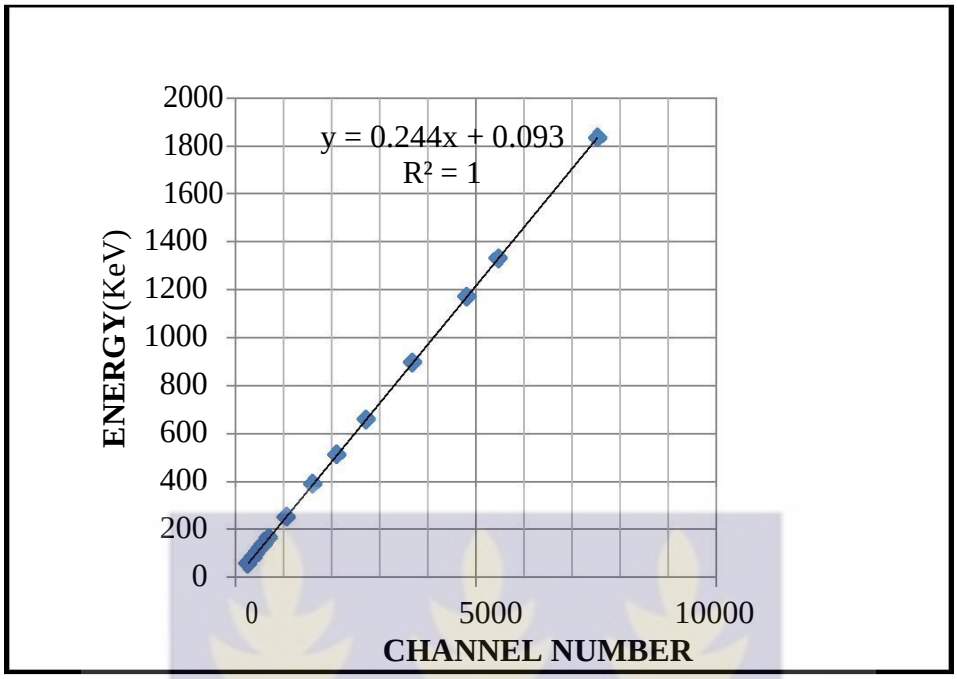


Figure 4.1: Energy calibration curve using mixed standard radionuclides (Czech Metrology Institute)

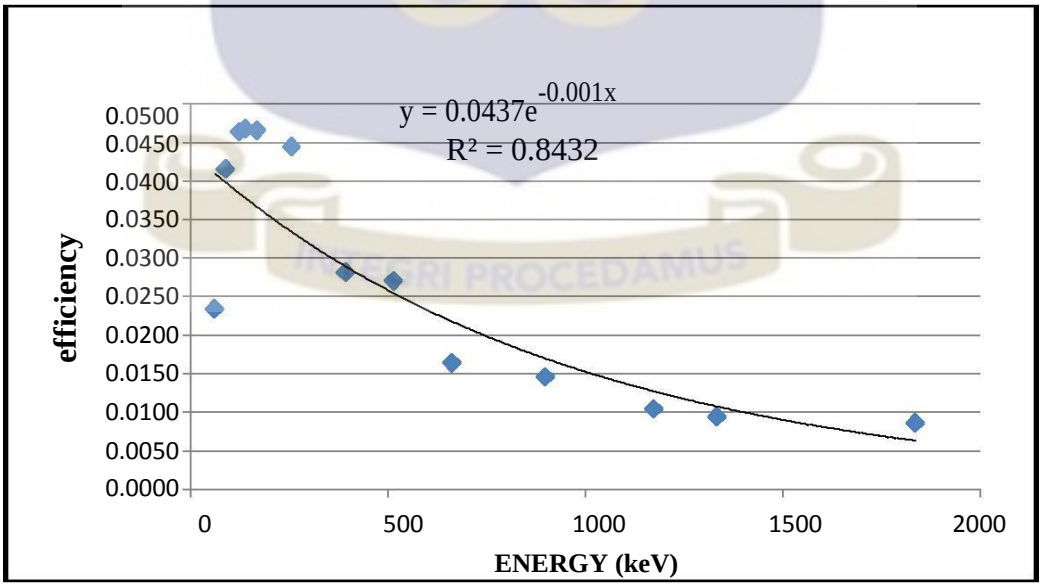


Figure 4.2: Efficiency calibration curve as a function of energy for mixed radionuclides.

Table 4.1: Minimum detectable activity of ^{232}Th, ^{226}Ra and ^{40}K

NUCLIDE	MDA (mBq/L)
^{232}Th	120
^{226}Ra	40
^{40}K	150

Table 4.2: Summary of activity concentrations and estimated annual effective doses in the bottled water samples

I.D	pH	ACTIVITY CONCENTRATION Bq/L			E_{ing} (mSv/a)
		^{40}K	^{232}Th	^{226}Ra	
L1	6.44	3.57±0.02	0.30±0.01	0.14±0.01	0.07
L2	6.32	5.36±0.05	0.44±0.20	0.08±0.01	0.10
L3	6.14	4.52±0.27	0.51±0.05	0.17±0.02	0.11
L4	5.65	4.55±0.32	0.45±0.03	BDL	0.10
L5	6.40	4.70±0.34	0.47±0.02	BDL	0.10
L6	5.97	4.37±0.28	0.46±0.03	BDL	0.10
L7	6.35	5.60±0.33	0.56±0.03	0.28±0.02	0.13
L8	5.94	4.36±0.43	0.56±0.03	BDL	0.11
L9	5.40	5.74±0.24	0.42±0.03	0.53±0.04	0.11
L10	5.02	5.05±0.26	0.37±0.02	0.18±0.02	0.09
L11	6.00	4.73±0.43	0.37±0.04	0.14±0.01	0.09
L12	5.50	4.67±0.24	0.45±0.02	0.16±0.01	0.10
L13	5.64	5.01±0.34	0.32±0.02	0.17±0.02	0.08
L14	5.80	5.41±0.41	0.36±0.03	BDL	0.08
L15	6.22	5.30±0.31	0.32±0.02	0.18±0.01	0.08
L16	6.12	4.98±0.35	0.45±0.03	0.19±0.02	0.11
Range	**5.02-6.44**	**3.57-5.74**	**0.30-0.56**	**0.00-0.53**	**0.07-0.13**
Mean	**5.93**	**4.87**	**0.43**	**0.14**	**0.10**
SD	**0.40**	**0.55**	**0.08**	**0.14**	**0.01**

Table 4.3: ANOVA table comparing the means of radionuclide concentrations

$F_{CRIT}=F_{(0.05,2,45)}=3.20$

SOURCE	SUM OF SQ	DF	VARIANCE	F_{cal}	$F_{(0.05,2,45)}$
Between	225.178	2	112.589	28147.253	3.20
Within	0.184	45	0.004		
TOTAL	225.362	47			

Table 4.4: systemic and random variances

Random variance(σ^2_{rand})	**0.004**	**$\sigma^2_{sys} >>> \sigma^2_{rand}$**
Systematic variance (σ^2_{sys})	7.040	

Table 4.5: Fishers LSD to determine source of significance difference

A-B	$\lvert\ddot{X}_A-\ddot{X}_B\rvert$	$\sqrt{[S^2_w(1/n_A+1/n_B)}$	t_{exp}	$t_{(0.05,45)}$
^{40}K-^{232}Th	4.44	0.152	29.21	1.679
^{40}K-^{226}Ra	4.73	0.152	31.12	
^{232}Th-^{226}Ra	0.29	0.152	1.91	

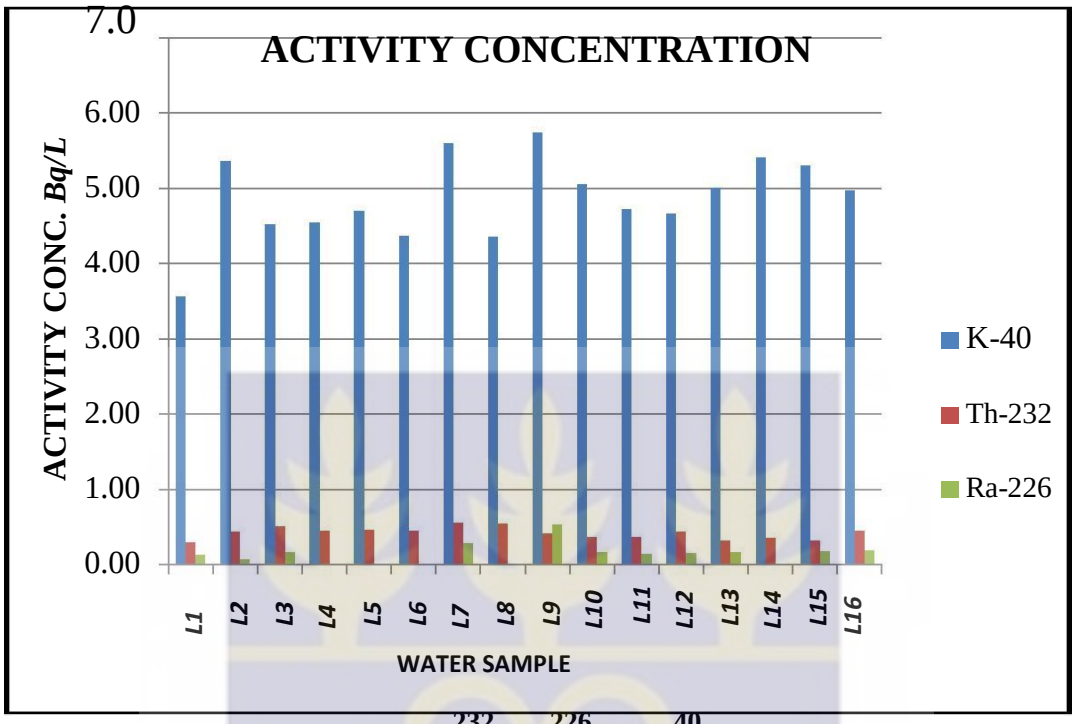


Figure 4.3: Activity concentrations of ^{232}Th, ^{226}Ra & ^{40}K in water samples

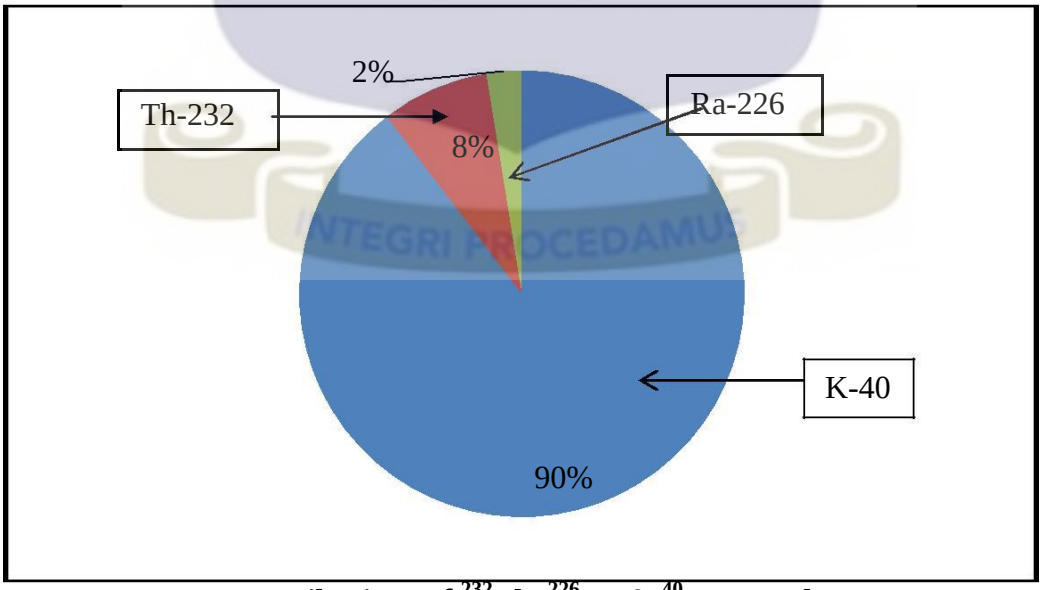


Figure 4.4: Percentage contributions of ^{232}Th, ^{226}Ra & ^{40}K to total gamma activity.

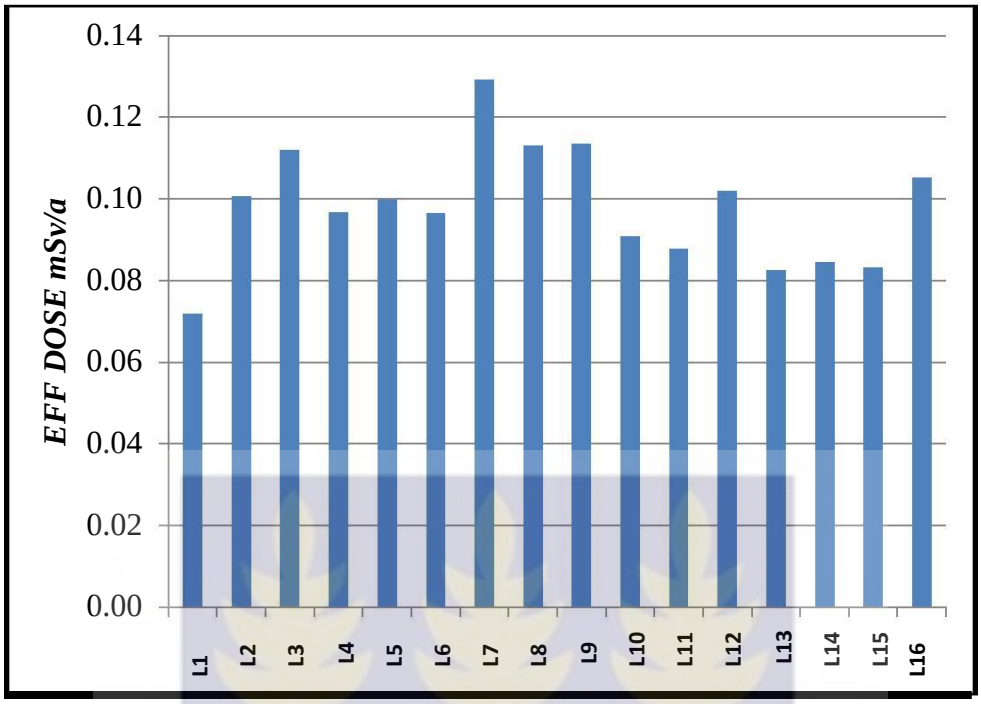


Figure 4.5: Estimated annual effective doses due to continuous ingestion of water.

Table 4.6: Physical analysis of water samples

I.D	Ph	T/^{0}C	Conductivity (µS/cm)	TDS (mg/L)	Alkalinity (mg/L)	Hardness (mg/L)
LI	6.44	25.6	874.0	480.7	14	16
L2	6.32	26.1	390.0	214.5	20	32
L3	6.14	25.9	602.0	331.7	24	36
L4	5.65	26.4	222.0	122.1	12	20
L5	6.4	27.0	121.9	67.1	12	16
L6	5.97	26.2	447.0	245.9	28	16
L7	6.35	25.8	578.0	317.9	24	36
L8	5.94	25.7	56.8.0	31.2	82	20
L9	5.40	26.4	381.0	209.6	18	16
L10	5.02	25.5	135.5	74.5	16	20
L11	6.00	25.9	73.5	40.5	10	16
L12	5.50	25.8	62.4	34.4	10	24
L13	5.64	26.4	290.0	159.5	14	8
L14	5.80	26.9	413.0	227.2	16	20
L15	6.22	26.5	524.0	231.4	20	24
L16	6.12	26.4	512.2	184.6	18	16

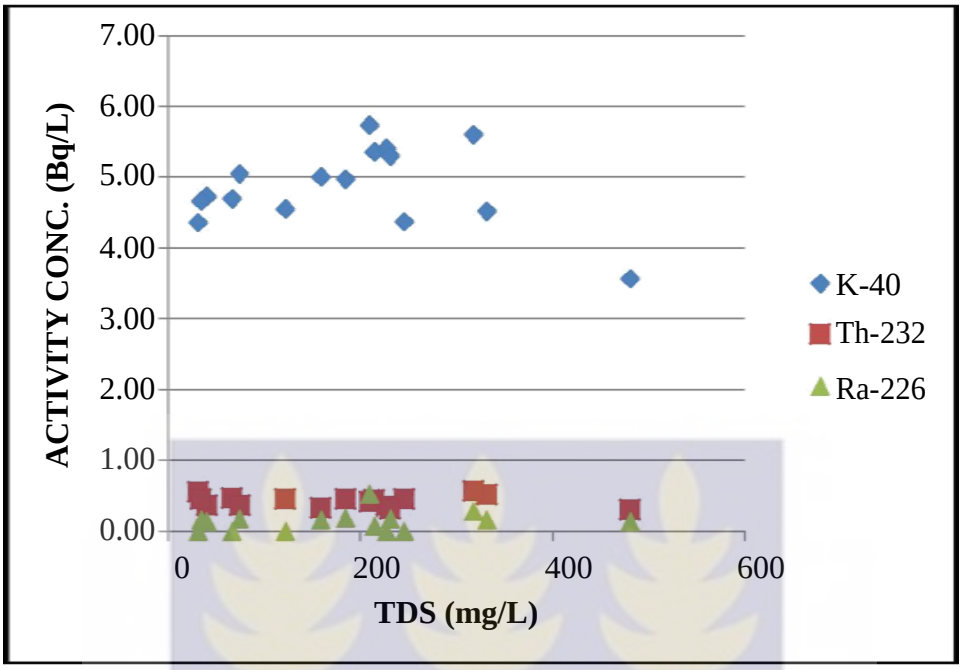


Figure 4.6: Relationship between activity concentrations & total dissolved solids

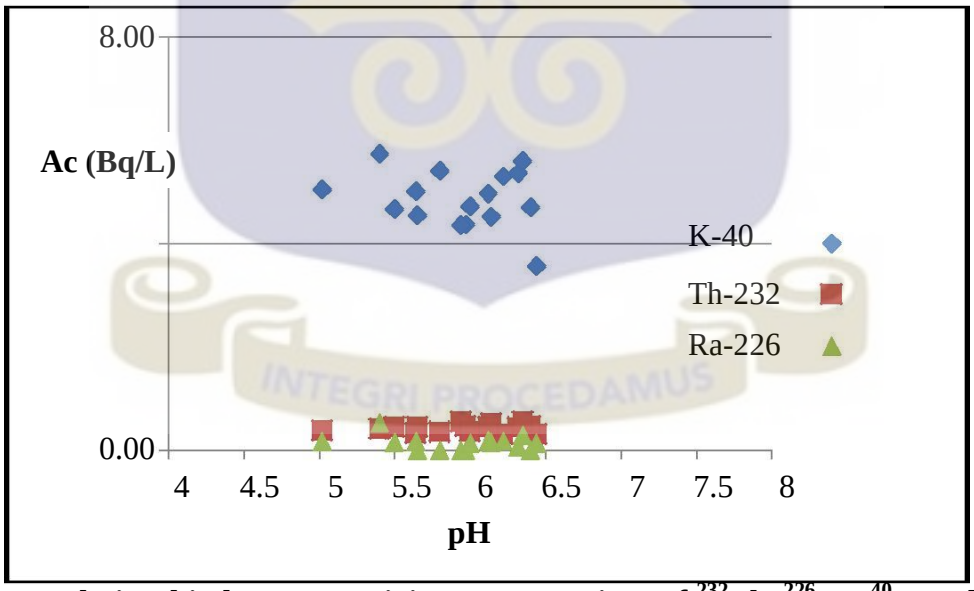


Figure 4.7: Relationship between activity concentrations of ^{232}Th, ^{226}Ra, ^{40}K and pH

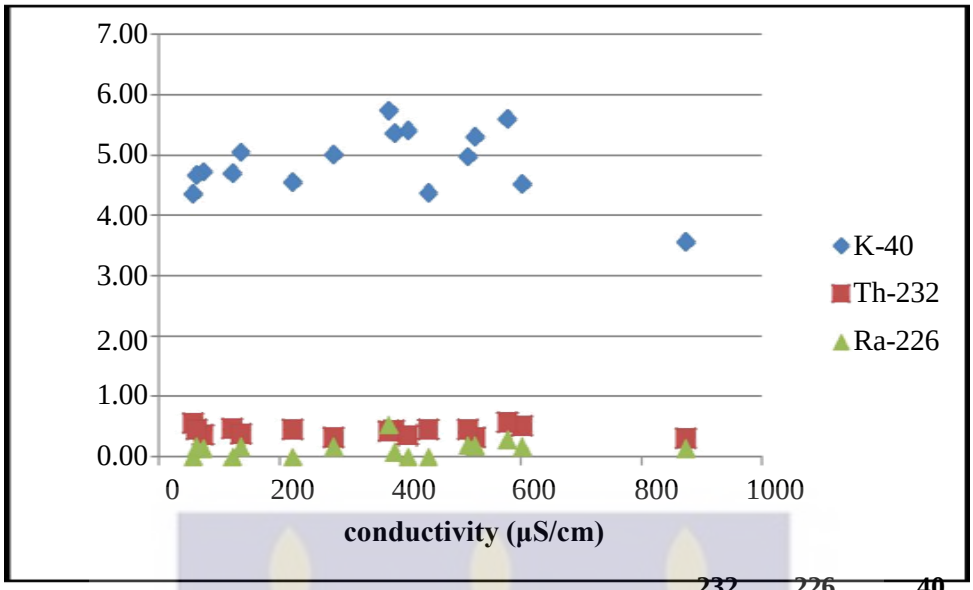


Figure 4.8: Relationship between activity concentrations of ^{232}Th, ^{226}Ra & ^{40}K and conductivity.

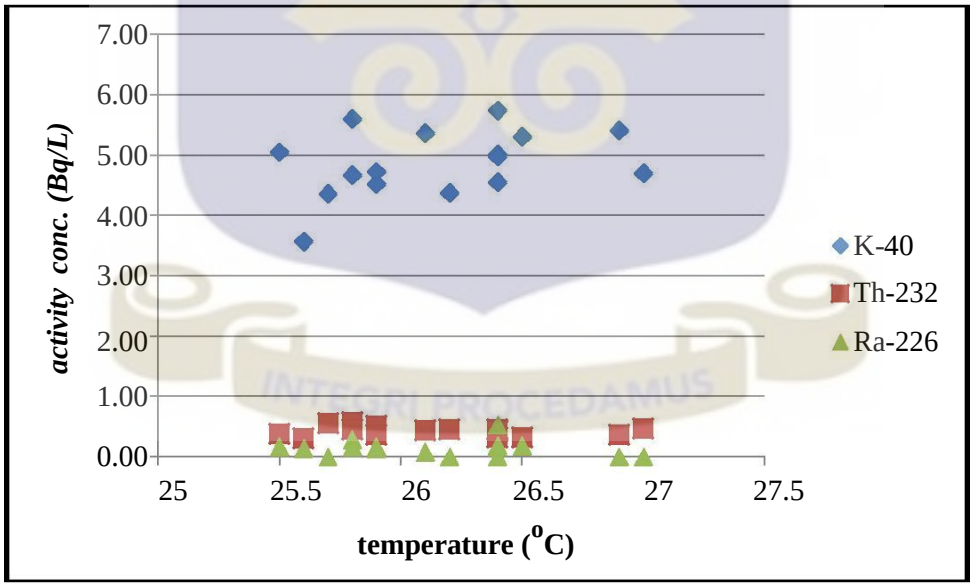


Figure 4.9: Relationship between activity concentrations of ^{232}Th, ^{226}Ra & ^{40}K and temperature

Table 4.7: Anion concentrations in the water samples

I.D	PO_4^{3-}	SO_4^{2-}	NO_3^-	Cl^-
	mg/L			
LI	0.099542	0.005336	0.007995	12.00
L2	0.083630	0.006018	0.013778	35.99
L3	0.099930	0.005144	0.009696	19.99
L4	0.082465	0.004814	0.009866	16.00
L5	0.098766	0.004946	0.006804	25.99
L6	0.080525	0.004781	0.011227	17.99
L7	0.097601	0.005127	0.007484	19.99
L8	0.080137	0.004709	0.010376	19.99
L9	0.097601	0.004940	0.006634	16.00
L10	0.082077	0.004748	0.007314	8.00
L11	0.097989	0.004929	0.012928	16.00
L12	0.082465	0.004781	0.005783	16.00
L13	0.099154	0.004836	0.009696	16.00
L14	0.082077	0.004627	0.009356	19.99
L15	0.080913	0.004676	0.007995	9.60
L16	0.093720	0.004726	0.008675	10.20

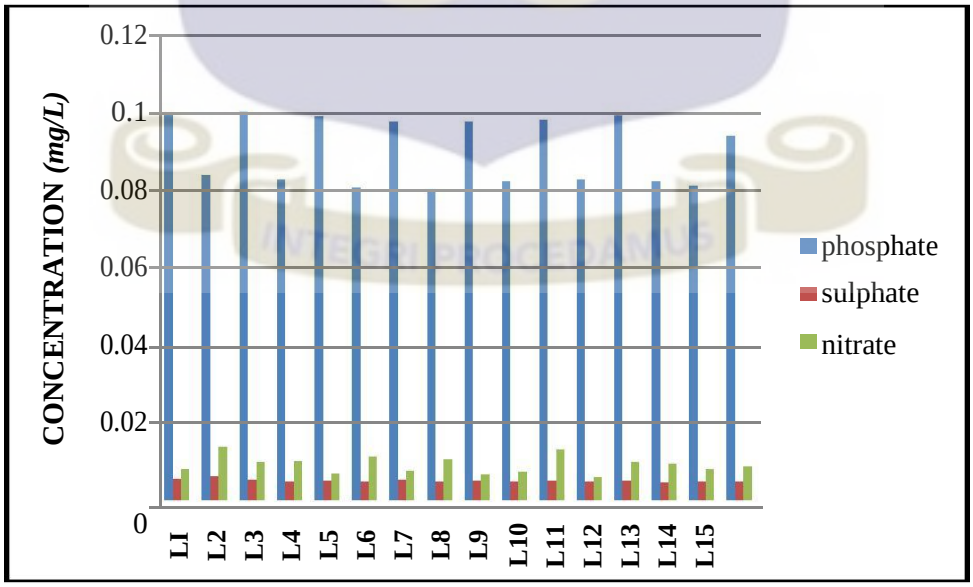


Figure 4.10: phosphate (PO_4^{3-}), sulphate (SO_4^{2-}), and nitrate (NO_3^-) concentrations (mg/L)

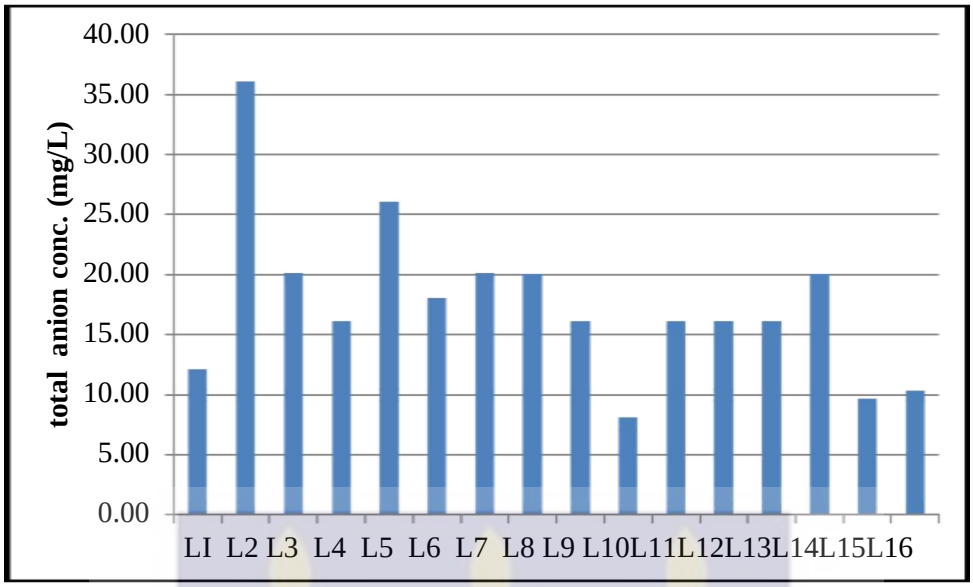


Figure 4.11: Total anion concentration (PO_4^{3-}, SO_4^{2-}, NO_3^-, Cl^-) in water samples

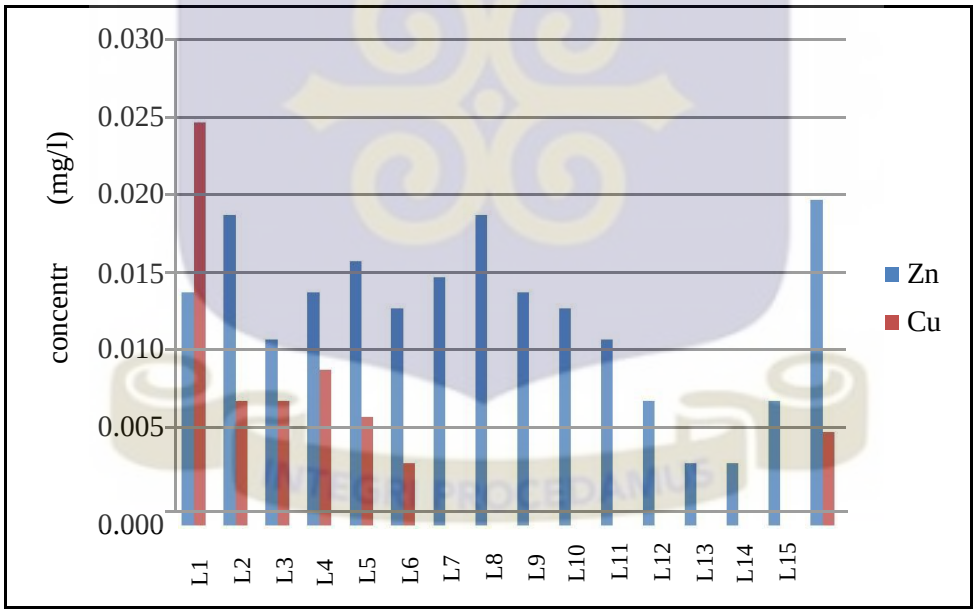


Figure 4.12: Zn and Cu concentrations in samples.

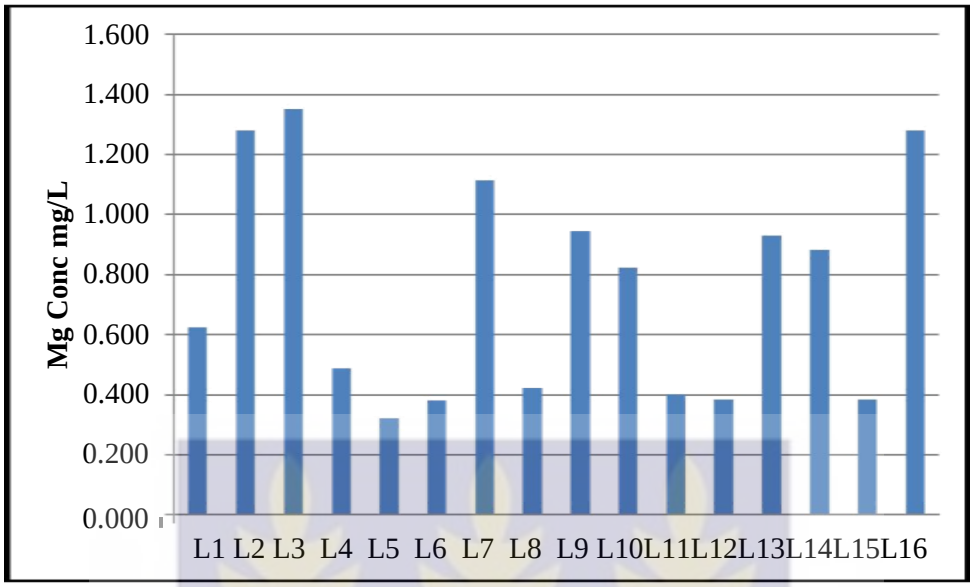


Figure 4.13: Magnesium concentrations in the water samples

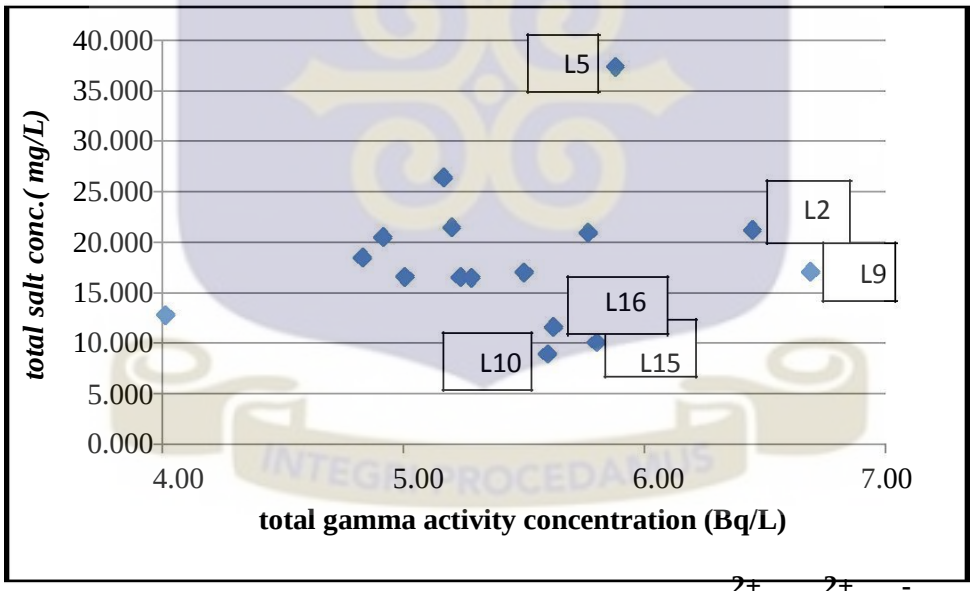


Figure 4.14: Relationship between total salt concentration (Ca^{2+}, Mg^{2+}, Cl^{-}) and total gamma activity concentration (^{232}Th, ^{226}Ra & ^{40}K)

Table 4.8: Fatality cancer and hereditary risk to adults

I.D	Fatality cancer risk $\times 10^{-7}$	Hereditary risk $\times 10^{-8}$	Total detriment $\times 10^{-7}$
L1	4.04	0.98	4.13
L2	5.65	1.38	5.79
L3	6.30	1.54	6.45
L4	5.43	1.32	5.56
L5	5.60	1.37	5.74
L6	5.43	1.32	5.56
L7	7.25	1.77	7.43
L8	6.35	1.55	6.51
L9	6.38	1.56	6.54
L10	5.11	1.25	5.23
L11	4.93	1.20	5.05
L12	5.73	1.40	5.87
L13	4.63	1.13	4.75
L14	4.75	1.16	4.87
L15	4.68	1.14	4.79
L16	5.91	1.44	6.05

Table 4.9: Radiation dose for water consumption for different age groups

ID	Age group exposure (mSv/a)					
	<1	1-2	2-7	7-12	12-17	>17
L1	0.2938	0.0458	0.0420	0.0420	0.0646	0.0719
L2	0.4164	0.0625	0.0580	0.0581	0.0890	0.1006
L3	0.4892	0.0725	0.0663	0.0659	0.1005	0.1121
L4	0.4226	0.0604	0.0561	0.0559	0.0849	0.0967
L5	0.4361	0.0623	0.0578	0.0577	0.0876	0.0998
L6	0.4265	0.0606	0.0562	0.0559	0.0849	0.0966
L7	0.5439	0.0837	0.0763	0.0760	0.1167	0.1292
L8	0.5170	0.0721	0.0665	0.0659	0.0996	0.1131
L9	0.4279	0.0747	0.0673	0.0675	0.1054	0.1136
L10	0.3593	0.0570	0.0526	0.0528	0.0815	0.0909
L11	0.3539	0.0551	0.0508	0.0510	0.0785	0.0878
L12	0.4304	0.0652	0.0598	0.0596	0.0913	0.1019
L13	0.3153	0.0511	0.0473	0.0477	0.0739	0.0825
L14	0.3360	0.0506	0.0476	0.0481	0.0738	0.0846
L15	0.3114	0.0513	0.0476	0.0481	0.0746	0.0833
L16	0.4374	0.0672	0.0616	0.0615	0.0944	0.1051

Table 4.10: statistical summary of water chemistry

I.D	pH	T/^{0}C	Cond/µS cm^{-1}	TDS /mgL^{-1}	Alk/ mgL^{-1}	Hard./ mgL^{-1}	PO_4^{3-}	SO_4^{2-}	NO_3^-	Cl^-	Zn	Cu	Mg	K-40	Th-232	Ra-226
L1	6.44	25.6	874	480.7	14	16	0.099542	0.005336	0.007995	12.00	0.015	0.026	0.624	3.57	0.30	0.14
L2	6.32	26.1	390	214.5	20	32	0.083630	0.006018	0.013778	35.99	0.020	0.008	1.280	5.36	0.44	0.08
L3	6.14	25.9	602	331.7	24	36	0.099930	0.005144	0.009696	19.99	0.012	0.008	1.350	4.52	0.51	0.17
L4	5.65	26.4	222	122.1	12	20	0.082465	0.004814	0.009866	16.00	0.015	0.010	0.487	4.55	0.45	-
L5	6.40	27.0	121.9	67.1	12	16	0.098766	0.004946	0.006804	25.99	0.017	0.007	0.322	4.70	0.47	-
L6	5.97	26.2	447	245.9	28	16	0.080525	0.004781	0.011227	17.99	0.014	0.004	0.381	4.37	0.46	-
L7	6.35	25.8	578	317.9	24	36	0.097601	0.005127	0.007484	19.99	0.016	-	1.113	5.60	0.56	0.28
L8	5.94	25.7	56.8	31.2	82	20	0.080137	0.004709	0.010376	19.99	0.020	-	0.421	4.36	0.56	-
L9	5.4	26.4	381	209.6	18	16	0.097601	0.004940	0.006634	16.00	0.015	-	0.943	5.74	0.42	0.53
L10	5.02	25.5	135.5	74.5	16	20	0.082077	0.004748	0.007314	8.00	0.014	-	0.823	5.05	0.37	0.18
L11	6.00	25.9	73.5	40.5	10	16	0.097989	0.004929	0.012928	16.00	0.012	-	0.401	4.73	0.37	0.14
L12	5.50	25.8	62.4	34.4	10	24	0.082465	0.004781	0.005783	16.00	0.008	-	0.385	4.67	0.45	0.16
L13	5.64	26.4	290	159.5	14	8	0.099154	0.004836	0.009696	16.00	0.004	-	0.930	5.01	0.32	0.17
L14	5.80	26.9	413	227.2	16	20	0.082077	0.004627	0.009356	19.99	0.004	-	0.883	5.41	0.36	0.00
L15	6.22	26.5	524	231.4	20	24	0.080913	0.004676	0.007995	9.60	0.008	-	0.385	5.30	0.32	0.18
L16	6.12	26.4	512.2	184.6	18	16	0.093720	0.004726	0.008675	10.20	0.021	0.006	1.280	4.98	0.45	0.19
min	5.02	25.5	56.8	31.2	10	8	0.080137	0.004627	0.005783	8.00	0.004	-	0.322	3.57	0.30	-
max	6.44	27.0	874	480.7	82	36	0.099930	0.006018	0.013778	35.99	0.021	0.026	1.350	5.74	0.56	0.53
mean	5.93	26.1	355.2	185.7	21.12	21	0.089912	0.004946	0.009100	17.48	0.013	0.004	0.751	4.87	0.43	0.14
SD	0.40	0.4	234.5	124.8	17.05	7.80	0.008535	0.000344	0.002233	6.77	0.005	0.007	0.369	0.55	0.09	0.14

CHAPTER FIVE

DISCUSSION

5.1 Sampling

There are more than twenty branded bottled water in Ghana but the decision to select the sixteen brands were due to the following;

- The availability and distribution in the country
- The market consistence of the brands
- Accessibility of the brands.

The availability has to do with the brand presence in all regions of the country. Some BW brands are made for specific localities and regions and do not have countrywide presence hence their rejection. In terms of consistency, certain brands have a reputation of pulling out of the market periodically. Some are out of business but not completely shut down. Accessibility issues have to do with the ease of BW acquisition and usage. Though they come in different capacities, 1.5L option was chosen so as to obtain enough volume for both the NORM determination by γ-spectrometry and physicochemical analysis.

Bottled water brands were obtained randomly and directly from the shelves so as to directly mimic the exact mode by which the brands were obtained. This would imply the estimated committed doses would represent consumer doses due to BW intake. The brand identities were removed and relabelled (Aappendix 1A) solely for objectivity purposes. These brands were already sealed with safety caps as well as additional polythene seals. Acidification (using HNO_3) before transportation as in the practice for freshwater samples was not done. The reason for not acidifying prior to transport was the fact that radionuclides that may stick to the container walls need not be reintroduced into the water since the consumer would not ingest it either.

5.2 γ-Ray Spectrometry

5.2.1 Energy & Efficiency Calibrations

Energy and efficiency calibrations were performed to establish the reliability and accuracy of the HPGe detector system using a mixed standard radionuclide (appendix B) with wide range of energies. Calibration curve for energy showed a perfect linear correlation (R^2=1) which means the detector system and the electronics are well synchronized and operating well as shown in Figure 4.1.

The calibration plot for efficiency was an exponential one with a strong correlation (R^2=0.84). Efficiency calibration is necessary for radionuclide quantification as it gives an idea about detection of events by a detector. The efficiency is estimated to be 84%

5.2.2 Activity Concentrations

Background measurements were performed using distilled/deionised water in a cleaned (acetone) 1L Marinelli beaker. The estimated activities were the minimum detectable activities (MDA) in Table 4.1. These values were used in background correction to ensure corrected activities were solely that of the sample.

In general, nuclides identified were ^{226}Ra (γ-ray lines of 351.92 keV of ^{214}Pb and 609.31, 1764.5 keV of ^{214}Bi), ^{232}Th (γ-ray lines of 238.63 keV of ^{212}Pb, 583.19 keV and 2614.53 keV of ^{208}TI and 911.21 keV of ^{228}Ac) and ^{40}K (γ-ray lines of 1460.83 keV). Higher activity concentrations were estimated for ^{40}K in the range of 3.57 Bq/L to 5.74 Bq/L. This was expected since ^{40}K is abundant in natural systems and could also be as a consequence of potassium ion-exchange resins used by some treatment facilities. Sample L9 showed higher potassium levels followed by L7, L2 and L14 (Figure 4.3). Though specific guidance values are not given for this nuclide due to the normally low risk levels associated, critical groups like children (<1) and patients suffering from renal failure, hypertension, diabetes etc. may be

susceptible to its presence. This means patients should consult their doctors for special advice.

Thorium-232 levels were about three times higher than ^{226}Ra with a mean reported value of 0.43Bq/L ranging from 0.30Bq/L to 0.56Bq/L. This was expected due to the fact that the most of the samples were slightly acidic and ^{232}Th is soluble in groundwater than in surface waters. It was highest in samples L7 and L8 with L3 following. ^{232}Th levels were below recommended guidance levels of 1Bq/L (WHO, 2011). Though radiotoxicity categorization had not been established for ^{232}Th, its long term health effects cannot be underestimated. The major concern to low exposure is the risk of lung and pancreatic cancer (US-EPA, 2015).

^{226}Ra levels were the lowest with a mean of 0.14Bq/L and maximum of 0.53Bq/L. Some showed no activity in the energy ranges of the reference daughter radionuclides and therefore classified as below detection limit (BDL). ^{226} Ra emits alpha particles with associated gamma rays. As long as it remains outside the human body, ^{226} Ra poses little hazard. If however ingested, its radioactivity may lead to an elevated risk of lung and bone cancer. It is chemically toxic at high concentrations and may affect critical organs like the kidney and lungs. The provisional guideline in drinking water is 1Bq/L (WHO, 2011). The measured values were far below this level.

Summarily activity concentrations were in the order ^{40}K > ^{232}Th > ^{226}Ra. An analysis of variance (ANOVA) conducted on the data showed far higher calculated F-value to the critical F-value (F_{cal}>>>F_{crit}) at the 0.05 significance level (Table 4.3, appendix C). This implies at least one of the data set is significantly different from the others. An attempt was made to establish if the difference is due to systemic variances (σ^2_{sys}) or random ones (σ^2_{rand}). The result (Table 4.4) proved that variance due to systemic difference between the samples is an order of magnitude greater

than the variance due to the methods precision ($\sigma^2_{sys} >> \sigma^2_{rand}$). This means the results are due to the inherent properties of the samples and not attributable to the γ-spectroscopy method. Again an attempt was made in determining which of the sample means resulted in the significant differences. A Fisher Least Square Differences (LSD) approach was used (Table 4.5) at 95% confidence interval. Significant systemic differences occurred between the means ($t_{exp} > t_{0.05,45}$) of the respective activity concentrations of ^{40}K, ^{232}Th and ^{226}Ra.

5.2.3 Committed Effective Dose (A_D)

The A_D was estimated from the activity concentrations of the identified radionuclides taking into consideration, the annual water consumption rate (IAEA, 1996.) and the appropriate ingestion dose conversion coefficients (ICRP, 2012). Various age groups were also considered as the critical group exist in this domain (Appendix 1D). The recommended effective dose is 0.1mSv/y (WHO, 2011: GSB, 1998). Generally there were low A_D estimated from ages 1 and above. For the adult group (>17yr), the maximum estimate was 0.1292mSv/y corresponding to sample L7. A_D estimates for this group were slightly closer to the guidance value which is expected mainly due to their high average water consumption rate. The preceding age group (12-17) also had relatively higher A_D though below the recommended value. The mean for this group was 0.0879mSv/y with an associated 0.0135 standard deviation. Ages 1-12 however showed very low annual doses, about 1.75 times lower than the recommended values. The one of concern is in the infants (<1yr); estimates were higher than recommended values with the lowest being 0.2948mSv/y and the highest of 0.5439mS/y, the mean estimate here was 0.4073mSv/y. Though this is high, it is important to note that about 95% is due to gamma activity from ^{40}K. A baby at this stage is supposed to be on exclusive breastfeeding for which reason it is not expected to be introduced to such activity 'loads'.

However, knowing the recent trend where busy mothers prefer to prepare infant formulas, bottled water may not be appropriate.

5.2.4 Relationship between Activity Concentrations (A_c) Some and Physical Parameters

Various physical parameters were analysed to establish their relationship with activity concentrations. These parameters are known to influence the availability and measurement of activity concentrations.

5.2.4.1. Activity Concentration (A_c) & pH

Though no health based guideline has been established for pH, it is important in water quality perceptions. The recommended range is 6.5-8 for drinking water but for bottled water where manufactures may deliberately alter the organoleptics, the pH might go beyond this range. The observed pH range was 5.02-6.44 (Table 4.6). The relationship between the activities and pH is shown in Figure 4.7. The sample data points were clustered in the pH range of 5.5-6.5 with the exception of one data point far below 5.5. This implies the radionuclides were predominantly present at pH 5.5-6.5 hence their identification. However no conclusion can be made on how pH increase or decrease could affect radionuclide availability since such studies was not conducted in this work. pH is logarithmic scale for expressing the H^+ concentration in a solution. It a range from 0-14 of which below 7 is classified as acidic, at 7 is neutral and above 7 is alkaline. One importance of pH is that it affects the solubility hence the mobility and availability of metals and radionuclides. It also has an effect on the toxicity of some elements.

5.2.4.2. Activity Concentration (A_c) & Total Dissolved Solids (TDS)

TDS is as a result of dissolved inorganic and organic substances in water. It affects the taste hence the acceptability requirements of consumers. Though there is no proposed health based guideline, TDS values below 600mg/L is usually acceptable (WHO, 2011). TDS values ranged from 31.2mg/L to 480.7mg/L (Table 4.6). This is far less than the conventional reference hence an unexpected effect on palatability of the water. Figure 4.6 shows the

relationship between TDS and activity concentrations. Generally there was positive linear correlation between TDS and activities. This might due to the fact that most of the samples (especially the NMW"s) were sourced from the same aquifer region (granitic aquifers of the pre-Cambrian basement). However there were exceptions: brands L1, L9 and L14 data points did not fit into the pattern. For L1 it was expected due to the fact that water treatment is done by naturally passing it through layers of sand, clay, limestone and granite. TDS is very important in gross alpha/beta measurements as it serves as a limiting factor but it has no effect in gamma spectroscopy since gamma rays can penetrate any thickness imposed by the dissolved solids.

5.2.4.3. Activity Concentration (A_c) & Conductivity

Ions present in water are constantly in motion and this creates a mild electric current which is measured conductance. Both natural and artificial processes that occur in raw water and during treatment could introduce inorganic Ions both of cationic and anionic nature which may influence the electrical conductivity. Figures 4.8 and 4.13 best describe the relationship between ions and activity. In Figure 4.8 activity concentrations showed strong positive correlations with conductivity with the exception of sample LI whose data was considered an outlier. A closer look at Figure 4.13 showed a slightly linear relationship with the exception of samples L2, L5, L9, L10, L15 and L16. As a rule, activity concentration tends to higher concentrations with higher mineralization however the exceptions could be due to the different treatment procedures employed.

5.3 Anion Concentrations

Figure 4.10 shows the concentrations of the above parameters in the water sample. This was done spectrophotometrically after running standards and calibration curves drawn (appendix E). Their concentrations were in the order PO_4^{3-} > NO_3^{-}>SO_4^{2-} but were all together below danger limits. Phosphates are very dominant in granite rocks and surface

waters. Radium predominantly exists in phosphate forms (together with uranium) and as such can be found in granite areas (Lieser, 2001). Nitrates in the infant are converted by the body to nitrites that oxidize blood haemoglobin to methaemoglobin. The altered bloods cells can no longer carry oxygen, which can result in brain damage or suffocation (WHO, 2011). Higher sulphate levels can induce laxative effects in consumers and hence it is less desired. Though there is no health based guidance level on this, 250mg/l is used conventionally as a benchmark. Chloride concentration was determined by argentometric titration and they were below conventional levels of 250mg/L. Higher chloride levels result in salty taste to water.

5.4 Risk Assessment

The ICRP risk assessment methodology (ICRP, 2007) was used in evaluating the fatality cancer and hereditary risk. The ICRP predicts that, with the availability of new data on dose-response due to low dose range, that below and around 100mSv, it is scientifically reasonable to assume that the incidence of cancer or hereditary effects will rise in direct proportion to an increase in the equivalent dose in the relevant organs or tissues (ICRP, 2007). The evaluation of risk covered only the exposure pathway considered in this study-ingestion.

The range of fatality cancer risk is 4.04-7.25($\times 10^{-7}$). This means at a minimum 4 persons out of 10million people would suffer fatal cancer on continuous ingestion of BW. The range of hereditary effect is 0.98-1.77 ($\times 10^{-8}$). A similar low risk analogy can be drawn to which the hereditary effects are extremely low. The total detriment is combination of both the fatality cancer risk and the hereditary risk hence the total detriment as in Table 4.6 can be said to be very low.

5.5 Heavy & Trace Metals

Atomic absorption spectroscopy (AAS) was used in the determination of Zn, Cu, Pb, Cd and Mg. Lead and cadmium were below detection limits as well as Cu being below detection limit in some of the samples. For magnesium a calibration curve was obtained (appendix E). However, zinc was present in all the samples with a higher level in L16 (table 4.10). Though there is no guideline level set for zinc, at about 4mg/L, it impacts bad taste and appear as oil on surface waters. Copper levels were below recommended levels of 2mg/L with the highest measure value occurring in sample L1. Copper has the ability of impacting colour and a bitter taste to drinking water for which reason a higher concentration would affect its taste hence the organoloeptics.

CHAPTER SIX

CONCLUSION & RECOMMENDATIONS

6.1 Conclusion

Sixteen brands of nationwide presence was analysed for natural radioactivity using gamma spectrometry. Activity concentrations of the NORMs analysed were generally low which resulted in low effective doses below recommended levels. ^{40}K activity concentrations were in the range of 3.57-5.47Bq/L, the highest occurring in sample L9. Similarly ^{232} Th activity concentrations were in the range of 0.30-0.56 Bq/L with the highest occurring in sample L8. ^{226}Ra was identified in eleven brands with the remaining below detection limit. The highest value (0.53Bq/L) occurred in sample L9. Comparison of the mean concentrations showed significant differences at α=0.05. The identified radionuclides contributed to systemic statistical differences. None of the radionuclides exceeded the maximum allowable averages for drinking water worldwide.

Radiation protection is premised on the prevention of deterministic effects and minimizing stochastic effects. This is done using a system of protection that requires justification of practice to ensure it produces a net benefit, optimisation of protection to keep exposures as low as reasonably achievable (ALARA) and the protection of individuals by imposing either dose limits or controls on the risks from potential exposures. Consequently, the potential exposure was evaluated by estimating the annual effective doses due to ingestion of BW by the population. The estimated committed effective doses were generally below 0.1mSv/a for all age groups with the exception of children <1yr. This should be situated in the context of the radionuclide's toxicity. However, protecting infants from associated health risks of exposure provides justification for additional costs that might be incurred in the re-examination of the water treatment procedures in the country.

Estimated lifetime cancer and hereditary risk was done using the ICRP risk assessment methodology (2007). The negligible cancer fatality risk value recommended by USEPA is in the range of 1×10^{-6} to 1×10^{-4}, however the estimated fatality cancer risk were far below the recommended minimum. Therefore bottled water on the Ghanaian market is radiologically safe and there is no need for special radiological assessment.

Relationship between Activity concentrations and some physicochemical parameters were established. The significant one was the conductivity parameter and how estimated activity concentrations tend to correlate. Higher mineralization in natural waters tends to introduce ions of different state and depending on the geochemistry of these systems, a significant amount is dissolved. This property is severely exploited by BWC"s for marketing purposes and influencing consumer perceptions.

The results from this study will serve as reference data for any future studies and also add up to data required to help develop guidelines for the regulation of NORM in Ghana.

6.2 Recommendations

- Determination of gross alpha/beta concentrations in BW on the Ghanaian market using gross alpha/beta counter.
- Radiochemical characterization of BW for naturally emitting alpha-emitters on the Ghanaian market using α-spectrometry.
- Periodic appraisal of treatment technologies used by bottled water companies. This should be enforced by the FDA and GSA
- Normal health and occupational protection measure are enough to protect against future radiological hazards. The radiation protection authority should maintain their surveillance.

REFERENCES

Agyekum W., (2002). Groundwater resources of Ghana with focus on the International Shared Aquifer Boundaries. CSIR-WRI. Proceedings of the international workshop in Tripoli, Libya, 2nd-4th June.

Awudu A. R., Glover E.T., Kpordzro R. (2011). Determination of radionuclides in underground water sources within the environments of University of Cape Coast. J. env. And Earth Sci. 3(3): 269-274.

Back W., Landa E.R. & Meeks L., (1995). Bottled water, spas & early years of Water Chemistry. Groundwater vol 33. Issue 4th ed. p 606-614

Cember & Johnson, (2009). Introduction to Health Physics. McGraw –Hill.4th edition.

Choppin G., Liljenzin J., Rydberg J, (2002). Radiochemistry and Nuclear Chemistry. Butterworth-Heinemann, 3rd Ed.

Codex alimentarius commission (2008). Codex standard for natural mineral waters. CODEX STAN 108-1981. Rome, Italy.

Dapaah-Siakwan & P. Gyan-Boakye (2000). Hydrogeological framework and borehole yields in Ghana. Hydrogeological journal. Vol 6. No.4. pp. 405-416.

Darko, E. O and Faanu, A. (2007). Baseline radioactivity measurements in the vicinity of a Gold Treatment Plant, J. App. Sci. and Tech., Vol. 10, Ghana.

Harvey David, (2000). Modern Analytical Chemistry 1st ed. McGraw Hill Company Inc.

Doria M. F., (2006). Bottled water versus Tapwater: Understanding Consumers" Preferences. Journal of water and health, 04.2

Dozol M. & Hagemann R., (1993). Radionuclide Migration in Groundwater: Review of the behavior of Actinides. J. pure appl. chem. 65.1081.

Dragani G, Draganic Z. D., Adloff J. P., (1990). Radiation and Radioactivity on the Earth Surface and Beyond. CRC press, Boca Raton, Florida

Dueñas C., Fernández M. C., Lieger E., Carretero J., (1997). Natural Radioactivity levels in bottled water in Spain. J. Water Res., vol. 31. No. 8, pp1919-1924.

Durance E. M., (1986). Radioactivity in Geology. Principles and Applications. Ellis Horwood, Chichester.

Norman E. B., (1994). Stellar Alchemy: The origin of the Chemical Elements. J. chem.educ. 71,813.

Faanu A., Darko E.O. & Ephraim J. H., (2011). Determination of Natural Radioactivity in soil and rock samples in a mining area in Ghana. J. Appl. Ecology, vol 19.

FAO, (2015). Irrigation in Africa in figures, AQUASTAT survey. Rome, Italy.

Gbadago J. K., Faanhof A., Schandorf C., (2011). Contribution of Natural Radionuclides in a domestic water of two critical gold mining communities in Ghana. J. Water Qual. Expo. Health.

Ghana National Commission for UNESCO, Water for Life Report (2008). Accra, Ghana.

Gilmore G. R., (2008). Practical Gamma Ray Spectrometry. 2nd ed. John Wiley & Sons Ltd.

Gyau-Boakye & Dappah-Siakwan, (2000). Groundwater as a source of rural water supply in Ghana. J. Appl. Sci. and Tech.. Vol.5, no.1&2. Pp77-86.

IAEA, (2001). Generic models for use in assessing the impact of discharges of radioactive substances to the environment. Safety report series 19, Vienna, Austria.

IAEA. (1989). Measurement of Radionuclides in Food and Environment: A Guidebook, IAEA-Technical Reports Series No. 295, Austria.

ICRP, 2007. The 2007 Recommendations of the International Commission on Radiological Protection. ICRP Publication 103. Ann. ICRP 37 (2-4).

ICRP, (2012). Compendium of dose coefficients based on ICRP publication 60. 1CRP publication 119. Ann. ICRP 41 (suppl.)

Jobbágy V., Dirican A., Wätjen U., (2013). Radiochemical Characterization of mineral water for a European interlaboratory comparison. Microchemical journal, 110, 675-680.

Junner N.R. & Hirst T. (1946). The geology and hydrology of the Volta basin. Gold Coast Geological Survey (Memoir 8).

Karamanis D., Stamoulis K., Ioannides K. G., (2007). Natural Radionuclides and Heavy metals in bottled water in Greece. J. Water Desalination 213, 90-97.

Kenkel J., (2003). Analytical Chemistry for Technicians, 3rd ed. CRC press LLC. Boca Raton, Florida.

Kortatsi B.K (1994): Groundwater Utilization in Ghana. Proceedings of international conference. Helsinki, Finland.

Lieser K. H., Ament A., Hill R., Singh R. N., Stingl U. & Thybusch B., (1990). Colloids in Groundwater and their influence on migration of trace elements and Radionuclides. Radiochim, hota. 49, 83.

Lieser K., (2001). Nuclear & Radiochemistry Fundamentals and Applications. Wiley-VCH, 2nd ed. Germany.

Loveland, Morrisey and Seaborg, (2006). Modern Nuclear Chemistry. Wiley & Son Inc, New Jersey.

Maddock A.G., Willis E.H., (1961). Atmospheric Activities and Dating Procedures. Adv. Inorg.radiochem.2, (287).

Manahan Stanley E. "Frontmatter", (2000). Env. Chemistry. 7th ed. Boca Raton. CRC press LLC.

Oyelude & Ahenkorah, (2012). Quality of Sachet Water and Bottled Water in Bolgatanga Municipality of Ghana. Journal of Applied Sciences, Engineering and Technology 4(9): 1094-1098.

Pradyot Patnaik, (2004). Deans Analytical Chemistry Handbook. 2nd ed. McGraw Hill Inc.

TISDA launch report, (May 2011).Ghana"s national water supply integrity studies, Ghana integrity initiative. Accra, Ghana.

United Nations, (2010). UNSCEAR 2008 report. Source and Effects of Ionizing Radiation, vol. 1. New York.

United Nations, (2013). The millennium development goals report 2013, New York.

USEPA. (2006). Edition of the Drinking Water Standards and Health Advisories, EPA 822-R-06-013, Washington DC.

Warner G. & Jabbar T., (2010). Natural radionuclides in Austrian bottled mineral waters. J. Radioanal. Nucl. Chem.., 286,329-324.

World Water Assessment Programme. 2009. The United Nations World Water Development Report 3: Water in a Changing World. Paris: UNESCO, and London: Earthscan

WHO, (2011). Guidelines for drinking- water quality, 4TH ed. Geneva, Switzerland.

APPENDIX 1

A **brands and assigned I.D**

BRAND	I.D	CATEGORY
Voltic	L1	NMW
Bel-aqua	L2	PW
Aqua fill	L3	NMW
Valley fresh	L4	NMW
Nero	L5	NMW
Bueno	L6	NMW
Verna	L7	NMW
Everpure	L8	PW
Special ice	L9	NMW
Vaettel	L10	NMW
Icepak	L11	PW
ESE	L12	NMW
Aquasplash	L13	PW
Ecospa	L14	NMW
Bonaqua	L15	PW
Ice cool	L16	PW

NB the arrangement is in no specific order of preference

B **mixed radionuclides used in energy & efficiency calibration**

radionuclides	channel no.	Gamma ray energy	Efficiency
^{241}Am	244.45	59.5412	0.0235
^{109}Cd	361.13	88.04	0.0416
^{57}Co	500.44	122.0614	0.0464
	559.4	136.4743	0.0468
^{139}Ce	679.78	165.864	0.0467
	1045.42	255.05	0.0445
^{113}Sn	1604.59	391.69	0.0282
^{85}Sr	2105.6	514.007	0.0271
^{137}Cs	2710.71	661.66	0.0165
^{88}Y	3679.58	898.042	0.0146
^{60}Co	4808.01	1173.237	0.0105
^{60}Co	5461.15	1332.501	0.0095
^{88}Y	7527.48	1836.063	0.0086

C **ANOVA Table**

SOURCE	SUM OF SQ	DF	VARIANCE	F_{cal}	$F_{(0.05,2,45)}$
Between	225.178	2	112.589	28147.253	3.20
Within	0.184	45	0.004		
TOTAL	225.362	47			

Systemic and random variances

Random variance(σ^2_{rand})	0.004	$\sigma^2_{sys} >>> \sigma^2_{rand}$
Systematic variance (σ^2_{sys})	7.040	

Fisher LSD test

A-B	$\lvert\ddot{X}_A-\ddot{X}_B\rvert$	$\sqrt{[S^2_w(1/n_A+1/n_B)}$	t_{exp}	$t_{(0.05,45)}$
^{40}K-^{232}Th	4.44	0.152	29.21	1.679
^{40}K-^{226}Ra	4.73	0.152	31.12	
^{232}Th-^{226}Ra	0.29	0.152	1.91	

D **Dose conversion factors (E_g) for ingestion. (ICRP, 2012)**

Radionuclide	**<1**	**1-2**	**2-7**	**7-12**	**12-17**	**>17**
^{232}Th	4.6e-06	4.5e-07	3.5e-07	2.9e-07	2.5e-07	2.3e-07
^{40}K	3.9e-08	4.2e-08	2.1e-08	1.3e-08	7.6e-09	6.2e-09
^{226}Ra	4.7e-06	9.6e-07	6.2e-07	8.0e-07	1.5e-06	2.8e-07

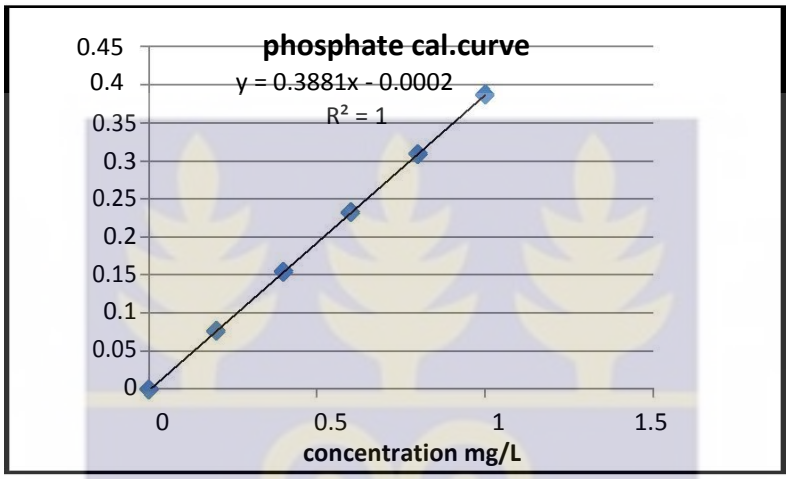
E **Water consumption rate (L/a). (IAEA, 1996)**

Age group	**<1**	**1-2**	**2-7**	**7-12**	**12-17**	**>17**
I_w	200	260	300	350	600	730

F

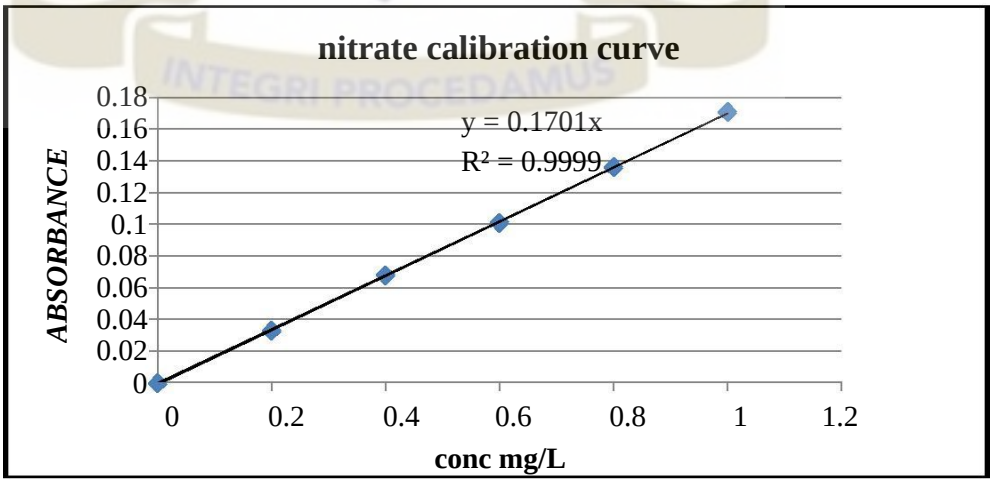
phosphate calibration data

CONC	ABS
0.0	0.000
0.2	0.077
0.4	0.155
0.6	0.233
0.8	0.310
1.0	0.388



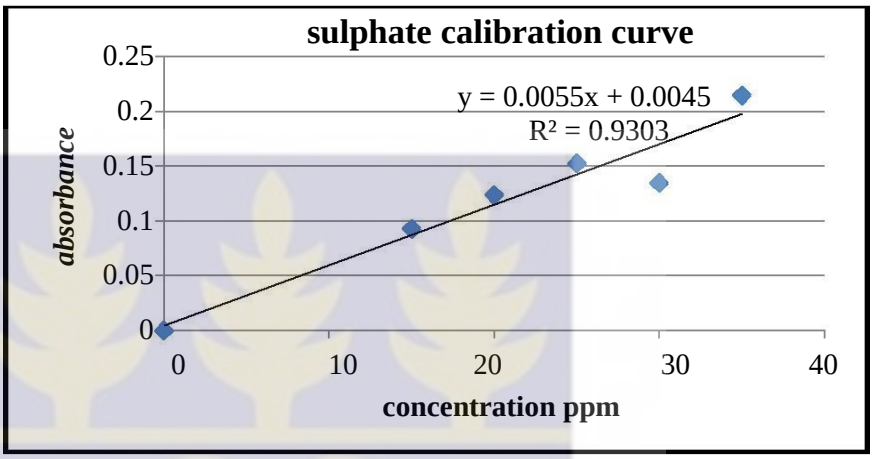
Nitrate calibration data

Conc	abs
0.0	0.000
0.2	0.033
0.4	0.068
0.6	0.101
0.8	0.136
1.0	0.171



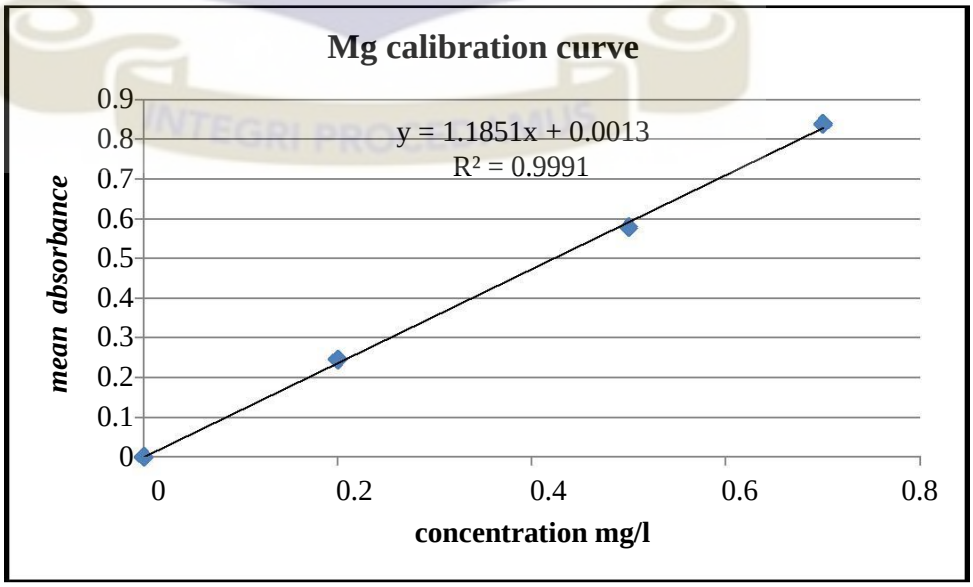
Sulphate calibration data

sulphate	abs
0	0
15	0.093
20	0.124
25	0.153
30	0.135
35	0.215



Mg calibration data

mg std	mean abs
0.0	0.0000
0.2	0.2460
0.5	0.5789
0.7	0.8393



CZECH METROLOGY INSTITUTE
INSPECTORATE FOR IONIZING RADIATION
Radiová 1, 102 00 Praha 10

CERTIFICATE

Cert. No: 9031 - OL - 146/14 Type: MBSS 2 Prod. No: 050214-1425039

Radionuclide	Half life days	Activity kBq	Combined standard uncertainty, %
Am-241	157800	4,694	1,1
Cd-109	462,6	14,54	1,4
Ce-139	137,5	1,355	1,1
Co-57	271,26	1,156	1,1
Co-60	1925,4	2,697	1,1
Cs-137	11019	2,689	1,3
Sn-113	115,1	4,000	2,2
Sr-85	64,78	4,570	1,5
Y-88	106,6	5,323	1,2

Mass: 980,0 g Density: 0,98 g/cm^3 Volume: 1000 cm^3

Radionuclide inpurities: gamma < 0,1 %

Reference date: 20.3.2014 Homogeneity better than: 1 %

Description:

Radioactive material is homogeneously dispersed in silicone resin. Composition of the matrix: C - 0,324 H - 0,0816 O - 0,216 Si - 0,379 (mass ratio).

Measuring method:

Preparation issues from standard ER solutions whose activities were determined by suitable absolute method. Final control is based on gamma spectrometry on HPGe detector.

Note:

As the criterion of homogeneity standard deviation of the acivity value of 1 cm^3 element was chosen (n=10). The volume is calculated from the mass and the density.

Date of the cetificate issue: 25.2.2014 Validity: 3 years

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Plate 1 : Standard radionuclide certificate (Czech Metrology Institute)