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DETERMINATION FOR LEVELS OF RADIONUCLIDES OF URANIUM, THORIUM AND POTASSIUM IN WATER, SEDIMENTS AND ALGAE SAMPLES FROM SELECTED COASTAL AREAS OF LAGOS, NIGERIA; USING ENERGY DISPERSIVE X-RAY FLOURESCENCE.

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ABSTRACT: *Concentration of some natural radionuclides were determined in water, sediments and green algae collected from selected coastal areas of Lagos, Nigeria over a period of two seasons (wet and dry) using Energy Dispersive X-ray Fluorescence (ED-XRF) techniques. This was done to highlight and ascertain possible radionuclide pollution. Using the ED-XRF technique, 46.10±1.34 ppm of Potassium was found in the sampled sediment during the dry season while Uranium, Thorium and Potassium were beyond the limit of detection during the wet season The ED-XRF technique showed that 31.40±0.14 ppm of Potassium was present in algae during dry the season. Uranium, Thorium and Potassium were beyond detection limit in the water samples using ED-XRF. The interactions of the wet and dry season showed that the nuclides of Uranium, Thorium and Potassium series are on the move and no significant changes in the concentration of the nuclides from wet to dry season. Potassium obtained are above the permissible levels by IAEA and may have health implication on the environment and persons living around the Coastal areas*.

KEYWORDS: Radionuclides, Energy Dispersive X-Ray Flourescence, Pollution.

INTRODUCTION

Radioactivity is caused by nuclides whose nucleus contains a specified number of protons and neutrons whereas any nuclei with an unfavourable proton/neutron ratio will undergo a nuclear disintegration to achieve a more stable configuration. (Balakrishina *et al*., 2007). This process is accompanied by the emission of radiation; such an unstable nuclide is referred as a radionuclide. The decay process proceeds at a well-defined rate characterized by the radionuclide considered. This attribute may be exploited to date materials, both geological and biological in nature, and to determine the kinetics of environmental processes such as water mixing and sediment deposition. Alternatively, artificial and natural radionuclides with enhanced concentration due to anthropogenic influences may be used as tracers for water masses. Some radionuclides deserve special consideration due to the threat they may pose as environmental pollutants when they undergo radioactivity, such radionuclides include the primordial nuclides of uranium-238, thorium-232, potassium-40 which are present since the formation of the universe often referred to as naturally occurring radionuclides and materials wherein they are present, (Cooper, 2006).

Uranium

Uranium is the most important element in nature. It exists in at least three isotopic forms, with mass numbers 234, 235 and 238. Another element of importance from the nuclear energy standpoint is thorium, with atomic number 90. It occurs in nature almost entirely as a single

nuclear species, with mass number 232. Thorium-232 is the parent of the thorium (4n) series. Its daughter,^{228}Th is formed through two intermediate nuclides, one of which is ^{228}Ra. Radium is far more mobile element than thorium, and the half- life of ^{228}Ra (6.7yrs) in sufficiently long to allow significant separation of ^{228}Th from the parent ^{232}Th. Its distribution is thus partially independent of the parent isotope and is more closely governed by the behaviour of ^{228}Ra.

Thorium

Thorium-232 is the parent of the thorium (4n) series. Its daughter, ^{228}Th is formed through two intermediate nuclides, one of which is ^{228}Ra. Radium is a far more mobile element than thorium, and the half- life of ^{228}Ra (6.7yrs) in sufficiently long to allow significant separation of ^{228}Th from the parent ^{232}Th. Its distribution is thus partially independent of the parent isotope and is more closely governed by the behaviour of ^{228}Ra. Thorium-230 and Thorium-234 are each daughter products of uranium isotopes, although with widely differing half- lives of 7.5 x 10^4 years and 24 days, respectively. They have a quite uniform source in sea water.

Potassium

Potassium, soft, silver –white metal is an important constituent of soil; it is also widely distributed in nature and is present in all plant and animal tissues. Potassium-40 is a naturally occurring radioactive isotope of potassium. Two stable (non-radioactive) isotope of Potassium exist, Potassium-39 and Potassium-41. Potassium-39 comprises most (about 93%) of naturally occurring Potassium-40 and Potassium–41 accounts for essentially the rest. Radioactive Potassium–40 comprises a very small fraction of about 0.012% of naturally occurring Potassium, Several radioactive isotopes of Potassium exist in addition to Potassium -40.These isotopes all have half-lives of less than one day. The half-life of Potassium-40 is 1.3 billion years, and decays to Calcium- 40 by emitting a beta particle with no attendant gamma radiation (89% of the time) and to the gas argon-40 by election capture (EC) with emission of an energetic gamma ray (11%of the time). Potassium–40 is an important radionuclide in terms of the dose associated with naturally occurring radionuclides. It is present in mineral waters and brines, and in various minerals such as carnalities, feldspar, saltpetre, greensand, and sylvite. Potassium is an important constituent of a fertile soil and is essential nutrient for plant growth and in the human diet. (Sparks, 2003,Kaplan, 2003).

Radiation in the environment can kill many organisms including human beings. Chemical and radioactive substances can cause cancer and as well as birth defects, (Norse 2006). The risk of impact on biota depends on a number of factors: type of radiation (α,β,γ,), the energy of radiation, the level of activity (distribution per unit time), the nuclides chemical and physical properties of the contaminated material and surrounding as well as properties relating to the species. The nuclides and some important parameters are shown on table 1.

Table 1: Overview of most important radionuclides with some important parameters.

Nuclide	Type of radiation	Half life	Energy.(MeV)	
^{40}k	β	1.28x10^{9}yrs	1.40	
The Uranium series				
^{238}U	α	4.47x10^{9} yrs	4.20	
^{226}Ra	α	1600 yrs		4.80
^{210}Pb	β	22.3yrs	<0.10	
^{210}Po	α	138 days		5.30
The Thorium series				
^{232}Th	α	1.41x10^{10} yrs	4.00	
^{228}Ra	β	5.75yrs		<0.10

Source :Norse, (2006).

Ionizing radiation can result in biological damage by cells dying or developing into cancer cells, but also by damaging DNA, thus entailing consequences for future generation. These are the sorts of effects of ionizing radiation that have been identified to date. (Parret,1998). The potential for biological damage depends on the amount of energy that is absorbed by the organism and depends on which radionuclide, the type of radioactivity, its chemical form, the route of exposure and the organism's biochemistry, (Polikarpov,1998). Knowledge on the processes and mechanisms of uptake, concentration levels and effects of natural radionuclide continues to be scanty. In view of this Aarkrog (1997) found that the difference in the uptake and concentrations of natural radionuclide was much larger between different species and trophic levels in the food chain than between different geographic regions. Materials that are exposed to radiation will have their atoms and molecule ionized. This means that the electrons in the atoms break away. The fact that radiation ionizes also implies that the energy of the radiation is deposited in the matter that it penetrates.

Alpha radiation (α) has a positive charge, short range and only penetrates organisms from their outside to a small degree. Internal alpha radiation may cause damage. Alpha particles are characterized by high energy loss in relation to transport distance, and therefore give high ionization density along the paths the particle is moving. Alpha particles have high linear energy transfer (LET) and therefore have greater potential to damage cells and tissue structure in living organisms than types of radiation with low LET.

Beta radiation (β) consists of free electrons with high velocity and energy. Beta radiation has a greater range than alpha particles and can penetrate skin, but this type of radiation has a much lower LET than alpha radiation. (Norse, 2006). Radioactive elements are not degraded in the environment and will emit radiation regardless of which other chemical components are being formed by them. Radioactive nuclide possesses the chemical properties characteristic for each individual element, and the fate of an individual nuclide will thus be determined by the element chemical properties (IAEA, 2008). Areas in proximity to the coast are the most important deposition areas for organic material. Here individual radionuclide will typically be

concentrated in the sediments, (Norse, 2006). These areas are the most biologically productive and important growing areas and habitats for fish mussels, crustaceans and birds. Table 2 below summarizes the phase distribution coefficient for the selected natural radionuclides. The phase distribution coefficient (Kd) is the ratio between the concentration of a nuclide in sediment and concentration of the same nuclide in water.
Elements with high affinity to organic or inorganic particles in the water will typically be concentrated in the sediment from which they can in turn be remobilized and re-suspended in the water column.

Table 2: Sources of Radiation and Class of Pollutants

Sources	Class of pollutants
Radioactivity	Nuclear derivatives
Petroleum	Man –generated fluxes
	= [Natural fluxes
Metals	Mercury, Lead, Other heavy metals (Pb, Al, Cd, Sc, Sn, Mn, Fe., La, V, Zn, Cu, Ag, Cr, Be, Sb, In, Tl, Co, Se Hg, W. Ga Ni, Cs, Ta. As, Mo, U.
Synthetic Organic	DDT and its residues
Chemicals	PCB (poly chlorinated biphenyls)
	Low molecular weight Halogenated hydrocarbons.
Marine Litter	Plastics, rubber, metal wastes.

Source: Duursima and Marchard, (1974)

The rationale for the above scheme arose from the pattern of investigations and generalization resulting therefore, (Duursima and Marchard, 1974). The transport routes and introduction of such pollutants could be further grouped into: Wind systems, River systems, Outfalls and Ships. Furthermore, because of their radioactive properties, many nuclides have important applications as indicators of the time- scales of various oceanic processes, such as water mixing and sediment accumulation. Interaction of dissolved material with sediments is an important factor in influencing the pathways of radioactive nuclides in estuarine and coastal waters. Because of the often complex patterns of transport, deposition and re-suspension of sediments and the process of sorption and description which may occur, settled sediments may frequently remove a considerable fraction of some nuclides, causing a reduction in concentration in solution and reducing availability to many organisms. But these are circumstances where associations with particulate material may increase uptake in some food chains, (Li, 1971). Problems concerning radioactive waste disposal and the exposure to radiation of ecosystem and human population have given rise to very many studies concerned with environmental monitoring, the uptake of nuclides by organisms and sediments and their movement in marine food chains.

INDICATORS

Indicators have been chosen for this determination: they include geological (sediments), biological (green algae) and Water.

Sediments

Sediment is any particulate matter that can be transported by fluid flow and which eventually is deposited as a layer of solid particles on the bed or bottom of a body of water or other liquid. Sedimentation is the deposition of a suspended material. Sediments are also transported by wind (eolian) and glaciers. Desert sand dunes and loess are examples of eolian transport. Oceans, and lakes accumulate sediment over time. The material can be terrigenuos (originating on the land) or marine (originating in the ocean). Many water-borne pollutant and nutrient species are predominantly associated with particulate matter that can settle and become sediment, (Sonon *et al*.,2007).

Green algae

Algae are photosynthetic lower plants which have no vascular tissues to carry differentiation, morphologically simplest organisms which possess a nucleus with a bounding membrane, recognizable chromosomes and also assimilate via the photosynthetic system which is basic to all plants containing chlorophyll a. Ecologically they are the most widespread of the photosynthetic plants, forming the bulk of the carbon assimilating, floating, around on the marine aquatic environment. Aquatic plants, rocks, sand and mud and even animals, e.g. mollusks and whales may have a coating of motile or attacked algae. The major importance of algae is that they fix carbon dioxide in habitats where few or no other photosynthetic plants occur. Thus in fresh waters and particularly in the open ocean they are essential to the food chain leading to fish. They are also important sources of chemical such as agar (used to cultivate bacteria, fungi, algae etc), alginic acid (used in food industry) and as food. (Porte *et al;* 1997).

Water

Water is the most abundant liquid on earth; it covers three quarters of the earth's surface. Human activities and settlements hinge on the availability of water. Our physical and biological environments hinge on water. As vapour, water absorbs radiation to influence the heat balance and temperature of the environment and brings moisture to the continents. As liquid, water erodes and shapes the land, transports and concentrate minerals and moderate climate. As solid (ice), water gouges glacier valleys and lakes, pulverizes rocks by expanding when it freezes and there by creates soils

USE OF SEDIMENTS IN RADIONUCLIDE RESEARCH

Sediments have been known to be the ultimate 'sinks' of metals discharged into aquatic and marine environments. They are admixtures of several component fractions of silt, alluvium, sand and clay; and are therefore difficult to be isolated. Some works had been done in the use of sediments of Kubani river located at Zaria to establish possible pollution from industrial and human activities, (Ewa *et al.,* 2004). Earlier works, Ewa *et al.,* (1992) revealed the presence of high concentrations of like: Sodium,(Na); Aluminium,(Al); Potassium,(K); Titanium,(Ti); Vanadium,(V); Manganese,(Mn); Barium,(Ba); Dysprosium,(Dy) in the sediments. Nwugo, (2001) determined the concentration of trace elements in commercial water samples. Inyang and Ekpo (2000) carried a survey to determine radioactivity, physical and chemical parameters of underground and surface water in Qua Iboe River estuary. These studies did not investigate

the radionuclides present in the waters and the sediments and any other biological species. Radionuclide of uranium and thorium series in rain water over several tropical storms was studied by Martin, (2003). His results revealed that the level of contamination was as a result of environmental fallout. Lozano *et al.,* (2002) studied the distribution of long-lived radionuclides of the Uranium series in the Sediments of a small river in a Uranium mineralized region of Spain. The half-life of Uranium nuclide gave rise to the discovery of thorium, Pa and Pb as contaminants. Balakrishna *et al.,* (2007) studied the distribution of Uranium-Thorium nuclides in the riverine and coastal environments of the tropical southwest coast of India. Their results showed < 25.00 + 0.2% ppm mean for all the ten sites analyzed. Croft and Hutchinson in 1999 studied the measurement of uranium, Thorium and potassium concentration in building materials. They discovered high concentration in samples of building blocks and roofing sheets and lower concentration in other materials as wood and ceiling boards. Khamrayeva *et al.*, (2008) worked on surface sediments collected from the coast of the sea of Marmara and the Black Sea around Instanbul using X-ray fluorescence and Neutron activation analysis techniques were used to investigate the extent of radionuclides contamination. Ergin *et al*., (1991) took samples from Golden Horn and Izmit Bay Sediments in Turkey and compared with those of Coastal sediments of Southern California and Gulf of Venice. Their results showed that Istanbul compared with these results from Ergin *et al.,* is not significantly contaminated with radionuclides. Miah *et al*., (1998) studied the distribution of radionuclides in soil samples in and around Dhaka City. The work revealed uneven distribution pattern and could result from terrain migration of ions in soil deposits and seepage. Heather *et al*., (1995) took a study in method development for the extraction of naturally occurring radionuclides in marine sediments. Various methods were outlined and tested with different yields. But it was remarked in this study that nuclear techniques, like the use of neutron activation analysis using a nuclear reactor was most preferred.

A review on the distribution of Uranium and thorium decay-series radionuclides in the environment has disclosed unequal distribution pattern due to different activities by man in the locations for the study. Movement of water bodies was attributed as a factor affecting such distribution. Uptake of Uranium and thorium series by water lily, Nymphaca violacea was studied by Cannor and Dobbins (1993). The results showed that water plants have a considerable amount of these radionuclides but could only cause a hazard if ingested or exposed to such. It was opined that consumption of aquatic plants and animals could pose an environmental threat. Such plants were discovered to be useful for remediation. (Schlosser *et al.,* 1999) studied terrestrial radiations and its environmental effects. He affirmed that the presence of radioactivity in the environment may be due to a variety of sources. Besides planned discharges arising from operations associated with nuclear fuel cycle, radionuclides may enter the environment as a consequence of accidental releases. The type of land and vegetation, and deposition mechanism, determine radionuclide behaviour in the terrestrial environment. United Nations Scientific Committee on the effects of Atomic Radiation (UNSCEAR) in 1993 reported the sources and effects of ionizing radiation. In this study, it was also revealed that the major sources of radiations are the long-lived terrestrial (primordial), radionuclides and the secondary radionuclides produced by their radioactive decay and belong principally to the three decay series of the Uranium, thorium and actinium; and are ubiquitously present in low concentration in soil and water as a result of weathering and erosion of rocks. In these result, Potassium-40,

a non-series primordial radionuclide, is also a major contribution to both internal and external exposure. However, the absorption of elemental potassium by the body is constantly under strict haemostatic control.

Naidu *et al.*, (2003), in their study revealed that the determinations using soils and sediment are particularly useful in the collection of information on the level of contamination. The environmental impact of metallic contaminants in soils and sediments is dependent both on the chemical species of the metals and the response of the matrix to biological and physicochemical conditions. These factors are responsible for the mobilization of the metals from solid into the aquatic phase and, hence, for the transport within the immediate vicinity, influencing the rate of dispersion, dilution, uptake and transfer into living system. Through human use of metallic elements, the contamination of the earth's surface occurred partly from localized problems associated with mining and initial ore processing, larger scale manipulation and refining, construction and manufacturing as well as waste disposal (Newson, 1992; Thornton, 1996, Sunder Land *et al.*, 2000).

It is important to predict the mobility of the radionuclide in soil systems, since this determines their transport in hydrobiological systems and their transfer into streams, surface water bodies and ground water. Once present in water courses, radionuclides might be taken up by fresh water plants and animal or human chinking water supplies. (Lake *et al.*,1984). Junior *et al.*, (2006); in their determination of radionuclides in the environment using gamma-spectrometry, found that environmental radioactivity is specifically predominant in soil and sediments and derived from 35the decay of the primordial radionuclides of ^{238}U, ^{235}U, ^{232}Th, ^{87}Rb & ^{40}K. However, the highest contribution to this radioactivity is due to the great number of decay products of ^{238}U and ^{232}Th. Xiaolin Hou, (2009) studied chemical species of inorganic elements in some marine algae by neutron activation analysis combined with chemical and biochemical separation techniques. It was found that alkali metals and chlorine were the main the ions in algae. The results indicated that the concentration of many trace elements, such as Zn, Fe, Sc, Th, are quite high. Radioactive pollution in ocean environments have indicated distribution of radionuclides; I–131, various uranium isotopes, Caesium – 137, Cobalt – 60, Sr – 90,Ruthenium – 160 and plutonium isotopes. Ecosystems considered include, coral reefs and atolls, planktonic zones in the open ocean, salt marshes, estuaries, coastal waters and the Mediterranean Sea. Sources of radioactive contamination examined include; atomic bomb blast, fossil fuel combustion, radioactive waste disposal and nuclear accidents.

Cynthia *et al.*,(1989) worked on biosorption of metals by algae and other microorganisms for a variety of reasons, including concern over potentially toxic and radioactive metals, their accumulation in the food chain, metal recovery techniques, contaminated water treatment methods, radionuclide clean-up procedures and precious metal recovery methods. Several algae strains have been characterized as to their ability to accumulate heavy metals. Sunta, (2004) studied the uptake of alpha and beta radiations in Mushrooms. They incorporated several radionuclide using laboratory and natural conditions into Mushrooms. Their results confirmed the uptake of metals/radionuclides under natural conditions: ^{137}/Cs >228, 230, 232, Th≈$^{234, 238}$ U≈ ^{90}Sr>> $^{239 + 240}$Pu. In view of the special ability of mushrooms and other green vascular plants to accumulate certain elements and radionuclides, they have already been suggested for

use in the mycogeochemical prospecting of metallic ores by Randa, (1989) and for monitoring environmental pollution by Poddubny et *al*., (1999). Mahmoud *et al*., (2005) employed NAA and EDXRF in multi-element determination in sandstone, qualitative and quantitative analysis of Aswan area in South Egypt was carried out. The EDXRF was used to compare the NAA as a non-destructive method. Na, K, Fe, Se, Cr, Co, Zr, Ce, La, Nd, Sm, Eu, Yb, Lu, Hf, Ta, Th and U were determined. Uranium–Thorium levels of the Kubani River (Zaria) sediments in the Nigerian basement complex have been determined; from the study, the probable contributory factors are either phosphate fertilizers used on the neighbouring farms or depositions from the North East trade winds blowing across the Sahara deserts across the Northern Nigeria Savannah region and the annual weathering of the basement granites, (Dim *et al*., 2000).

RADIONUCLIDE RESEARCH WITH ALGAL FORMS

When the pollutant type is known or well under stood certain indicators are more effectively used (Phillips et al, 1993). The use of indicators, indicator species or indicator communities, generally benthic macro invertebrates, fish and /or algae are used. Certain aquatic plants have also been used as indicator species for pollutants (Phillips and Rainbow, (1993); Batiuk *et al.*, 1992). Macro invertebrates are most frequently used (Rosenberg and Resh, 1993). Biochemical, Genetic, Morphological, and Physiological changes in certain organisms have been noted as being related to particular environmental stressors and can be used as indicators. The presence or absence of an indicator or of an indicator species or indicator community reflects environmental conditions. Absence of a specie is not as meaningful as it might seen as there may be reasons other than pollution, that result in its absence (e.g. predation, competition or geographic barriers which prevented it from ever being at the site; Phillips *et al*., (1993). Algae or seaweed have been known to concentrate most metals/ radionuclide in the tissues, Algal growth is dependent on sunlight and nutrient concentrations. An abundance of algae is indicative of nutrient pollution, (De-Lange, 1994). Algae are sensitive to some pollutants at level which may not visibly affect other organisms in the short term or may affect other Communities at higher concentrations. As an advantage, algae have very short life cycles and rapid reproduction they are most directly affected by physical and chemical environmental factors, (Plafkin *et al*, 1989). The biosorption of nuclides by algae and other microorganisms has been of interest for a variety of reasons, including concern over potentially toxic metals accumulation in the food chain, metal recovery techniques from process and industrial steams, contaminated water treatment methods, radionuclide clean up procedures, and precious metal recovery methods. (Mahan *et al.,* 1999). Several algae strains have been characterized as to their ability to accumulate heavy metal but most of these studies have concentrated on the biosorption of particular algae for a particular metal or on the mechanism of adsorption. Only recently have studies focused on the utilization of algal biomass as a preconcentration technique for ultra trace.

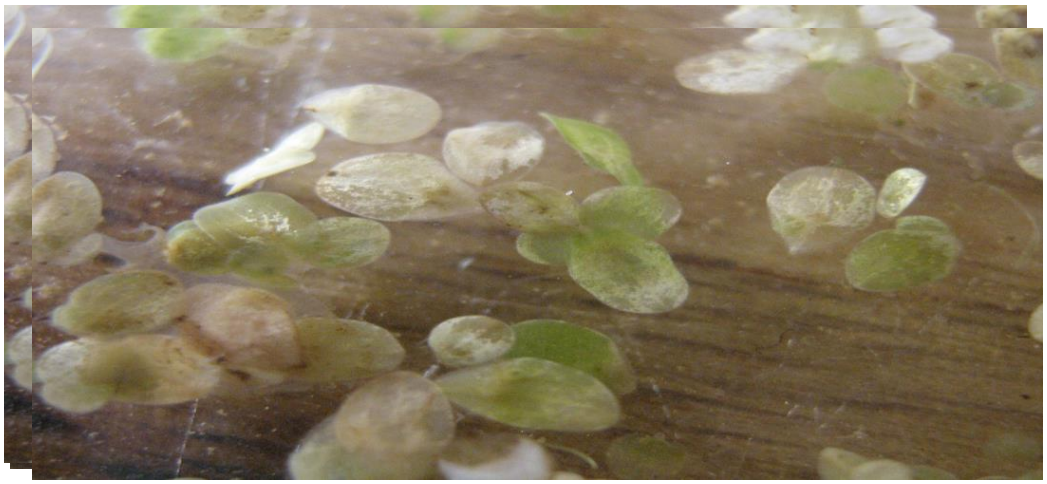

Fig. 1: Green Algae (genus species) in contact with media.

Biosorption occurs for essentially every element with the relative affinities decreasing in the order: Pb> Fe > Cu> Cd > Zn > Mn > Mo > Sr > Ni > V > Se > As > Co for chorella pyrenoldosa. Other algae strains (stichococcus bacillaris and Chlamydomonas) displayed similar adsorption behavior Uranium sorption studies were carried out using natural sample. The bioaccumulation was demonstrated using pettigera membranes as a function of time and pH, (Johnson *et al.*, 1998). Analysis of the artificial radionuclide in marine samples requires a chemical separation due to its low concentration. Sea weeds as algae were used for the recoveries of TC using the inductively coupled Plasma mass spectrometry, (Jose *et al*, 2004). Algae as lower plants have a significant influence on the environmental fate of radionuclides in aquatic and terrestrial ecosystem with a multiplicity of physico-chemical and biological mechanisms effecting changes in mobility and speciation. Physico-chemical mechanisms of removal include association with extracellular material metabolites and cell-walls which are features of living and dead organisms. Metabolism dependent mechanisms of radionuclide immobilization include sulphide precipitation, transport and intracellular compartmentation. In addition chemical reduction to less soluble forms can result in immobilization. Microbial processes involved in radionuclide solubilization include autotrophic and heterotrophic leaching and complexation by siderophores and other metabolites. Such mechanisms are important component of biogeochemical cycles for radionuclides and should be considered in any analyses of environmental radionuclide contamination. In addition, several microorganism based biotechnologies are receiving interest as potential treatment methods, (Gadd, 2002). Various studies showing the concentration of radionuclides in marine system was highest, occurred in algae and benthic organisms. Values essentially reflect weapon fallout, (Goldschemidt and Vertes, 1995). The natural uptake of nutrients by plant has been utilized in specific remedial-phytotechnological terms such as in phytostabilization, rhizofilteration, phytoextraction, rhizodegradation, phytovolatilization (Higgy, 2002). Similarly, the inherent ability of algae to incorporate radionuclides on specific binding sites of their tissues have been adopted in bioremediation applications such as in: biostimulation, mineralization, bioaugmentation, chelation and sequesterization, (Chowhurry *et al.*, 2005). Algae represent an important part of the ecosystem and play a major role in nutrient cycling in both aquatic and terrestrial ecosystem. The radiological half life is an important factor in opting for remediation;

if the half life is relatively short, it may lead to the effective disappearance of the contaminant in a practical amount of time. Conversely, if the half life is relatively long, it may necessitate regulated disposal.

Prasad and Oliveira, (2003) studied metal hyperaccumulation in plants and discovered that aquatic species have the ability to remove heavy metals and radionuclides from water. The roots of Indian mustard are effective in the removal of Cd, Cr, Cu. Ni, Pb and Zn and sunflower removes Pb, U, ^{137}Cs and ^{90}Sr from hydroponic solution. Aquatic plants in freshwater, marine and estuarine system act as receptacle for several metals. In this paper, Genes responsible for metal hyperaccumulation in plant tissues have been identified and cycloned. Dushenkov *et al.*, (1997) studied the removal of Uranium from water using terrestrial plants; in their preliminary laboratory experiments and treatability studies indicated that the roots of terrestrial plants could be efficiently used to remove Uranium from aqueous streams (rhizofiltration). One strategy that is being pursued to tackle the international problem of actinide contamination of soil sediment and water is to use microbial activity to fix these radionuclides into insoluble form that cannot be readily dispersed; (Yohey, *et al*., 2002). They were able to show that uraninite (UO_2) particles could be formed from uranium in sediments by bacterial reduction. Some agricultural lands located in the Vromos Bay area, near the black sea coast, SE, Bulgaria, have been contaminated with radioactive elements (Uranium, radium and thorium) and toxic metals (copper, calcium and lead) as a result of mining and mineral processing of polymetallic ores. Laboratory experiments carried out on soil samples from these lands revealed that an efficient remediation of the soil was achieved by an in situ treatment method based on the activity of the indigenous soil micro flora, (Groudev, *et al.*, 2004). Lloyd and Lovley, (2001) in their study of microbial detoxification of metals and radionuclides found out that microorganisms have important roles in the biogeochemical cycling of toxic metals and radionuclides. Recent advances have also been made in understanding metal- microbe interactions and new applications of these processes to the detoxification of metal and radionuclide contamination have been developed, (Entry *et al.*, 2004). The majority of the radionuclides generated by the nuclear fuel cycle can be removed during established remediation processes. However among the long lived, alpha emitting actinides, neptunium (v) is recalcitrant biotechnological methods. Apart from the uses of algae, citrobacter sp, has been used in the removal of ^{237}Np as well as its daughter ^{233}Pa (protactinium), (Lloyd *et al.*, 2000). Haas *et al*.,(1998); studied bioaccumulation of metals by lichens (uptake of aqueous uranium by pettigera membranacea as a function of time and pH); thus revealing the highest concentration of biosorbed U, relative to solution U activity, of any lichen reported to date. They found in this work that Uranium sorption was strongest in the pH range 4—5 with maximum sorption occurring at a pH of 4.5 Lichens are successful colonizers in extreme terrestrial habitat world-wide, including metalliferous environments. Their ability to accumulate metals has led to their use in monitoring radionuclide fallout from Chernobyl and uranium uptake from dust resulting from mining, (Mclean *et al.,* 1998). Accumulation of metals/radionuclides by microalgae and cyanobacteria may consist of two phases: metabolism-,independent binding to cell walls/extracellular polysaccharide (biosorption) followed or accomplished by intracellular uptake which may be energy-dependent. Both phases can be affected by environmental factors, e.g. changes in pH, salinity, nutritional regions and suspended clay minerals, (Garnham *et al.,* 1994).

DESCRIPTION OF SAMPLING LOCATION

The area under study is Lagos metropolis, the state capital of Lagos state, former Figure 2: Map of Lagos showing sampled locations
Administrative Federal Capital of Nigeria and current Commercial Federal Capital. It lies on latitude $+6^0$ 27' 11'' and longitude $+3^0$ 23' 45'' to the south western part of Nigeria. It shares boundaries with Ogun state in the North and East and with Republic of Benin in the west. It

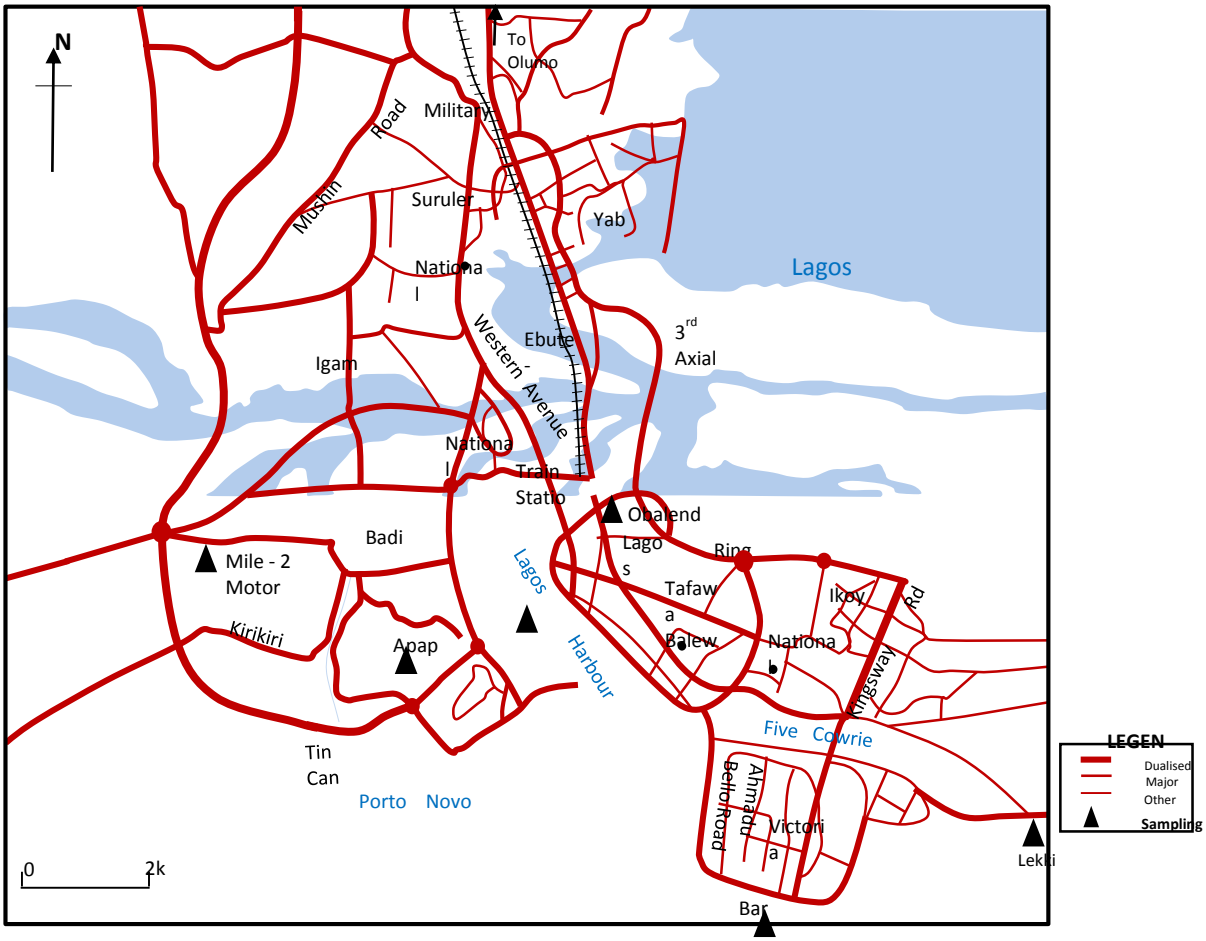

Figure. Lagos Showing Sampling
Source: Geological Survey

stretches for 180km along the coast of the Atlantic Ocean in the south. Lagos state, the smallest state in Nigeria occupies an area of 3,577Sq km. 22% or 787 Sq km, part of which consists of lagoons and creeks (canals). The ilupeju layout of the Lagos metropolis houses most of the industries where industrial activities take place. All the rivers that run into the River Niger and Benue, in turn drain into the Atlantic Ocean with all the pollutants. The Atlantic Ocean is kinetic and due to its non-static nature transports pollutants from other parts of the world and as such the coastal samples from these sites are equally polluted, hence could be useful in the pollution studies. Lagos, Nigeria is bound on the South by the Atlantic Ocean and all the major rivers and their tributaries run their wastes to the sea. The sea and the linkages (canals) are a major source of water supply and aquatic animals for human consumption. It may be possible that the

coastal waters of Lagos are contaminated with consequent radiations resulting from human activities and sea transport. It is therefore necessary to determine the concentration of the radionuclides in these water bodies and study the seasonal variations in the levels so as to educate the residents of the possible health implication. Radiations from radionuclide, alpha & beta, are high Linear Energy Transfer (LET) radiations, hence they deposit their energy at short distances and cause serious biological effects for the organs and tissues they interact with. Therefore, there is the need to determine the concentrations of the radionuclides present in some environmental samples. (Ekpo, 2000, Santschi, 1989). The choice of sampling location was borne out of the interest for total radionuclide pollution in the coastal waters of Lagos as there has not been any established data on the amount of radionuclides present in these Coastal waters.

Sampling

Samples were collected in the month of February, (dry season) and August, (wet season) respectively from six designated areas in the Lagos metropolis namely: Bar beach, Lekki beach, Mile 2 Canal. Lagos Harbour, Apapa Canal, and Ijeh Canal as shown in figure.3.1

Water

The water samples were collected in polyethylene plastic containers. The containers were washed with soap solution rinsed with dilute HCl acid solution in ratio 1:1. The acid washing was done by adding 100ml of the acid solution into the bottles and then rinsed with deionised water and dried, (Greenberg, 1992). The water samples, ten samples from a particular site was sampled by taking water from the top and bottom (about 2 metres) then mixed together to form a representative sample, of six samples

Sediments

The assessment of sediments remains the most critical pathway for monitoring and evaluating contamination of the aquatic environment. Representative samples using the stratified random sampling method, (Williams 2004) was adopted; sampling was done using the coring method, (Ewa *et al*., 2004). In collecting the sediments, the profile is taken into consideration as the radionuclide total concentration is of interest. Samples were taken at two depths; upper and lower layer about two feet. Ma clean hand-auger was used to collect the sediments. A total of ten samples from five points were collected from a site at a distance of about 20 metres, they were thoroughly mixed together and made to represent a composite sample. The samples were immediately stored in plastic containers and labeled. A total of sixty (60) samples were reduced to six (6) composite samples for each season.

Algae

Conspicuous green algae were sampled in six plastic containers with perforated lids for oxygen intake and were in contact with their environmental media enroute Kaduna within about 12hrs as they have very short cycle, (Plafkin *et al.,* 1989). The samples were filtered and dried to constant weight in an oven at 50-70^{o}C for two hours, (Victor, 2004). A homogenized 5g of Algae powder was prepared for Neutron Activation and ED-XRF analysis.

METHODOLOGY

Sample Preparation For Energy Dispersive X-Ray Flourescence Water, Sediments And Green Algae

(i) Water

The preserved water samples were filtered and 100mls was taken for EDXRF analysis. 2% ammonium pryolidin-1-dithiocarbamate, $C_5 H_{12} N_2 S_2$ (APDC) was added to the acidified samples (pH<2) with resultant precipitation and was filtered through a 0.22µm filter paper disc using a suction pump. The precipitate was allowed to dry, subjected to 10 tonnes hydraulic press and placed on a Si (Li) detector. (Injuk and Grieken, 1993).

(ii) Sediments and Algae:

Samples were ground to powder manually with mortar and pestle to grain size of less than 63µm. pellets were prepared from 0.2–0.30g powder mixed with three drops of organic binder (Polyvinylchloride, PVC dissolved in toluene) and subjected to 10 tonnes with a SPECAC hydraulic press machine. Measurement were performed using an annular 25mm Si- ^{109} Cd as the excitation source that emits Ag-K X-rays (22.1 KeV). The system consists furthermore of a canberra Si (Li) detector with a resolution of 170 eV for the 5.90 KeV line coupled to a computer controlled ADC-card, (IAEA, 1996).

Quantitative analysis of the samples was carried out using Emission-Transmission (ET) method for which a number of quantification methods has been developed and applied, (Funtua, 2007).

RESULTS AND DISCUSSION

Analysis for Radionuclides in Water

The results for the levels of radionuclides in water samples obtained (using EDXRF) from the sampling sites during dry and rainy (wet) seasons are presented in tables 3 and 4 (ppm). From table 3, it was revealed that Potassium, Vanadium, Chromium, Manganese, Cobalt, Nickel, Copper, Zinc, Gallium, Lead and Rubidium were detected at a concentration range of 4.5 ±0.2— 6.57 ±0.2; 45.0 ±10.2—162 ±20.62; 111.0 ±100.2—150.7 ±0.48; 154.0 ±0.91— 1480 ±110.0; 6.91 ±0.70; 140 ±12.82; 12.70 ±0.62—1690 ±100.2; 100;4 ±62.9; 0.92 ±1.02; 100.71 ±0.41— 400 ±19.54 and 1120 ±120.3 respectively while table 4 showed that only Iron, Zirconium and Molybdenum were detected at concentration range of 2.31 ±0.29—10.60 ±0.64; 10.81 ±4.61 and 0.17 ±0.058 at ML2, LG.HB and Apapa canal respectively. The detection of these radionuclides at these sites could be due to effluent run-offs from domestic. The environmental impact of radionuclides in biological (algae) and geological (sediment) and water samples is dependent both on the chemical species of the nuclides and the response of the matrix to biological and physicochemical conditions. These factors are responsible for the mobilization of the nuclides from solid into the aquatic phase, and hence, for the transport within the immediate vicinity influencing the rate of dispersion, dilution, uptake and transfer into living systems, (Naidu et al, 2003). The low concentration of nuclide in ppm recorded in this work can be attributed to the movement of water bodies and the constant dispersion as compared to the work of Sharif *et al.*,1994 and Cochran *et al.*, 2008.

Table 3: Concentration of nuclides (ppm) in water samples during dry season.

	BB	LB	ML2	LG HB	AP.C	IJ.C
K	BDL	BDL	4.51±0.2	BDL	BDL	6.57±0.02
Ca	BDL	BDL	BDL	BDL	BDL	BDL
V	BDL	BDL	BDL	45±10.2	102±18.6	162±20.62
Cr	BDL	BDL	BDL	150.7±0.48	111.0±100.2	BDL
Mn	BDL	BDL	BDL	1480±110.0	BDL	154±0.91
Fe	BDL	BDL	BDL	BDL	BDL	BDL
Co	BDL	BDL	6.91±0.70	315 ±0.68	BDL	BDL
Ni	BDL	BDL	BDL	BDL	140±12.82	BDL
Cu	BDL	BDL	12.70±0.62	BDL	BDL	1690±100.2
Zn	BDL	BDL	BDL	BDL	BDL	100.4±62.9
Ga	BDL	BDL	BDL	BDL	0.92±1.02	BDL
As	BDL	BDL	BDL	BDL	BDL	BDL
Se	BDL	BDL	BDL	BDL	BDL	BDL
Pb	BDL	BDL	100.71±0.41	BDL	400±19.54	120±0.2
Rb	BDL	BDL	BDL	BDL	BDL	1120±120.3
Sr	BDL	BDL	BDL	BDL	BDL	BDL
Zr	BDL	BDL	BDL	BDL	BDL	BDL
Mo	BDL	BDL	BDL	BDL	BDL	BDL

BDL – Below the Detection Limit

Key: B.B-Bar Beach; LK.B-Lekki Beach; ML2-Mile2; LG.HB-Lagos Harbour; AP.C-Apapa Canal; IJ.C- Ijeh Canal.

Table 4: Concentration of radionuclide (ppm) in water sampled during rainy (wet) season

	B.B	LK.B	ML2	LG.HB	AP.C	IJ.C
K	BDL	BDL	BDL	BDL	BDL	BDL
Ca	BDL	BDL	BDL	BDL	BDL	BDL
Cr	BDL	BDL	BDL	BDL	BDL	BDL
Mn	BDL	BDL	BDL	BDL	BDL	BDL
Fe	BDL	BDL	4.51±2.87	2.31±0.29	10.60±0.64	BDL
Co	BDL	BDL	BDL	BDL	BDL	BDL
Ni	BDL	BDL	BDL	BDL	BDL	BDL
Cu	BDL	BDL	BDL	BDL	BDL	BDL
Zn	BDL	BDL	BDL	BDL	BDL	BDL
Ga	BDL	BDL	BDL	BDL	BDL	BDL
As	BDL	BDL	BDL	BDL	BDL	BDL
Se	BDL	BDL	BDL	BDL	BDL	BDL
Pb	BDL	BDL	BDL	BDL	BDL	BDL
Rb	BDL	BDL	BDL	BDL	BDL	BDL
Sr	BDL	BDL	BDL	BDL	BDL	BDL
Zr	BDL	BDL	10.81±4.61	BDL	BDL	BDL
Mo	BDL	BDL	BDL	BDL	0.17±0.058	BDL

BDL – Below the Detection Limit

Key:B.B-Bar Beach; LK.B-Lekki Beach; ML2-Mile2; LG.HB-Lagos Harbour; AP.C-Apapa Canal; IJ.C- Ijeh Canal.

SEDIMENTS

The result for the presence and concentration of nuclides in the sediments for both season using ED-XRF technique are presented in tables 5 and 6. Potassium was detected at a concentration of 4610±134 ppm in the sediments sampled at Ijeh canal while uranium and thorium were beyond detection limit. The presence of potassium in this sample during the dry season could be from anthropogenic sources or attributed to increased human activities.

Table 5: Concentration of radionuclides (ppm) in dry season sediments using the EDXRF.

Nuclides	BB	LB	ML2	LG HB	AP.C	IJ.C
K	BDL	BDL	BDL	BDL	BDL	4610±134
Ca	BDL	BDL	BDL	BDL	26100±781	55200±10,500
Ti	BDL	BDL	BDL	BDL	BDL	BDL
Fe	BDL	BDL	BDL	BDL	BDL	38400±963
V	BDL	BDL	BDL	BDL	BDL	BDL
Cu	BDL	BDL	BDL	BDL	BDL	37300±138
Fe	2210±13.0	3490±400	BDL	3650±402	280±3.22	BDL
Zr	235±13.0	336±14.70	BDL	369±15.4	142±11.2	BDL
Nb	BDL	BDL	BDL	BDL	BDL	BDL
Zn	BDL	BDL	BDL	BDL	BDL	BDL
Pb	BDL	BDL	BDL	BDL	BDL	1560±127
Sr	BDL	BDL	BDL	BDL	BDL	519±90.0
Y	BDL	BDL	BDL	BDL	BDL	BDL
U	BDL	BDL	BDL	BDL	BDL	BDL
Zr	BDL	BDL	BDL	BDL	BDL	69.1±13.7

BDL = Beyond Detection Limit.

Key:B.B-Bar Beach; LK.B-Lekki Beach; ML2-Mile2; LG.HB-Lagos Harbour; AP.C-Apapa Canal; IJ.C- Ijeh Canal.

Table 6: Concentrations of radionuclides (ppm) in Wet (rainy) season sediments using ED-XRF.

Nuclide	B.B	LK.B	ML2	LG.HB	AP.C	IJ.C
K	BDL	BDL	BDL	BDL	BDL	BDL
Ca	BDL	BDL	BDL	BDL	BDL	6750 ±215.0
Fe	3480±94.4	4750±106.0	7430±98.4	3140±94.60	8940±101.0	2600±133.0
Ni	BDL	BDL	BDL	BDL	BDL	BDL
Zn	BDL	BDL	BDL	BDL	BDL	696 ±207
Pb	BDL	BDL	BDL	631.0.0±217	BDL	BDL
Rb	BDL	BDL	BDL	BDL	BDL	BDL
Zr	148±29.0	103±26.50	628±37.50	BDL	245±34.8	156±28.40

BDL = Beyond Detection Limit.

Key: B.B-Bar Beach; LK.B-Lekki Beach; ML2-Mile2; LG.HB-Lagos Harbour; AP.C-Apapa Canal; IJ.C- Ijeh Canal.

ALGAE

The concentration of nuclides in the dry season using ED-XRF technique presented in table 7 showed that the important nuclides, uranium and Thoriun were beyond the detection limit.

Table 7: Concentrations of radionuclides (ppm) in dry season algae samples using ED-XRF.

	B.B	LK.B	ML2	LG.HB	AP.C	IJ.C
K	BDL	BDL	BDL	BDL	BDL	314 ±0.14
Ca	BDL	BDL	BDL	BDL	750 ±0.54	640 ±0.24
Ti	BDL	BDL	BDL	BDL	BDL	BDL
Na	BDL	BDL	BDL	BDL	BDL	410 ±0.13
U	BDL	BDL	BDL	BDL	BDL	BDL
Cu	BDL	BDL	BDL	BDL	BDL	BDL
Fe	415 ±0.5	220 ±0.78	BDL	315 ±0.68	BDL	BDL
Zr	112 ±0.12	BDL	BDL	BDL	BDL	BDL
Nb	BDL	BDL	BDL	BDL	BDL	BDL
Zn	BDL	BDL	BDL	BDL	BDL	BDL
Pb	BDL	BDL	BDL	BDL	BDL	BDL
Sr	BDL	BDL	BDL	BDL	BDL	BDL
Y	BDL	BDL	BDL	BDL	BDL	BDL
U	BDL	BDL	BDL	BDL	BDL	BDL
Zr	BDL	BDL	BDL	BDL	BDL	BDL

BDL – Below the Detection Limit

Key:B.B-Bar Beach; LK.B-Lekki Beach; ML2-Mile2; LG.HB-Lagos Harbour; AP.C-Apapa Canal; IJ.C- Ijeh Canal.

Statistical Analysis to Study Seasonal Interaction of Sampled Locations and Concentration of Nuclides.

In the study of seasonal interaction for the concentration of the nuclides, it was observed that three main clusters were formed (fig.3). The first cluster was seen between BB-dry and LK-wet. The second cluster comprised of BB-wet,ML2-wet, LG.HB-wet and AP.C-wet. The third cluster has LK-dry, LG.HB-dry and AP.C-dry, IJC-dry, ML2-dry and IJC-wet. This shows that variables within the same clusters have similar properties while variable belonging to different clusters have dissimilar properties. The criterion is that variables within clusters have minimum variance. This can be compared with the findings of Ward 2008; Einax et al, 2007, 1998, Vernet 1991; Simeonov et al; 2006 and Smolinski et al; 2008.

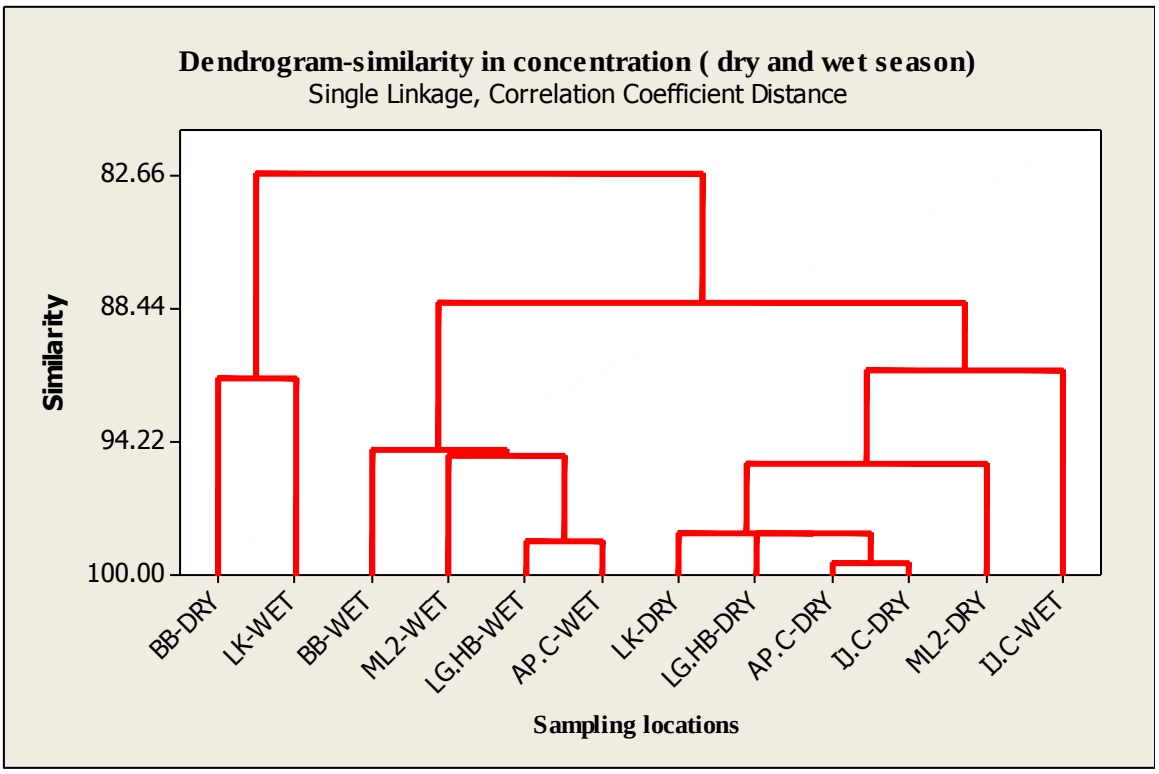

Fig. 3 Showing Cluster analysis for nuclides (dry and wet season)

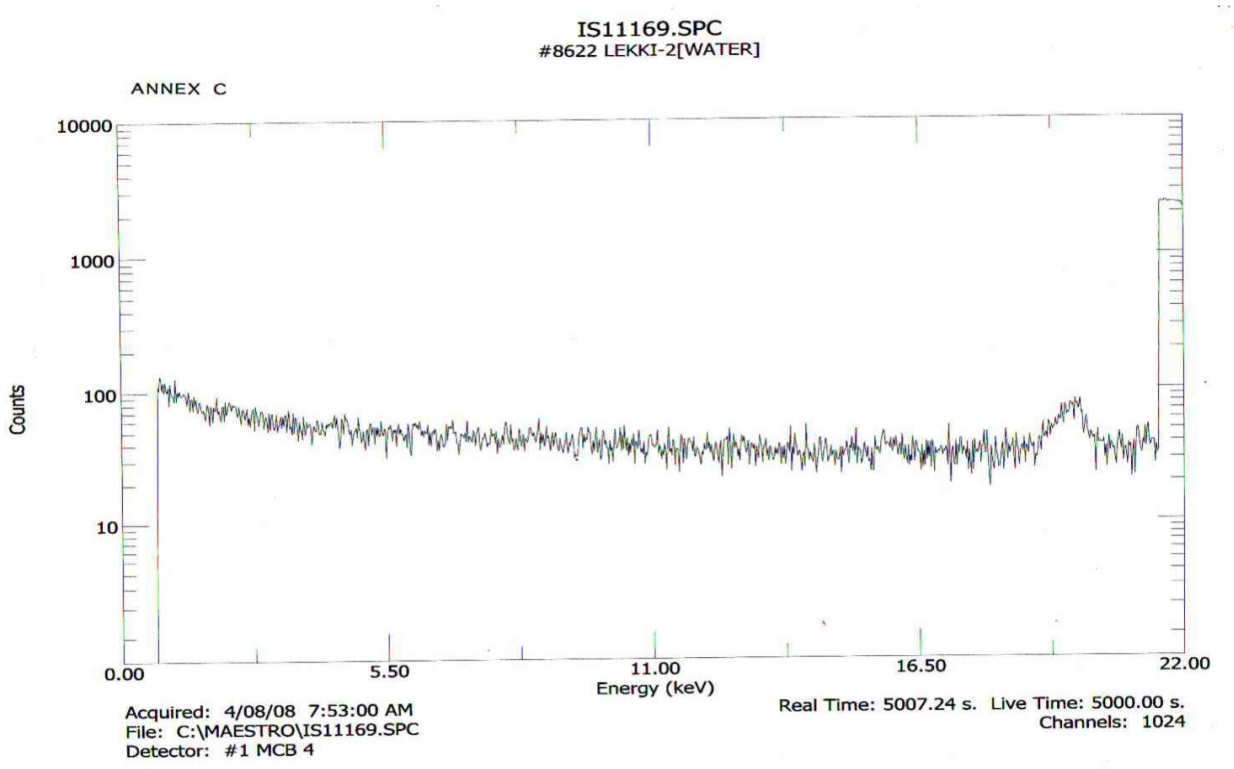

Fig. 4: Spectrum of EDXRF analysis of water sample from Lekki Beach-Wet season

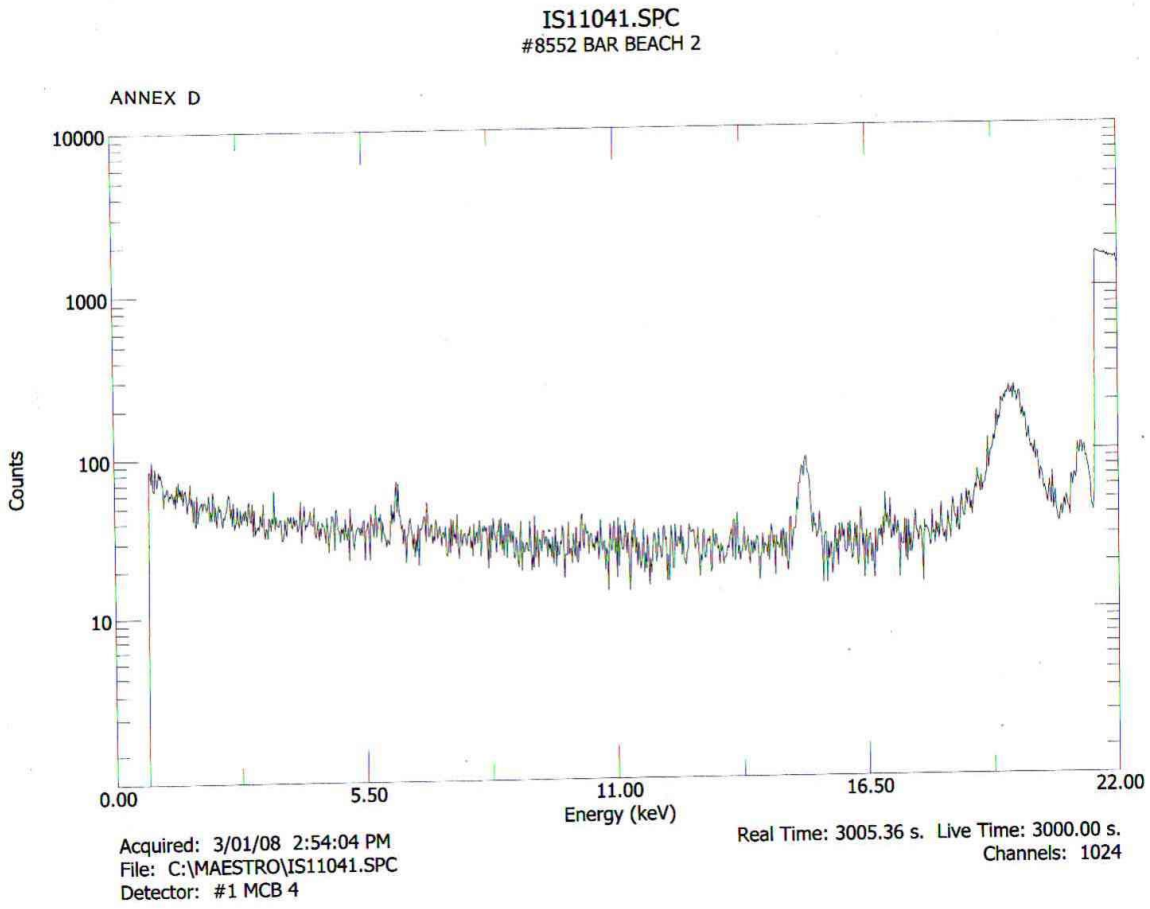

Fig. 5: Spectrum of EDXRF analysis of Water sample from the Bar Beach—dry season

The low concentration levels recorded in figure 3 and 4 could be attributed to the following reasons (Omale, 2012):

(i) Plankton synthesis in surface water of lakes and oceans may regulate the concentration of ‘’nutrient–type’’ elements e.g. Cu, Zn, Ni, Be, Se, and As.

(ii) Bacterial degradation of organic carbon in subsurface waters and surface sediments regulates the redox potential of the local environment and thereby, may control the concentration of “redox sensitive” and nutrient-type elements e.g. Mn, Co, Cr, U, V. However the redox condition in a particular environment, do not affect all radioactive and stable trace elements the same way. In general, elements involved with the Fe,Co, and Mn, redox cycles (eg Co and Mn) are mobilized in reducing (anoxic) environments while others are mobilized in oxidized (oxic) environment (e.g Cr, Se, U, Pu, V).

(iii) Particle settling through a lake estuary or ocean water column will control the behaviour of certain radionuclide by removing them from the dissolved phase through the formation of nuclide/ particle/surface site complexes. Such “scavenging-type” nuclides includes Fe, Mn, Co, Cr, Pb, Pu, Sn, Pa, and Th. For a particular radionuclide, the extent, of scavenging by sinking particle depends on the chemical composition of the particle surface.

(iv) Dissolved organic carbon (DOC) peptization and POC (particulate organic carbon) coagulation reactions can thus regulate the concentration of organically–complexed elements eg, Cu, Pb, and Hg. Such reactions are particularly important in coastal waters with high organic loadings and estuarine system with large ionic strength gradient.

(iv) Clay reconstitution reactions can regulate the concentration of element in sediments which have special affinities for clay in minerals e.g Si, Al, and B.

For open water bodies, it is the particle flux through the system which is most effective at regulating the concentration of trace metals with relatively simple chemical properties, However factors such as particle –particle interaction appear to play an important role as well (Omale, 2012)

CONCLUSION

Qualitative and quantitative analysis for nuclides of ^{238}U, ^{232}Thorium and ^{40}K series has been determined in sediment, algae and water samples collected from six locations in Lagos State, Nigeria using Energy dispersive X-Ray florescence techniques. The values obtained were below the permissible levels. The statistical study of the seasonal variables and the nuclides showed that there was no correlation between them. This culminated to the use of multivariate analysis. The dendrograms showed (clusters) that the seasons in the coastal areas especially Lagos have no clear cut boundaries and overlap is a common occurrence. The wave movement from the Atlantic Ocean enhances constant motion and dilution/mixing of pollutants in all directions. This may account for the low concentration of some of the nuclides as seen from the tables of results. It can be concluded that the interactions of the wet and dry seasons in this research have shown that the nuclides are on the move and no significant change in the level of the nuclides from wet to dry season, hence the concentration levels of these will have no serious consequences on terrestrial life. Some of the nuclides could however not be detected because of their short half lives.

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