

Research article

# CLUSTER ANALYSIS FOR SEASONAL VARIATIONS IN LEVELS OF RADIONUCLIDES OF POTASSIUM-40, URANIUM-238 AND THORIUM-232 SERIES IN THE SEDIMENTS FROM SELECTED COASTAL AREAS OF LAGOS-NIGERIA

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## ABSTRACT

Concentration of some natural radionuclides were determined in sediments collected from selected coastal areas of Lagos, Nigeria over a period of two seasons (wet and dry) using Neutron Activation (NAA) technique. This was done to highlight and ascertain possible radionuclide pollution. The results obtained for nuclides that were successfully determined using the energy of emission characteristics of each nuclide in all the samples include; Ti, V, Mn, K, As, Br, La, Yb, Np, Sc, Cr, Fe, Co, Zn, Rb, Cs, Ba, Eu, Lu, Hf, Ta, Sb, Pa, Ce, Ni, Cu, Ga, Pb and Sr. The mean concentration of daughter nuclides in the sampled sediments during the dry season using the neutron activation (NAA) technique were  $39.05 \pm 17.7$ — $67.4 \pm 13.40$  ppm for potassium ( $^{42}_{19}\text{K}$ ),  $2.31 \pm 0.31$ — $8.73 \pm 4.10$  ppm for uranium ( $^{239}_{92}\text{U}$ ) and  $1.15 \pm 0.07$ — $3.50 \pm 0.15$  for Thorium  $^{233}_{91}\text{Th}$ ; while the concentration of these radionuclides and daughter nuclides were  $24.68 \pm 3.33$ — $55.73 \pm 56$  ppm,  $1.0 \pm 0.20$ — $1.70 \pm 0.30$  and  $2.10 \pm 0.30$ — $4.10 \pm 0.60$  ppm respectively for  $^{42}_{19}\text{K}$ ,  $^{239}_{92}\text{U}$  and  $^{233}\text{Th}$  during the wet season. The interactions of the wet and dry season showed that the nuclides of Uranium-238, Thorium-232 and Potassium-40 series are on the move and no significant change in the concentration of the nuclides from wet to dry season. The results obtained were statistically analysed for seasonal interaction. However, the concentrations of the daughter nuclides of Uranium, Thorium, and Potassium obtained are above the permissible levels by IAEA and may have health implication on the environment and persons living around the Coastal areas. **Copyright © acascipub.com, all rights reserved.**

**Keywords:** Cluster Analysis, Radionuclide and Sediments

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## INTRODUCTION

A nuclide is an atom 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.*,2001). This process is accompanied by the emission of radiation; such an unstable nuclide is referred to 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 pose as environmental pollutants when they undergo radioactivity. Such radionuclides include the primordial nuclides of uranium-238, thorium-232, and potassium-40 which has been present since the formation of the universe. Radioactive nuclides undergo spontaneous change at a definite rate, which varies with the nature of the nuclide. The unstable nucleus emits a characteristic particle, (or radiation) and is thereby transformed into a different nucleus, which may (or may not) also be radioactive. Nuclides which owe their instability to their high mass may emit either positively charged alpha particle, which are identical with helium nuclei and consist of two protons and two neutrons, or negatively charged beta particles, which are the same as electrons. The nucleus itself does not contain electrons, and in radioactive beta decay, the electron arises from the spontaneous conversion of a neutron into a proton and an electron (Glasstone, 1967)

## URANIUM, THORIUM AND POTASSIUM

### URANIUM

At present, uranium is the most important radioactive element in nature. It exists in at least three isotopic forms, with mass numbers 234, 235 and 238. The Uranium (4n+2), Thorium (4n) and Actino-Uranium (4n + 3) series have as their parent nuclides Uranium -238, Thorium – 232 and Uranium-235 respectively. Each parent gives rise to a complex chain of decay products.

### THORIUM

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 232Thorium-232 is the parent of the thorium (4n) series. Its daughter, <sup>228</sup>Th is formed through two intermediate nuclides, one of which is <sup>228</sup>Ra. Radium is a far more mobile element than thorium, and the half- life of <sup>228</sup>Ra (6.7yrs) is sufficiently long to allow significant separation of <sup>228</sup>Th from the parent <sup>232</sup>Th. Its distribution is thus partially independent of the parent isotope and is more closely governed by the behaviour of <sup>228</sup>Ra. Thorium-230 and Thorium-234 are each daughter products of Uranium Isotopes, although with widely differing half- lives of  $7.5 \times 10^4$  years and 24 days, respectively.

### 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 the element. Two stable (non-radioactive) isotopes of potassium exist namely; Potassium-39 and Potassium-41. Potassium-39 comprises most (about 93%) of naturally occurring potassium while 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 the element exist in addition to Potassium -40. These isotopes all have half-lives of less than one day. However, 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 electron capture (EC) with emission of energetic gamma rays (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).

Radiation in the environmental can kill many organisms including human beings. The risk of impact on biota depends on a number of factors: type of radiation ( $\alpha, \beta, \gamma$ ), the energy of radiation, the level of activity (distribution per unit time), the nuclides chemical properties, 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. (Norse,2003).

Nuclide	Type of radiation	Half life	Energy.(MeV)
<sup>40</sup> K	$\beta$	1.28x10 <sup>9</sup> yrs	1.40
<b>The Uranium series</b>			
<sup>238</sup> U	$\alpha$	4.47x10 <sup>9</sup> yrs	4.20
<sup>226</sup> Ra	$\alpha$	1600 yrs	4.80
<sup>210</sup> Pb	$\beta$	22.3yrs	<0.10
<sup>210</sup> Po	$\alpha$	138 days	5.30
<b>The Thorium series</b>			
<sup>232</sup> Th	$\alpha$	1.41x10 <sup>10</sup> yrs	4.00
<sup>228</sup> Ra	$\beta$	5.75yrs	<0.10

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 ( $\alpha$ ) 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 ( $\beta$ ) 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, 2003).

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, 1990). 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, 2003). These areas are the most biologically productive and important growing areas and habitats for fish mussels, crustaceans and birds. Table 1.4 below summarizes the phase distribution coefficient for the selected natural radionuclides. The phase distribution coefficient ( $K_d$ ) 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.

## RADIONUCLIDES AND MARINE POLLUTION

The chemical composition of ocean waters presently is being wholly influenced by man's activities. The use of materials in industry, agriculture, and everyday life is responsible for the mobilization of huge tons of materials annually on the earth's surface. In addition, the combustion of fossil fuels introduces tons of carbon dioxide and lesser amounts of other gases; much of these eventually enter the sea. As a consequence, the makeup of our surrounding is altered measurably (Goldberg, 1972).

The oceans receive a substantial fraction of these materials either by the deliberate or unintentional actions of man. In addition to three main routes of transport for substances from the continents to the oceans (winds, rivers and glaciers) society has added two more: ships and out falls pipes which carry domestic and industrial wastes. Two characteristics of marine system influence their ability to accommodate the wastes provided by Society. Firstly, the time scales for the retention of materials is long. It can retain both dissolved and particulate phases for times ranging from years to hundreds of millions of years. Thus, substances injected today may still be evident many generations later. Secondly, biological and geological process occurring in the marine environment is able to concentrate materials from sea water into living and non-living phases respectively to a remarkable extent ( Santschi *et al.*, 1997). This is always serious a risk because if the oceans are used as a disposal site, highly toxic materials will be concentrated in the biomass and aquatic animals. There is consideration of the potential return to man though ingestion of sea food. The transport paths to the ocean from the continents, emphasises both global dispersion resulting from atmospheric transport and the more localized effects produced by rivers and outfalls. The main aim of this work is to determine the concentration levels of some natural radionuclides in sediments collected from selected coastal areas of Lagos-Nigeria and also to highlight and ascertain possible radionuclide pollution in the selected coastal areas.

## METHOD

### NEUTRON ACTIVATION METHODOLOGY

The method involves the use NIRR -1; a lower nuclear reactor, which has highly enriched uranium as fuel, light water as moderator and beryllium as reflector. A detail description of the reactor and the irradiation facility has been enumerated by Jonah *et al.*, (2006). The associated facility for radioactivity measurement is a gamma ray data acquisition system. It consists of horizontal dip-stick high-purity germanium (HPGe) detector, (Jonah *et al.*, 2006). Neutron activation analysis has been established as a powerful tool for the determination of trace elements in a variety of matrices. The need of a sensitive multi elements analysis method is essential to carryout successful geological investigation. Over the years, various analytical methods have been used but each method has different limitations, e.g. sample preparation, sample dissolution and limited number of accessible elements. Due to its high sensitivity and great accuracy, the multi element neutron activation analysis technique has been widely applied all over the world (Ewa, I.O.B, 1992; Haskin and Schmidt, 1967; Herderson, 1984; Laul, 1984).

**Table 2:** Routine irradiation and measuring regime for NIRR-1. (Jonah *et al.*, 2006).

Neutron flux irradiation channel	Procedures	$T_{irr}$	$T_d$	$T_m$	Activation products
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1x10 <sup>11</sup> n/cm <sup>2</sup> s/outer irradiation channels (B4, A2)	S1	2min	2-15min	10min	<sup>28</sup> Al, <sup>27</sup> Mg, <sup>38</sup> Cl, <sup>49</sup> Ca, <sup>66</sup> Cu, <sup>52</sup> Ti, <sup>52</sup> V, <sup>116</sup> In
	S2	2min	3-4hrs	10min	<sup>24</sup> Na, <sup>42</sup> K, <sup>165</sup> Dy, <sup>56</sup> Mn, <sup>152</sup> Eu
5x10 <sup>11</sup> n/cm <sup>2</sup> s/inner irradiation channels (B1,B2, B3, A1)	L1	6hrs	4-5d	30min	<sup>24</sup> Na, <sup>42</sup> K, <sup>76</sup> As, <sup>82</sup> Br, <sup>140</sup> La, <sup>153</sup> Sm, <sup>198</sup> Au, <sup>239</sup> Np(U), <sup>72</sup> Ga, <sup>122</sup> Sb, <sup>46</sup> Sc, <sup>141</sup> Ce, <sup>60</sup> Co, <sup>51</sup> Cr, <sup>134</sup> Cs, <sup>152</sup> Eu, <sup>177</sup> Lu, <sup>131</sup> Ba, <sup>86</sup> Rb, <sup>182</sup> Ta, L2
	L2	6hrs	10-15d	60min	<sup>175</sup> Tb, <sup>233</sup> Pa(Th), <sup>65</sup> Zn, <sup>50</sup> Fe, <sup>181</sup> Hf

T<sub>irr</sub> – time for irradiation, T<sub>d</sub>

## METHOD OF DATA ANALYSIS

### CLUSTER ANALYSIS

Cluster Analysis (Tryon, 2002) encompasses a number of different algorithms and methods for grouping objects of similar kinds, into respective categories. It is an exploratory data analysis tool which aims at sorting different objects into groups in a way that the degree of association between two objects is maximal if they belong to the same group. Cluster analysis can be used to discover structures in data without providing explanation or interpretation. In general, whenever one needs to classify a “mountain” of information into manageable meaningful lots, cluster analysis is of great utility. The result or output of agglomerative hierarchical clustering which is a commonly used clustering technique is usually represented by a tree like structure known as the dendrogram. We have vertical and horizontal orientations; top of tree represents one single group (root) of all data points and the bottom individual stems are given. Dendrograms are built usually from bottom to top but it is read from top to bottom (Oladipo, 1987).

### DESCRIPTION OF STUDY LOCATION

The area under study is Lagos metropolis, the state capital of Lagos state, former Administrative Federal Capital of Nigeria and current Commercial Federal Capital. It lies on latitude +6° 27' 11" and longitude +3° 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 stretches for 180km along the coast of the Atlantic Ocean in the south. Lagos state, Nigeria occupies an area of 3,577 Sq km. About 22% or 787 Sq km of the total area consists of lagoons and creeks (canals) which are influenced by the sub-equatorial climate with a rainfall of 2500mm per annum. It has double maxima of rainfall-June/July and September/October with conventional rainfall. It has temperature of about 27°C, with a low annual range of 2-3 °C and a relative humidity of 90%. It has a long period of wet season between 6-8 months and 3-4 months of dry season. All the rivers, e.g.Ogun, Osun, Osse, Niger and Benue drain into the Atlantic Ocean with all the transported 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 pollution studies.

### SAMPLING

Samples were collected in the month of February, (dry season) and August 2007, (wet season) respectively from six designated areas in the Lagos metropolis namely: Bar beach (BB), Lekki beach (LK.B), Mile 2 Canal ( ML2.C). Lagos Harbour (LG.HB), Apapa Canal (AP.C), and Ijeh Canal (IJ.C).



Figure. Lagos Showing Sampling Locations.  
Source: Geological Survey Dept.Lagos,2006.

Figure 1: Map of Lagos Sampling Locations . Δ

## 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). Sediment Samples were collected at the surface and at a depth about two metres using Maclean hand-auger. A total of ten samples were obtained from five points from each location at an interval of about 20 metres apart, to make a composite sample. This was repeated for all for all the locations to form six samples. 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.

Approximately 0.20 g of sample (sediments or algae) was weighed and wrapped in pre-cleaned polyethylene films to avoid contamination. The polyethylene films and rabbit capsules were cleaned by soaking in 1:3 nitric acid and water for three (3) days and washed with deionized water. Two schemes were adopted based on the half-life of product radionuclide. For the nuclides leading to short-lived activation products, the samples are each packed and sealed in 7cm<sup>3</sup> rabbit capsules and sent for irradiation via pneumatic pressure in turn in an outer irradiation channel where the spectrum is soft. The choice of outer irradiation channel is to eliminate corrections due to nuclear interferences caused by the threshold reactions, notably Mg in the presence of Al; Al in the presence of Si; and Na in the presence of P. this is due to the proximity of the inner channel miniature neutron source (MNS) to the core leading to relatively higher ratio of fast – to- thermal neutrons. For nuclides leading to long-lived activation products samples wrapped in polyethylene. Films are packed in a stack inside the 7cm<sup>2</sup> rabbit capsule and sealed for irradiation. Samples are irradiated for 6hrs in any of the inner irradiation to take the advantage of the maximum value of thermal neutron flux in the inner channels. Radioactivity measurement of indirect radionuclides was



performed by the PC-based gamma-ray spectrometry set up. Following the short irradiation regime the first round of counting is performed for 10mins (i.e. S1) after a waiting time of 2-15mins. The second round of counting was also carried out for 10mins following the short irradiation regime (i.e. S2) after a waiting period of 3-4hrs. It should be noted that the neutron flux setting was raised for biological reference materials irradiation was raised to  $5 \times 10^{11}$  n/cm<sup>2</sup> in order to increase the detection sensitivities for analysis of nuclides using S1 and S2.

With respect to the long irradiation regime, the first round of counting is carried out for 30mins following the long irradiation (i.e. L1) after a waiting period of 4-5 days. The second round of counting was performed for 60mins (i.e. L2) after a cooling time of 10-15 days. A description of the irradiation and counting regimes adopted for NIRR-1 facilities as well the radionuclide of interest are given in Table 2 (Jonah *et al.*, 2006).

## RESULTS AND DISCUSSION

### RESULTS FOR ANALYSED SAMPLES (WET & DRY SEASONS)

#### SEDIMENTS

The results for the presence and concentration of radio nuclides in the sediments sampled during the wet (rainy) and dry season using NAA are presented in tables 3 and 4 respectively. The mean concentration (ppm) of Potassium, Uranium (<sup>239</sup>Np) and Thorium (<sup>233</sup>Pa) during wet (rainy) season varied between 2486±333—5513±562; 1.0±0.20—1.70±0.3 and 2.1±0.3—4.1±0.6 respectively. This high concentration of the radionuclides during this period is an indication of increased inflow of nuclides into the sampled sites through run- off from industries and river tributaries. During this dry season, the mean concentrations (ppm) also varied between 674±13.40—3905±177; 2.31±0.31—8.73±4.1 and 1.147±0.065— 3.495±0.154 respectively. Elevated levels of potassium and iron in these sites could be associated with automobile waste found in the environment. Mechanical, industrial and commercial activities are carried out on a daily basis at these sites. This result compared well with the results obtained in the concentration of radio nuclides entering an estuary of the Australian coastal sediments (Cooper, 2003).

**Table 3:** Mean concentration levels (ppm) of nuclides and daughter nuclides in sediments obtained during dry season using the NAA.

	Nuclide	B.B	LK.B	ML2	LG.HB	AP.C	IJ.C
Mg	<sup>27</sup> Mg	BDL	BDL	BDL	BDL	BDL	669.4±210
Al	<sup>28</sup> Al	964±102	135±20	1041±16.07	1202±102	1098±10.98	5281±420
Ca	<sup>49</sup> Ca	821±28	1072±136	875±16.5	BDL	636.5±85.83	4243±420
Ti	<sup>51</sup> Ti	BDL	2228±60.16	1418±14.2	BDL	BDL	468±75
V	<sup>52</sup> V	BDL	5.163±0.37	3.092±0.60	BDL	1.257±0.19	6836±144
Mn	<sup>56</sup> Mn	78.20±22.1	270.7±4.6	102.7±11.32	224.2±2.02	43.21±1.81	BDL
Dy	<sup>165</sup> Dy	BDL	BDL	BDL	BDL	BDL	BDL
Na	<sup>24</sup> Na	1180±38	290±37.71	1430±12.37	19900±139	BDL	2188±35.01
K	<sup>42</sup> K	BDL	BDL	674±13.40	BDL	3370±727.92	3905±177
As	<sup>46</sup> As	BDL	2.80±0.27	11±2	0.92±0.41	0.2±0.1	4.50±0.35
Br	<sup>82</sup> Br	7.5 ± 0.1	12.40±0.8	15.0±0.81	6.02±0.41	5.24±0.23	10.20±0.8
La	<sup>140</sup> La	1.87±0.02	4.20±0.04	18±0.78	1.80±0.02	8.21±0.28	4.20±0.91
Sm	<sup>153</sup> Sm	BDL	BDL	BDL	BDL	BDL	BDL
Yb	<sup>175</sup> Yb	BDL	BDL	0.0694±0.019	BDL	BDL	0.133±0.04

U	<sup>239</sup> U	BDL	BDL	8.73±4.1	2.31±0.31	3.42±0.07	3.721±0.41
Sc	<sup>46</sup> Sc	0.7492±0.05	6.356±2.94	0.49±0.03	900.1±15.3	95.15±5.9	5.876±0.99
Cr	<sup>51</sup> Cr	2.450±0.362	BDL	0.70±0.30	650±31.2	80.16±15.79	11.53±0.90
Fe	<sup>59</sup> Fe	BDL	12890±5310	2914±271	40280±2362	22920±1054	44580±936
Co	<sup>60</sup> Co	BDL	BDL	BDL	17.28±4.46	12.96±2.16	3.577±0.22
Zn	<sup>65</sup> Zn	377.9±16.63	BDL	170.8±10.59	BDL	458.14±21.99	3853±50.09
Rb	<sup>86</sup> Rb	BDL	BDL	BDL	BDL	BDL	6.930±1.93
Cs	<sup>134</sup> Cs	BDL	10.71±5.13	0.043±0.022	BDL	BDL	0.2914±0.11
Ba	<sup>131</sup> Ba	72.47±28.55	BDL	BDL	BDL	672.3±110.26	BDL
Eu	<sup>152</sup> Eu	0.020±0.007	BDL	BDL	2.892±0.95	0.9189±0.31	0.041±0.014
Lu	<sup>177</sup> Lu	BDL	BDL	BDL	8311±0.11	0.2011±0.07	0.042±0.05
Hf	<sup>181</sup> Hf	151.5±4.55	0.2387±0.16	43.21±2.72	BDL	BDL	66.23±4.3
Ta	<sup>182</sup> Ta	1.141±0.22	0.2387±0.16	24.03±16.79	0.4782±0.44	0.3853±0.17	1.820±0.63
Sb	<sup>122</sup> Sb	BDL	BDL	BDL	BDL	0.5625±0.43	BDL
Th	<sup>233</sup> Pa	3.479±0.11	BDL	1.147±0.065	BDL	BDL	3.495±0.154
Ce	<sup>141</sup> Ce	BDL	BDL	BDL	213.28±4.46	BDL	BDL

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:** Mean concentration levels (ppm) of nuclides and daughter nuclides in sediments obtained during wet season using the NAA.

Elements	Nuclide	B.B	LK.B	ML2	LG.HB	AP.C	IJ.C
Mg	<sup>27</sup> Mg	BDL	BDL	BDL	BDL	BDL	BDL
Al	<sup>28</sup> Al	4480±33.2	3529±25.8	5963±44.1	6342±30.8	7683±56.1	9650±70.4
Ca	<sup>49</sup> Ca	BDL	4931±98.6	BDL	BDL	BDL	4350±39.6
Ti	<sup>51</sup> Ti	BDL	BDL	1899±27.2	BDL	1732±28.9	9892±21.07
V	<sup>52</sup> V	BDL	6.0±1.2	10.0±2.0	BDL	BDL	BDL
Mn	<sup>56</sup> Mn	30±2	23.0±1.4	52.0±2.3	17.4±1.0	41.3±2.0	163±7
Dy	<sup>165</sup> Dy	BDL	BDL	BDL	BDL	BDL	BDL
Na	<sup>24</sup> Na	3559±177.9	3441±172	3441±172	861±43	1170±59	1182±59
K	<sup>42</sup> K	BDL	BDL	BDL	2486±333	4714±542	5513±562
As	<sup>46</sup> As	1.5±0.3	BDL	BDL	BDL	BDL	BDL
Br	<sup>82</sup> Br	12±1	8.3±1.0	8.3±1.0	0.6±0.2	2.4±0.3	15±1
La	<sup>140</sup> La	2.1±0.3	2.3±0.3	2.3±0.3	2.0±0.3	4.1±0.1	8.5±0.6
Sm	<sup>153</sup> Sm	BDL	BDL	BDL	BDL	BDL	BDL
Yb	<sup>175</sup> Yb	BDL	BDL	1.0±0.3	BDL	BDL	BDL



U	<sup>239</sup> U	BDL	BDL	1.7±0.3	BDL	1.0±0.2	1.5±0.4
Sc	<sup>46</sup> Sc	0.30±0.04	0.4±0.1	1.4±0.1	0.40±0.04	1.3±0.1	2.0±0.1
Cr	<sup>51</sup> Cr	BDL	BDL	BDL	BDL	14.0±3.0	BDL
Fe	<sup>59</sup> Fe	3882±30.3	1802±40.0	1802±40.0	2256±29.1	3532±32.5	3450±64.6
Co	<sup>60</sup> Co	3.7±0.5	BDL	1.1±0.3	BDL	2.0±0.4	3.6±0.5
Zn	<sup>65</sup> Zn	BDL	BDL	BDL	BDL	BDL	2704±17.6
Rb	<sup>86</sup> Rb	BDL	BDL	BDL	BDL	38±9	BDL
Cs	<sup>134</sup> Cs	BDL	BDL	BDL	BDL	BDL	1.3±0.4
Ba	<sup>131</sup> Ba	BDL	148±38	BDL	BDL	359±72	BDL
Eu	<sup>152</sup> Eu	BDL	BDL	164±49	BDL	BDL	BDL
Lu	<sup>177</sup> Lu	BDL	BDL	BDL	BDL	BDL	BDL
Hf	<sup>181</sup> Hf	BDL	BDL	14.0±1.3	14.0±1.3	BDL	2.5±0.4
Ta	<sup>182</sup> Ta	BDL	BDL	0.5±0.1	BDL	BDL	BDL
Sb	<sup>122</sup> Sb	BDL	BDL	BDL	BDL	BDL	BDL
Th	<sup>233</sup> Pa	BDL	BDL	4.1±0.6	4.1±0.6	BDL	2.1±0.3

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

The concentrations obtained for daughters nuclides of <sup>238</sup>U (<sup>239</sup>Np) and <sup>232</sup>Th (<sup>233</sup>Pa) in the samples are higher (Tables 3 and 4) than the permissible contaminant levels reported for <sup>238</sup>U, <sup>232</sup>Th, <sup>40</sup>K which are 35 30, 400 Bqkg<sup>-1</sup> respectively and 20-30 µg/l, UNSCEAR 2000). The mean activities can be calculated using equation 1 below. The concentration unit in ppm can be calculated from measured activity values using the empirical equation:

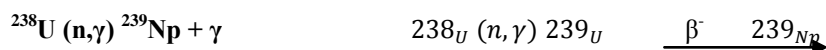
$$M \text{ (ppm)} = \frac{[C M_w] t_{1/2}}{N_{AV} \ln 2} \times 10^6 \quad \text{eqn ( i)}$$

C is measured in Becquerel per kilogram of the radionuclides, M<sub>w</sub> the molecular mass (g/mol), N<sub>AV</sub> the Avogadro's number and t<sub>1/2</sub> the half life in seconds.( Abbady *et al.*,2005).

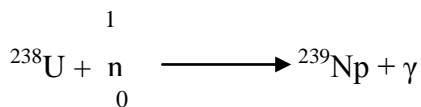
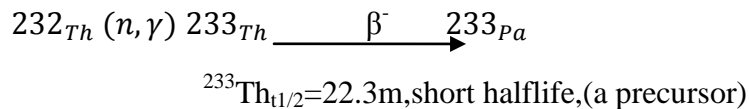
**Table 5: Activity Concentration (mean) Bq Kg<sup>-1</sup> (UNSCEAR 2000)**

	<sup>238</sup> U	<sup>232</sup> Th	<sup>40</sup> K
Worldwide Average	35	30	400

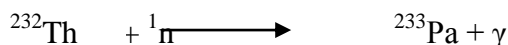
The irradiation of the mother nuclides of uranium and thorium in the samples did not yield the fission products but produced <sup>239</sup>Np and <sup>233</sup>Pa thus:



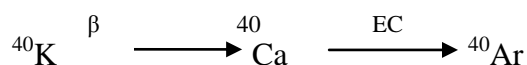
$^{239}\text{U}_{t/2}=23.47\text{m}$ ; unstable with short  $t^{1/2}$  (a precursor)



Similarly



Potassium decays by beta emission or k-capture. These results compares favourably with the findings of Glasstone and Sesonske, 1981 and Chowhury *et al.*, 2005.



### STATISTICAL ANALYSIS OF THE DATA.

In the study of seasonal interaction for the concentration of the nuclides, it was observed that three main clusters were formed (Fig. 2). 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 2003; Einax *et al.*, 1997, 1998, Vernet 1991; Simeonov *et al.*, 2002 and Smolinski *et al.*, 2002.

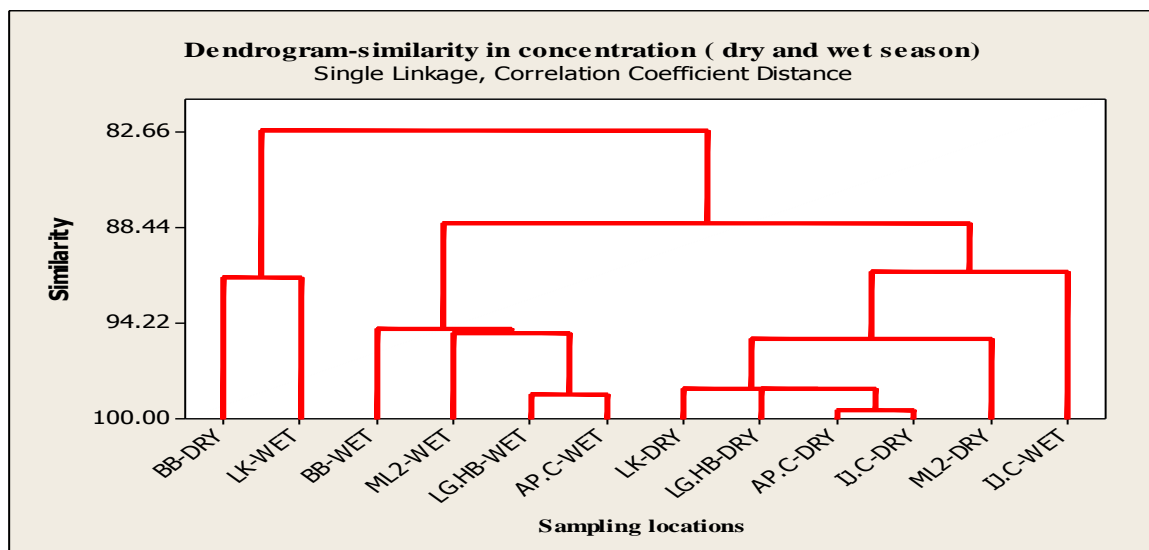


Fig. 2 Showing Cluster analysis for nuclides (dry and wet season)

## CONCLUSION

Qualitative and quantitative analysis for nuclides of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  series has been determined in sediments samples collected from six locations in Lagos State, Nigeria using Neutron Activation technique. The values obtained are above the maximum permissible levels of  $30\mu\text{g/l}$ . The statistical study of the seasonal variables and the nuclides showed that there was no correlation between them. This culminated to the use of cluster analysis. The dendrogram showed (clusters) that the seasons in the coastal areas especially Lagos has 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. The interactions of the wet and dry seasons in this research have shown that the nuclides of Uranium-238, Thorium-232 and Potassium-40 series are on the move and no significant change in the level of the nuclides from wet to dry season; but the concentrations of the daughter nuclides of Uranium, Thorium, and Potassium obtained are above the permissible levels by IAEA and may have health implication on the environment and persons living around the Coastal areas.

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## REFERENCES

- [1] Aarkrog, A (1997): "A Comparison of doses from  $^{137}\text{Cs}$  and  $^{210}\text{Po}$  in marine food" : A major international study. *Journal of Environmental Radioactivity* 43 (1); 69-90.
- [2] Abbadly Adel., EL-Arabi A., and Abbadly A., (2005): Heat production from radioactive rocks elements in igneous and metamorphic in eastern desert, Egypt. *Arab Journal of Nuclear Science*; 38 ( 2 ), 287-297
- [3] Balakrishna, R., Sarin,M.M., and Manjunatha,B.R. (2001): Distribution of U- Th nuclides in the Riverine and Coastal Environments of the tropical south west coast of India; *Journal of Environment Radioactivity*, 57, 1, 21-33
- [4] Cooper, M.B. (2003): Naturally occurring radioactive materials (NORM) in Australian Industries review of current inventories and future Generation. Report prepared for the radiation health and safety Advisory Council, ER006
- [5] Einax, J. W., Zwanziger, H.W., and Geib, S., (1997): *Chemometrics in Environmental Analysis* (Wiley-VCH, Weinheim) 33.
- [6] Einax, J. W., and Soldt, U., (1999): Geostatistical and Multivariable methods in assessment of polluted soils. *Chemom Intel. Lab. Syst.* 46, 79.
- [7] Ewa, I.O.B. (1992): Characterization of trace contaminant in Nigerian coals using NAA, Ph.D. thesis, ABU Zaria.
- [8] Ewa, I O.B., Oladipo, M,O,A, and Seydou Hankouraou, (2004): Determination of Heavy elements in Nigerian River Sediments using the Energy Disperse X-Ray Fluorescence Technique, *Nig. Journal of Physics* 16,2.
- [9] Glasstone, S. (1967). *Source Book on Atomic Energy*; Van Nostrand R Reinhold Coy, 3rd Edition 13-18.
- [10] Goldberg, E.D (1972) In: the changing chemistry of the ocean "Wiley Inter Sc. Div, New York, 1032.

- [11] Haskin, L.A and Schmidt, B.A.(1967): Rare Earth distribution in: Researches in Geochemistry, Vol. 2, Abelson P.H. (Ed.) John Wiley, New York, 234-258.
- [12] Henderson, P, (1984): Rare Earth Element Geochemistry, Elsevier, Amsterdam, 63-114.
- [13] Jonah S.A., Umar I.M. Oladipo M.O.A., Balogun G.I. and Adeyemo D.J. (2006).
- [14] Standardization of NIRR 1 Irradiation and counting facilities for instrumental neutron activation analysis. Applied Radiation and Isotopes 64, 818 – 822.
- [15] Laul, J.C (1984): Rare Earth element behavior in the development of energy resources. Proc. 5th Int. Conf. Nuclear Methods in Environ and Energy Research, Univ. of Missouri U.S.A CONF-840408
- [16] Norse Decom A.S. (2003): Naturally Occurring Radionuclides in the marine environment an overview of current knowledge with emphasis on the North Sea Area; 26 – 48.
- [17] Oladipo, M. O. A., (1987): Trace element analysis of Corinthian Pottery and related clays. Ph.D. Thesis, University of Manchester.
- [18] Parret, A. (1998): Pollution impact on North Seas fish stocks, Science of the Total Envi. 68,34, 78-79.
- [19] Polikarpov, J. (1998): Conceptual model of responses of organisms, populations and ecosystems to all possible dose rates of ionizing radiation in the environment. Radiation Prot. Dosim 75(1-4):181-185
- [20] Santschi, P.H and Honeyman, B.D (1997). Radionuclide's in Aquatic Environments; radiation. Phys. Chem.. 34, 2, 216 -219.
- [21] Simeonov V., Einax J.W., Stanimirova I. (2002): Environmetric modelling and interpretation of river water monitoring data; and Bioanal Chem. 374, 898.
- [22] Smolinski A., Wakzak B., Einax J.W. (2002) Hierarchical Clustering extended with visual complements of environmental data set. CILS, 64, 45.
- [23] Tryon, R. C., (2002): A Cluster Analysis. Ann Arbor, MI. Edwards Brothers. 16
- [24] UNSCEAR (2000): United Nations Scientific Committee on the Effects of Atomic Radiation (2000): Sources and effects of ionizing radiation. Report to the General Assembly, 4. Annex B. 60
- [25] Vernet, J.P (1991): Heavy metals in the environment. Elsevier, Amsterdam, 45.
- [26] Ward, J.H. (2003) "Hierarchical grouping to optimize an objective function" Journal of the American Statistical Association, 58(301); 236-244
- [27] Williams, G.C. (2004): Sampling Techniques, 3rd Edition. New York, 89-92