



# Journal of Applied Sciences

ISSN 1812-5654

**science**  
alert

**ANSI***net*  
an open access publisher  
<http://ansinet.com>

## Measurement of Natural Radioactivity in the Clays Consummated in Côte d'Ivoire using Gamma-ray Spectrometry

<sup>1</sup>Coulibaly Vamoussa, <sup>1</sup>Sei Joseph, <sup>1</sup>Kouame N'Dri, <sup>2</sup>Koua Aka Antonin,  
<sup>1</sup>Oyetola Samuel and <sup>3</sup>Brun Stéphane

<sup>1</sup>Laboratoire de Chimie des Matériaux Inorganiques (LCMI),  
UFR SSMT, Université Félix Houphouët-Boigny, 22 BP 582, Abidjan 22, Côte d'Ivoire

<sup>2</sup>Laboratoire de Physique Nucléaire et de Radioprotection,

UFR SSMT, Université Félix Houphouët-Boigny, 22 BP 582, Abidjan 22, Côte d'Ivoire

<sup>3</sup>Commissariat à l'Énergie Atomique (CEA), Laboratoire de Radioanalyse et de Chimie de l'Environnement,  
Saclay, Bat 524 P146/Point Courrier 84, 91191 Gif-sur-Yvette Cedex, France

**Abstract:** The presence of radionuclides in natural materials was one of the major causes of external and internal exposure to ionizing radiation (gamma rays). The knowledge of the radioactivity levels in these commonly used materials was of great importance in the assessment of possible radiological risks to human health. The purpose of this study was to determine the natural radioactivity due to <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K of some clay samples consummated in Côte d'Ivoire for their therapeutic virtues by using gamma spectrometry. The activity concentration of <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K ranged from 19.0±8.2 to 54.8±20.8 Bq kg<sup>-1</sup> (with a mean of 33.6±13.2 Bq kg<sup>-1</sup>), from 12.8±3.5 to 42.3±12.1 Bq kg<sup>-1</sup> (with a mean of 31.3±8.5 Bq kg<sup>-1</sup>) and from 16.0±59.2 to 790±245 Bq kg<sup>-1</sup> (with a mean of 314.1±101.7 Bq kg<sup>-1</sup>), respectively. Radium equivalent activities and various hazard indices were also calculated to assess the radiation hazard. The Radium equivalent activity (Ra<sub>eq</sub>) ranged from 90.2±28.4 to 130.3±43.8 Bq kg<sup>-1</sup> (with an average of 102.6±33.1 Bq kg<sup>-1</sup>), was lower than the limit of 370 Bq kg<sup>-1</sup>. The calculated values of external hazard index (H<sub>ex</sub>) 0.24±0.08-0.35±0.12 and internal hazard index (H<sub>in</sub>) 0.32±0.11-0.50±0.18 were also lower than unity. The annual effective dose ranged from 52.2±16.3 to 73.8±24.8 μSv y<sup>-1</sup> with a mean of 59.6±19.1 μSv y<sup>-1</sup> whereas the effective dose by ingestion varied from 17.1±6.2 to 30.8±11.1 μSv y<sup>-1</sup> with an average of 21.3±7.6 μSv y<sup>-1</sup>. These values were lower than the limit of 1 mSv y<sup>-1</sup>. From this study, it was found that the use of the investigated clay samples for their therapeutic virtues did not induce significant radiation hazards.

**Key words:** Natural radioactivity, gamma spectrometry, activity concentration, hazard indexes, effective dose engaged, clays colloids

### INTRODUCTION

Clay minerals being soil colloids are very widespread in the terrestrial crust. Their basic structural elements are similar: sheets of corner-sharing oxygen tetrahedral with Si<sup>4+</sup> and generally some Al<sup>3+</sup> as central cations and sheets of edge-sharing octahedral in which oxygen and hydroxyl surround a variety of possible di or trivalent cations (mainly Mg<sup>2+</sup>, Fe<sup>2+</sup>, Al<sup>3+</sup> and Fe<sup>3+</sup>).

In addition to these major elements, one meets in their bosom many chemical elements including the alkali, alkaline-earth, metals of transition, lanthanides and actinides. These elements are either in isomorphous substitutions in their network, either in the inter layer space where they play the role of compensatory ions,

either to the adsorbed state at the surface of the clay particles. They can also belong to other associated minerals. Some of these chemical elements notably uranium, thorium, potassium have unsteady cores and confer to the clay minerals a natural radioactivity whose importance depends on their concentration. The population whom is exposed to them directly via the ingestion or inhalation pathways can receive external and internal dose.

The knowledge of concentration and distribution of the radionuclides in these minerals are of interest because it provides useful information in the monitoring of environmental radioactivity. Importance of this subject has given rise to numerous studies on the radioactivity in soils (Pourcelot *et al.*, 2003; Laubenstein and Magaldi,

2008; Al-Hamarnah and Awadallah, 2009; Montes *et al.*, 2012), in the building materials (Hewamanna *et al.*, 2001; Petropoulos *et al.*, 2002; Pavlidou *et al.*, 2006; Turhan, 2008; Kumar *et al.*, 1999; Ravisankar *et al.*, 2012), in foodstuffs (Santos *et al.*, 2002; Bolca *et al.*, 2007) and in groundwater (Amin *et al.*, 2011).

In Côte d'Ivoire, the "Société pour le Développement Minier" (SODEMI) listed several clays deposits through the country. These materials are used in several domains such as pottery, building materials (tiles, bricks...), ceramics, health.

The object of this study was to determine the chemical composition as well as the radioactivity of some consummated clay samples in Côte d'Ivoire for their therapeutic virtues namely by pregnant women. In order to appreciate the risks bound to this practice and to develop standards concerning their exploitations and uses, different parameters relative to radiation hazards have been calculated and compared to the standard limits.

## MATERIALS AND METHODS

**Clay sampling:** The studied eight clay samples come from Anyama and Bingerville, two commons of the district of Abidjan (Côte d'Ivoire). Anyama is situated at 10 km North-West while Bingerville is located at 12 km South-West of Abidjan.

These localities are localized in the sedimentary basin and the clays are supposed to be formed after sedimentation of alluvial products eroded from the uppermost layer of the Precambrian shelf (Le Bourdiec, 1958).

Anyama is situated in a plateau area and the studied green clay (labelled AVA) is dominated by chlorite, illite and quartz with minor amounts of other minerals including smectite (Coulbaly *et al.*, 2012). It is commercialized by the local population for its therapeutic virtues. It is used by internal way and also by external way to treat many diseases such as whitlow, athlete foot and stomach disease. This green clay is also used for soap production. For this study, the only one sample has been collected to about 2 m of depth from mineral deposit and dried in air as that sold.

Bingerville is situated in the coastal lagoon and the seven clay samples are labeled as follows:

**LBF** : White lokpo  
**LRF** : Red lokpo  
**LMF** : Brown lokpo  
**LVF** : Purple lokpo

**LJPF** : Yellow lokpo  
**LJFF** : Dark yellow lokpo  
**LNF** : Gray lokpo

They are dominated by kaolinite with relative important amounts of quartz, illite and goethite (Coulbaly *et al.*, 2012) and have the particularity to be eatable (generally by pregnant women) after manning. They are also used for soap preparation and other beauty care. The samples were taken from the site of exploitation according to their color; they suffer the same heat treatment as those sold, commonly called "Lokpo". This treatment involves cleaning of the clays to rid them of the impurities and heating the sample in an oven built in clay and powered by firewood for 3 to 5 days. This operation often gives the clay material a pleasant and smells appetizing.

For the different analyzes, the samples have been dried at 40°C during 24 h in a steam room, ground and sieved through 80 µm mesh. A portion of each sample was used for chemical composition analysis while the remaining part was used for natural radioactivity determination.

**Chemical analysis:** The chemical analysis in total rock was carried out by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) for major elements and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) for trace elements after fusion with LiBO<sub>2</sub> and dissolution in HNO<sub>3</sub>.

The total adsorbed and structural (structural OH) water contents were determined by thermogravimetric analysis at 1200°C.

**Radioactivity measurement:** The activity measurements were made using a typical high resolution gamma-ray spectrometer. The system comprises a high-purity n-type coaxial germanium (HPGe) detector with a relative photo peak efficiency of 60%. About 100 g of each sample were placed in cylindrical plastic container 75 mm in diameter and 15 mm in height. They were hermetically sealed and stored for 3 weeks before counting, allowing time for <sup>226</sup>Ra and <sup>232</sup>Th to reach equilibrium with their respective progenies. The accumulation time for gamma ray spectra measurement was 18 h. Prior to sample measurement, the laboratory background was determined and peak corrections were performed.

The concentrations of various nuclides of interest were determined in Bq kg<sup>-1</sup> using the counted spectra.

The activity concentration of <sup>40</sup>K was measured directly by its own gamma ray at 1460.7 keV, while activities of <sup>226</sup>Ra and <sup>232</sup>Th were calculated based on the weighted mean value of their respective decay products in equilibrium.

## RESULTS AND DISCUSSION

### Chemical analysis

**Major elements:** The major elements expressed in weight percentage of oxides are given in Table 1. All samples contain qualitatively the same elements. Sample AVA

differs from those of Bingerville by its high SiO<sub>2</sub> content and its low Al<sub>2</sub>O<sub>3</sub> content. It also contains significant quantity of MgO, Fe<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O.

Excepted LJFF, the samples of Bingerville have relatively homogenous composition with SiO<sub>2</sub> content ranging from 45.73 to 57.05%, Al<sub>2</sub>O<sub>3</sub> from 25.2 to 34.4%, Fe<sub>2</sub>O<sub>3</sub> from 2.3 to 4.92%. Sample LJFF is characterized by its very high Fe<sub>2</sub>O<sub>3</sub> (26%) content and low concentration of silica (42.7%) and alumina (18.33%).

**Trace elements:** The trace elements expressed in ppm are given in Table 2. They are in the majority constituted of

Table 1: Chemical composition of the major elements in weight percent

Sample	Colour	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O
AVA	Green	61.58	17.21	7.42	0.08	3.84	0.04	0.46	2.38	0.75	nd	5.74
LBF	White	52.83	29.74	2.34	nd	0.29	nd	0.11	1.17	1.06	0.08	12.03
LRF	Red	51.06	30.18	4.48	0.00	0.22	nd	0.11	1.16	1.13	0.06	11.97
LMF	Brown	56.55	25.44	4.25	0.01	0.36	nd	0.08	1.01	1.10	0.08	11.46
LVF	Purple	45.73	34.41	4.92	nd	0.07	nd	0.06	0.57	1.12	0.09	13.12
LJPF	Yellow	55.33	27.81	3.97	0.00	0.24	nd	0.06	0.77	0.94	0.21	11.40
LNF	Black	57.05	25.22	2.23	0.01	0.37	nd	0.07	0.97	1.03	0.10	13.02
LJFF	Dark-yellow	42.71	18.33	26.02	nd	0.14	nd	0.05	0.63	0.87	0.12	11.69

nd: Not determined, AVA: Green clay of Anyama, LBF: White lokpo, LRF: Red lokpo, LMF: Brown lokpo, LVF: Purple lokpo, LJPF: Yellow lokpo, LJFF: Dark yellow lokpo, LNF: Gray lokpo of Bingerville

Table 2: Chemical composition of trace elements in ppm

Samples	As	Ba	Be	Bi	Cd	Ce	Co	Cr	Cs	Cu	Dy	
AVA	nd	523.1	1.03	0.15	nd	52.53	32.92	138.10	5.00	43.87	4.23	
LBF	7.77	313.8	1.28	0.35	0.13	120.40	3.53	163.10	7.33	19.34	4.79	
LRF	12.26	299.3	1.24	0.40	0.15	53.07	3.17	160.00	5.76	12.97	2.49	
LMF	4.55	21.1	0.98	nd	0.30	30.42	29.50	94.58	0.51	83.51	7.58	
LVF	18.27	159.4	1.13	0.48	0.14	90.75	3.33	173.70	2.05	7.45	2.16	
LJPF	14.67	283.9	1.42	0.28	0.15	418.10	2.38	160.70	5.10	11.90	8.09	
LNF	12.53	291.7	1.78	0.33	0.20	132.50	21.24	149.60	6.39	19.24	8.09	
LJFF	10.75	146.5	1.22	0.25	0.12	29.97	3.09	159.20	3.86	34.63	2.33	
Samples	Er	Eu	Ga	Gd	Ge	Hf	Ho	In	La	Lu	Mo	Nb
AVA	2.44	1.39	20.44	4.56	1.89	2.88	0.85	nd	21.15	0.38	nd	5.17
LBF	2.24	2.16	34.59	6.29	2.04	5.49	0.83	nd	50.75	0.36	1.073	12.53
LRF	1.50	0.77	37.13	2.61	1.89	5.74	0.49	nd	31.88	0.29	1.21	13.32
LMF	4.41	2.01	20.18	7.05	1.76	5.06	1.57	nd	11.93	0.69	0.38	10.85
LVF	1.14	0.96	40.35	2.73	1.57	5.39	0.38	nd	48.98	0.20	2.64	15.79
LJPF	2.84	5.08	26.87	13.31	2.32	6.30	1.16	nd	185.60	0.36	0.58	11.20
LNF	3.75	3.16	28.66	10.29	2.17	6.70	1.43	nd	53.53	0.54	1.03	13.45
LJFF	1.43	0.63	22.28	2.25	1.79	4.64	0.48	nd	17.35	0.26	0.55	10.78
Samples	Nd	Ni	Pb	Pr	Rb	Sb	Sm	Sn	Sr	Ta	Tb	
AVA	24.98	100.20	4.58	6.07	86.12	1.09	5.05	1.07	60.52	0.45	0.69	
LBF	49.81	22.52	17.98	13.46	62.08	0.59	9.29	2.79	88.88	1.14	0.91	
LRF	18.80	23.19	18.91	5.53	56.74	0.62	3.24	2.90	71.36	1.19	0.41	
LMF	21.34	52.18	4.65	4.49	13.05	0.21	6.11	2.19	274.10	0.89	1.20	
LVF	29.11	25.47	29.98	9.25	24.59	0.71	4.43	3.04	87.10	1.58	0.40	
LJPF	140.50	16.08	100.84	41.91	46.72	0.47	23.56	2.12	131.00	1.00	1.76	
LNF	64.59	96.75	19.21	16.03	63.61	0.64	12.95	2.71	92.55	1.17	1.50	
LJFF	12.51	14.34	8.66	3.44	36.81	0.426	2.47	2.02	31.58	0.95	0.37	
Samples	Th	Tm	U	V	W	Y	Yb	Zn	Zr			
AVA	3.47	0.37	1.02	104.20	1.57	25.21	2.52	138.20	105.8			
LBF	9.22	0.33	1.85	103.10	1.73	20.00	2.22	33.98	196.6			
LRF	9.88	0.24	1.95	108.80	1.94	13.63	1.72	37.10	207.2			
LMF	0.81	0.67	0.39	259.30	nd	44.02	4.39	91.68	213.4			
LVF	13.00	0.18	2.28	150.20	1.98	9.89	1.26	34.05	194.6			
LJPF	8.31	0.37	2.11	151.70	1.40	24.56	2.35	26.07	246.0			
LNF	9.13	0.55	1.96	97.54	1.66	36.75	3.63	39.12	259.2			
LJFF	7.54	0.23	3.98	90.96	1.31	13.60	1.64	66.18	178.7			

nd: Not determined, AVA: Green clay of Anyama, LBF: White lokpo, LRF: Red lokpo, LMF: Brown lokpo, LVF: Purple lokpo, LJPF: Yellow lokpo, LJFF: Dark yellow lokpo, LNF: Gray lokpo of Bingerville

alkali, alkaline-earth, metals of transition, lanthanides and actinides. Their uranium content ranges from 0.39 to 3.98 ppm and the high content is observed in the sample LJFF while the lowest is observed in the sample LMF. The thorium content ranges from 0.81 to 13 ppm and the high content is observed in the sample LVF while the lowest is observed in the sample LMF.

**Activity concentration:** The most important source of natural radiation exposure is caused by the gamma rays emitted from members of the uranium and thorium decay chains and radioactive potassium ( $^{40}\text{K}$ ) occurring naturally in soil colloids including clay minerals. In the  $^{238}\text{U}$  series, the decay chain segment starting from radium ( $^{226}\text{Ra}$ ) is radiologically most important and therefore, reference is often made to  $^{226}\text{Ra}$  instead of  $^{238}\text{U}$  (Ravisankar *et al.*, 2012).

The activity concentrations of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  in  $\text{Bq kg}^{-1}$  dry weight are given in Table 3 while in Fig. 1, the activity concentrations of the examined samples are compared. The radioactivity concentrations of the three nuclides are relatively homogenous in the different samples of Bingerville but they are different from those of the sample of Anyama. The latest sample is characterized by very low concentration in  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and a very high concentration in  $^{40}\text{K}$ , in agreement with the chemical analysis. The activity concentrations of  $^{226}\text{Ra}$  and  $^{232}\text{Th}$  are in the same ranges and are lesser than the activity concentration of  $^{40}\text{K}$ .

As can be seen from the results, the lowest value of  $^{226}\text{Ra}$  concentration is  $19.0 \pm 8.2 \text{ Bq kg}^{-1}$  measured in sample AVA while the highest value for the same radionuclide is  $54.8 \pm 20.8 \text{ Bq kg}^{-1}$  measured in sample LBF.

The observed minimum and maximum  $^{232}\text{Th}$  activity concentration were respectively  $12.8 \pm 3.5 \text{ Bq kg}^{-1}$  in sample AVA and  $42.3 \pm 12.1 \text{ Bq kg}^{-1}$  in sample LVF.

Activity concentration of  $^{40}\text{K}$  varies from  $160.0 \pm 59.2 \text{ Bq kg}^{-1}$  in sample LVF to  $790 \pm 245 \text{ Bq kg}^{-1}$  in sample AVA.

For building materials including clay materials, the world average values are 35, 30 and  $400 \text{ Bq kg}^{-1}$ , respectively for  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  (UNSCEAR, 2000). The activity concentration of  $^{40}\text{K}$   $790 \pm 245 \text{ Bq kg}^{-1}$  in sample AVA exceeds the normal level and is due to the presence of illite in the sample.

The average values of activity concentration of the investigated samples for  $^{226}\text{Ra}$  ( $33.6 \pm 13.2 \text{ Bq kg}^{-1}$ ),  $^{232}\text{Th}$  ( $31.3 \pm 8.5 \text{ Bq kg}^{-1}$ ) and  $^{40}\text{K}$  ( $314.1 \pm 101.7 \text{ Bq kg}^{-1}$ ) are in the ranges of the corresponding typical world averages for the said nuclides, respectively.

The natural radioactivity levels measured in the investigated samples are comparable and within the range

Table 3: Activity concentration due to  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  in the investigated samples

Samples	Radioactivity concentration ( $\text{Bq kg}^{-1}$ )		
	$^{226}\text{Ra}$	$^{232}\text{Th}$	$^{40}\text{K}$
AVA	$19.0 \pm 8.2$	$12.8 \pm 3.5$	$790.0 \pm 244.9$
LBF	$54.8 \pm 20.8$	$39.8 \pm 11.4$	$241.0 \pm 86.8$
LRF	$29.0 \pm 11.3$	$29.3 \pm 7.6$	$250.0 \pm 80.0$
LVF	$33.0 \pm 14.2$	$42.3 \pm 12.1$	$160.0 \pm 59.2$
LMF	$25.0 \pm 10.5$	$31.3 \pm 8.3$	$300.0 \pm 96.0$
LJPF	$33.0 \pm 12.2$	$34.3 \pm 8.8$	$260.0 \pm 83.2$
LJFF	$39.0 \pm 14.4$	$28.0 \pm 7.4$	$220.0 \pm 70.4$
LNF	$35.8 \pm 13.6$	$32.8 \pm 8.5$	$292.0 \pm 93.4$
Average	$33.6 \pm 13.2$	$31.3 \pm 8.5$	$314.1 \pm 101.7$

AVA: Green clay of Anyama, LBF: White lokpo, LRF: Red lokpo, LMF: Brown lokpo, LVF: Purple lokpo, LJPF: Yellow lokpo, LJFF: Dark yellow lokpo, LNF: Gray lokpo of Bingerville

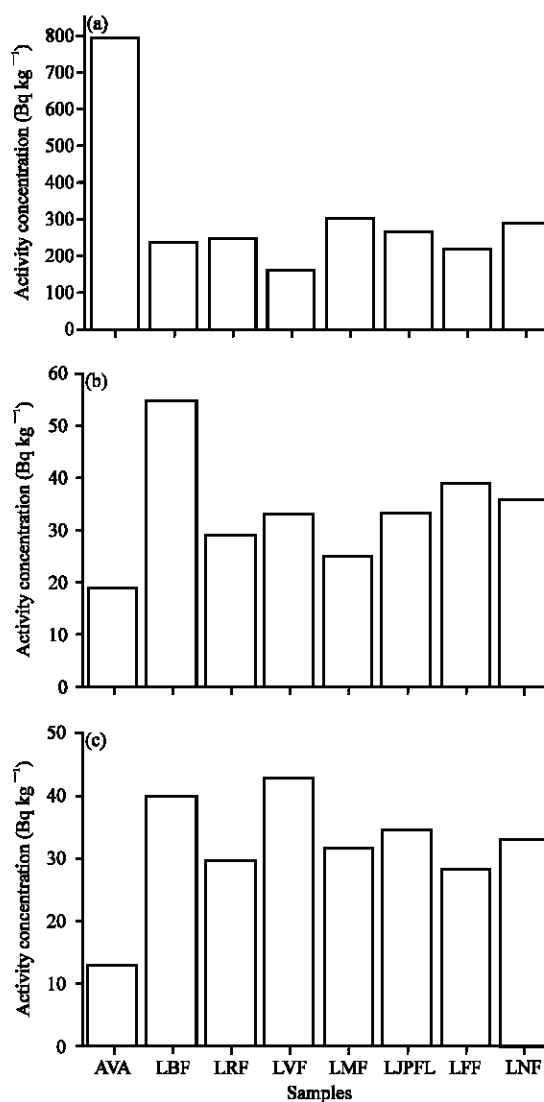


Fig. 1(a-c): Different clay samples (a)  $^{40}\text{K}$ , (b)  $^{226}\text{Ra}$  and (c)  $^{232}\text{Th}$  accounted for their activity concentration

reported for other countries. Righi and Bruzzi (2006) found 23-24 Bq kg<sup>-1</sup> for <sup>226</sup>Ra, 30-36 Bq kg<sup>-1</sup> for <sup>232</sup>Th and 540-590 Bq kg<sup>-1</sup> for <sup>40</sup>K in red clay roofing tiles (regions of northern Italy). In mean, 33±20 Bq kg<sup>-1</sup> for <sup>226</sup>Ra, 37±17 Bq kg<sup>-1</sup> for <sup>232</sup>Th and 511±158 Bq kg<sup>-1</sup> for <sup>40</sup>K are found in clay bricks (Upper Egypt) (Ahmed, 2005).

However, the activity concentrations for <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K measured in the investigated samples are higher than those found in the clays used in building materials of Namakkal (Ravisankar *et al.*, 2012).

**Radium equivalent activity;** As the distribution of natural radionuclides in samples is not uniform, a common radiological hazard index has been introduced in order to compare the specific activities of materials containing different amounts of <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K. This index used to obtain the sum of those activities, is called Radium equivalent activity (Ra<sub>eq</sub>) and is given by the relation below (Beretka and Mathew, 1985):

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

where A<sub>Ra</sub>, A<sub>Th</sub> and A<sub>K</sub> are respectively the activity concentration of the radionuclides <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K.

The above formula is based on the estimation that 370 Bq kg<sup>-1</sup> of <sup>226</sup>Ra, 259 Bq kg<sup>-1</sup> of <sup>232</sup>Th or 4810 Bq kg<sup>-1</sup> of <sup>40</sup>K produce the same gamma dose rate (Stranden, 1976).

The calculated values of Radium equivalent activity (Ra<sub>eq</sub>) for the different samples are shown in Table 4. These values vary from 90.2±28.4 Bq kg<sup>-1</sup> (sample LRF) to 130.3±43.8 Bq kg<sup>-1</sup> (sample LBF) with an average of 102.6±33.1 Bq kg<sup>-1</sup>. This estimated value is lower than the recommended maximum value of 370 Bq kg<sup>-1</sup> (UNSCEAR, 2000).

**The external and internal hazard indices:** The external hazard index (H<sub>ex</sub>) is a criterion to access the radiological suitability of a material. The model, proposed by Krieger (1981), defines the external hazard index as follows:

Table 4: Radium equivalent activity, external and internal hazard indices values of the studied clay samples

Samples	Ra <sub>eq</sub> (Bq kg <sup>-1</sup> )	H <sub>ex</sub>	H <sub>in</sub>
AVA	98.1±32.1	0.27±0.09	0.32±0.11
LBF	130.3±43.8	0.35±0.12	0.50±0.18
LRF	90.2±28.4	0.24±0.08	0.32±0.11
LVF	105.9±36.1	0.30±0.10	0.38±0.14
LMF	92.9±29.7	0.25±0.08	0.32±0.11
LJPF	102.1±31.2	0.28±0.08	0.37±0.12
LJFF	96.0±30.4	0.26±0.08	0.37±0.12
LNF	105.2±33.0	0.28±0.09	0.38±0.13
Average	102.6±33.1	0.28±0.09	0.37±0.13

AVA: Green clay of Anyama, LBF: White lokpo, LRF: Red lokpo, LMF: Brown lokpo, LVF: Purple lokpo, LJPF: Yellow lokpo, LJFF: Dark yellow lokpo, LNF: Gray lokpo of Bingerville, Ra<sub>eq</sub>: Radium equivalent activity, H<sub>ex</sub>: External hazard index, H<sub>in</sub>: Internal hazard index

$$H_{ex} = \frac{A_{Ra}}{370 \text{ Bq kg}^{-1}} + \frac{A_{Th}}{259 \text{ Bq kg}^{-1}} + \frac{A_K}{4810 \text{ Bq kg}^{-1}}$$

where, A<sub>Ra</sub>, A<sub>Th</sub> and A<sub>K</sub> are respectively the activity concentration of <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K. The value of H<sub>ex</sub> must not exceed the limit of unity to keep the radiation hazard insignificant.

The internal hazard index (H<sub>in</sub>) gives the internal exposure to carcinogenic radon and its short-lived progeny. It is given by the following formula:

$$H_{in} = \frac{A_{Ra}}{185 \text{ Bq kg}^{-1}} + \frac{A_{Th}}{259 \text{ Bq kg}^{-1}} + \frac{A_K}{4810 \text{ Bq kg}^{-1}}$$

The values of H<sub>in</sub> must also be less than unity to have negligible hazardous effect of radon and its short-lived progeny to the respiratory organs (Al-Hamarneh and Awadallah, 2009).

From the results (Table 4), the calculated values for H<sub>ex</sub> and H<sub>in</sub> vary from 0.24±0.08 to 0.35±0.12 and from 0.32±0.11 to 0.50±0.18, respectively. The lowest value is found in sample LRF for H<sub>ex</sub> and in sample AVA for H<sub>in</sub> while the highest values are in sample LBF.

The average values (0.28±0.09) for H<sub>ex</sub> and (0.37±0.13) for H<sub>in</sub>, being lower than unity indicated that the hazardous effects of these radiations are negligible.

**External gamma absorbed dose rates and annual effective dose:** The external absorbed dose rate, D<sub>ext</sub> (nGy h<sup>-1</sup>) contribution from <sup>226</sup>Ra, <sup>232</sup>Th and <sup>40</sup>K at 1 m above the ground was estimating using the equation (Farai *et al.*, 2006; Jibiri and Biere, 2011):

$$D_{ext} = 0.427 A_{Ra} + 0.662 A_{Th} + 0.043 A_K$$

The annual effective dose rate E<sub>ext</sub> (μSv y<sup>-1</sup>), resulting from the absorbed dose rate values and taking into account the conversion coefficient from absorbed dose in air to effective dose and the outdoor occupancy factor, was calculated using the following relation (Al-Hamarneh and Awadallah, 2009):

$$E_{ext} (\mu\text{Sv y}^{-1}) = D_{ext} (\text{nGy h}^{-1}) \times 24 \text{ h} \times 365.25 \text{ d} \times 0.2 \times 0.7 \text{ Sv Gy}^{-1} \times 10^{-3}$$

The conversion coefficient from Gy h<sup>-1</sup> to Sv h<sup>-1</sup> gives the equivalent human dose in Sv h<sup>-1</sup> from the absorbed dose rate in air (Gy h<sup>-1</sup>) while the occupancy factor gives the fraction of the time an individual is exposed to outdoor radiation. The conversion coefficient recommended by the UNSCEAR (2000) is 0.7 Sv Gy<sup>-1</sup> and the occupancy factor is 0.2 which suggests that people spent 20% of their time outdoors.

The results of these calculations are given in Table 5. The external absorbed dose rate in air outdoors  $D_{ext}$  and the annual effective dose  $E_{ext}$  values vary from  $42.6 \pm 13.3$  to  $60.1 \pm 20.2$  nGy  $h^{-1}$  and from  $52.2 \pm 16.3$  to  $73.8 \pm 24.8$   $\mu Sv y^{-1}$ , respectively. The lower values are registered in sample LRF and the highest are in sample LBF. The average values of the absorbed dose rate in air and the calculated annual effective dose are found to be  $48.6 \pm 15.6$  nGy  $h^{-1}$  and  $59.6 \pm 19.1$   $\mu Sv y^{-1}$ , respectively.

The absorbed dose rate in air outdoors from terrestrial gamma ray in normal circumstances is about 57 nGy  $h^{-1}$  while the worldwide average annual effective dose is approximately 70  $\mu Sv$  (UNSCEAR, 2000). The values calculated for the investigated samples are in good agreement with the average worldwide limits.

**Annual effective dose by ingestion:** The consumption by ingestion of the materials is a source of exposure to the rays emitted by the radionuclides. The effective dose by ingestion of the materials is given by the formula (Cazala *et al.*, 2006):

$$E_{ing} = \sum_j A_j \times q \times h_{j,ing}$$

Where:

- $E_{ing}$  (Sv  $y^{-1}$ ) = Annual effective dose by ingestion
- $q$  = Quantity of matter ingested (kg  $y^{-1}$ )
- $h_{j,ing}$  = Effective dose engaged by unit of incorporation of the radionuclide  $j$  (Sv Bq $^{-1}$ ) ingested

For  $^{226}Ra$ ,  $^{232}Th$  and  $^{40}K$ , the coefficients of effective dose engaged by unit incorporated by ingestion (Sv Bq $^{-1}$ ) are  $2.8 \times 10^{-7}$ ,  $9.2 \times 10^{-8}$  and  $6.2 \times 10^{-9}$ , respectively.

While admitting a yearly consumption of 1.5 kg, the relation becomes:

Table 5: External gamma absorbed dose rates, annual effective dose and annual effective dose by ingestion of the studied clay samples

Samples	$D_{ext}$ (nGy $h^{-1}$ )	$E_{ext}$ ( $\mu Sv y^{-1}$ )	$E_{ing}$ ( $\mu Sv y^{-1}$ )
AVA	50.6±16.4	62.1±20.1	17.1±6.2
LBF	60.1±20.2	73.8±24.8	30.8±11.1
LRF	42.6±13.3	52.2±16.3	18.6±6.5
LVF	49.0±16.6	60.1±20.4	21.2±8.2
LMF	44.3±14.1	54.4±17.3	17.6±6.4
LJPF	48.0±14.6	58.9±17.9	21.0±7.1
LJFF	44.7±14.1	54.8±17.3	22.3±7.7
LNF	49.6±15.5	60.8±19.0	22.3±7.8
<b>Average</b>	<b>48.6±15.6</b>	<b>59.6±19.1</b>	<b>21.3±7.6</b>

AVA: Green clay of Anyama, LBF: White lokpo, LRF: Red lokpo, LMF: Brown lokpo, LVF: Purple lokpo, LJPF: Yellow lokpo, LJFF: Dark yellow lokpo, LNF: Gray lokpo of Bingerville,  $D_{ext}$  (nGy  $h^{-1}$ ): External absorbed dose rate,  $E_{ext}$  ( $\mu Sv y^{-1}$ ): Annual effective dose rate,  $E_{ing}$  ( $\mu Sv y^{-1}$ ): Annual effective dose rate by ingestion

$$E_{ing} = 1.5 \times (2.8 \times 10^{-7} A_{ra} + 9.2 \times 10^{-8} A_{th} + 6.2 \times 10^{-9} A_K)$$

The values calculated for the investigated samples are given in Table 5. The observed values vary from  $(17.1 \pm 6.2 \mu Sv y^{-1})$  in sample AVA to  $(30.8 \pm 11.1 \mu Sv y^{-1})$  in the sample LBF. The average value calculated is  $21.3 \pm 7.6 \mu Sv y^{-1}$ . This value is lower than the admissible value of 1 mSv  $y^{-1}$ .

### CONCLUSION

The radioactivity concentrations of  $^{226}Ra$ ,  $^{232}Th$  and  $^{40}K$  measured in the investigated clay samples of Côte d'Ivoire have been determined by gamma ray spectrometry. The specific activity, radium equivalent activity, radiation hazard indices, external annual dose and dose by ingestion have been determined for each sample in order to assess the radiological hazard.

These different parameters calculated in the present study are within the recommended safety limits. The clays studied do not pose any significant radiation hazard and hence can be consummated.

This investigation can serve as model for more extensive studies of the same subjects.

### REFERENCES

Ahmed, N.K., 2005. Measurement of natural radioactivity in building materials in Qena city, Upper Egypt. *J. Environ. Radioact.*, 83: 91-99.

Al-Hamarneh, I.F. and M.I. Awadallah, 2009. Soil radioactivity levels and radiation hazard assessment in the highlands of northern Jordan. *Radia. Measure.*, 44: 102-110.

Amin, R.M., F.A. Khalil and M.A.K. El Fayoumi, 2011. Natural radioactivity and chemical concentrations in Egyptian groundwater. *Environ. Monit. Assess.*, 173: 29-35.

Beretka, J. and P.I. Mathew, 1985. Natural radioactivity of Australian building materials, waste and by-products. *Health Phys.*, 48: 87-95.

Bolca, M., M.M. Sac, B. Cokuysal, T. Karali and E. Ekdal, 2007. Radioactivity in soil and various foodstuffs from the Gediz River Basin of Turkey. *Radia. Meas.*, 42: 263-270.

Cazala, C., B. Cessac and D. Gay, 2006. Methodological guide for the acceptance of waste with natural radioactivity in classified installations for disposal. Report DEI/SARG/2006-009, pp: 1-52.

Coulbaly, V., J. Sei, S. Oyetola, M.T. Sougrati and J.C. Jumas, 2012. Iron speciation in the clays consummated in Cote d'Ivoire: A transmission mossbauer spectroscopy study. *Asian J. Applied. Sci.*, 5: 460-472.

- Farai, I.P., R.I. Obed and N.N. Jibiri, 2006. Soil radioactivity and incidence of cancer in Nigeria. *J. Environ. Radioact.*, 90: 29-36.
- Hewamanna, R., C.S. Sumithrarachchi, P. Mahawatte, H.L.C. Nanayakkara and H.C. Ratnayake, 2001. Natural radioactivity and gamma dose from Sri Lankan clay bricks used in building construction. *Applied Radiat. Isot.*, 54: 365-369.
- Jibiri, N.N. and P.E. Biere, 2011. Activity concentrations of  $^{232}\text{Th}$ ,  $^{226}\text{Ra}$  and  $^{40}\text{K}$  and gamma radiation absorbed dose rate levels in farm soil for the production of different brands of cigarette tobacco smoked in Nigeria. *Iran. J. Radiat. Res.*, 8: 201-206.
- Krieger, R., 1981. Radioactivity of construction materials. *Betonwerk Fertigteil-Techn.*, 47: 468-473.
- Kumar, V., T.V. Ramachandran and R. Prasad, 1999. Natural radioactivity of Indian building materials and by-products. *Applied Radiat. Isot.*, 51: 93-96.
- Laubenstein, M. and D. Magaldi, 2008. Natural radioactivity of some red Mediterranean soils. *Catena*, 76: 22-26.
- Le Bourdiec, P., 1958. Contribution to geomorphological study of sedimentary basin and coastal regions of Cote d'Ivoire. *Eburnean Stud.*, 7: 7-97.
- Montes, M.L., R.C. Mercader, M.A. Taylor, J. Runco and J. Desimoni, 2012. Assessment of natural radioactivity levels and their relationship with soil characteristics in undisturbed soils of northeast of Buenos Aires province, Argentina. *J. Environ. Radioact.*, 105: 30-39.
- Pavlidou, S., A. Koroneos, C. Papastefanou, G. Christofides, S. Stoulos and M. Vavelides, 2006. Natural radioactivity of granites used as building materials. *J. Environ. Radioact.*, 89: 48-60.
- Petropoulos, N.P., M.J. Anagnostakis and S.E. Simopoulos, 2002. Photon attenuation, natural radioactivity content and radon exhalation rate of building materials. *J. Environ. Radioact.*, 61: 257-269.
- Pourcelot, L., D. Louvat, F. Gauthier-Lafaye and P. Stille, 2003. Formation of radioactivity enriched soils in mountain areas. *J. Environ. Radioact.*, 68: 215-233.
- Ravisankar, R., K. Vanasundari, A. Chandrasekaran, A. Rajalakshmi, M. Suganya, P. Vijayagopal and V. Meenakshisundaram, 2012. Measurement of natural radioactivity in building materials of Namakkal, Tamil Nadu, India using gamma-ray spectrometry. *Applied Radiat. Isot.*, 70: 699-704.
- Righi, S. and L. Bruzzi, 2006. Natural radioactivity and radon exhalation in building materials used in Italian dwelling. *J. Environ. Radioact.*, 88: 158-170.
- Santos, E.E., D.C. Lauria, E.C.S. Amaral and E.R. Rochedo, 2002. Daily ingestion of  $^{232}\text{Th}$ ,  $^{238}\text{U}$ ,  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{210}\text{Pb}$  in vegetables by inhabitants of Rio de Janeiro City. *J. Environ. Radioact.*, 62: 75-86.
- Stranden, E., 1976. Some aspects on radioactivity of building materials. *Phys. Norv.*, 8: 167-173.
- Turhan, S., 2008. Assessment of the natural radioactivity and radiological hazards in Turkish cement and its raw materials. *J. Environ. Radioact.*, 99: 404-414.
- UNSCEAR, 2000. Sources and effects of ionizing radiations. Report to the General Assembly with Scientific Annexes. United Nations, New York, USA.