Radiological and X-Ray Fluorescence Spectrometric Analyses of Selected Inorganic Fertilizers in Zaria Kaduna State, Nigeria: Source of Possible Environmental Pollution

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Abstract: ***This work investigated the presence and concentrations of heavy metals and the specific activity concentrations of radionuclides in selected inorganic fertilizers purchased from Zaria, Kaduna State, Nigeria using X-ray Fluorescence and gamma ray spectrometric techniques. The average concentrations of Cr, Ni, Si, V, and Zn were within the ranges in agricultural soils, except Sambuka fertilizer which recorded 72mg/kg average Cr concentration higher than in agricultural soils. The ^{40}K activity concentration of the fertilizers ranged from 101Bq/kg to 2,481Bq/kg with a mean of 566Bq/kg. The ^{226}Ra activity concentration ranged from 22.99 Bqkg-^{1} to 34.48Bqkg^{-1} with a mean of 28.36±1.96 Bqkg^{-1}. ^{232}Th has mean activity concentration of 57.33 ± 0.74Bqkg^{-1} ranging from 40.71 to 77.10Bqkg-^{1}. The air absorbed dose rate ranged from 53.91 to 144.90nGyh^{-1} with a mean of 72.31nGy h^{-1} which is higher than 51nGy/h Benchmark. The annual effective dose rate had an average of 88.37 µSvy^{-1} ranging from 60.51 to 178.23µSvy^{-1}.The Raeq ranged from 113.06 to 207.69Bqkg^{-1} with a mean activity concentration of 134.84±3.130Bqkg^{-1}which is far below the 370Bq/kg Benchmark. The H_{ex} and H_{in} averaged 0.48 and 0.39 with ranges from 0.398 to 0.83 and 0.29 to 0.77 respectively.***

Key words: Elemental; Environmental Pollution; Inorganic Fertilizers; Natural radioactivity; Gamma Spectroscopy

1. Introduction

Fertilizers are very important in agriculture for sustaining soil fertility and productivity to fight hunger [1]. However, they constitute an important source of heavy metals to the environment in addition to other sources of anthropogenic activities such as mining, smelting, steel, iron and chemical industries [2]. Nitrogen- Phosphorous-Potassium (NPK) fertilizers are in association with natural radioactive materials (Uranium-234, Thorium-232, and Potassium-40) and heavy metals and other radionuclides transferred from phosphate ore during fertilizer production [3].

The accumulation of heavy metals and radioactive materials in the soil above their threshold levels due to excessive use of phosphate fertilizers becomes an increased indestructible poison in the environment [4]. Plants pick up these contaminants and the consumption of these plant materials by humans and animals pose some health problems like cancer and autoimmune disease. Heavy metals in small quantities referred to as trace elements are however, nutritionally essential for healthy life. For instance Iron, Copper, Manganese and Zinc or some form of these metals are commonly found in foodstuff, in fruits and in vegetables and in commercially available multivitamins which aid in maintaining good health as reported by National Institute of Safety and Health, [5].

Heavy metals also find industrial application in the manufacture of insecticides, batteries, and steel [5]. However, heavy metals become toxic when their concentrations are above threshold levels because they cannot be metabolized by the body and tend to accumulate mostly in the soft tissues especially in kidney and liver. They may enter the human body through food, water, air or may be absorbed through the skin when humans contact them in agriculture and in manufacturing, pharmaceutical and industrial settings [5].

For healthy life, organisms require varying amounts of heavy metals such as Iron, Cobalt, Manganese, Copper, Molybdenum and Zinc. These are also required by humans in small amounts for instance Iron is a component of blood which aid in oxygen transportation and copper is a component of chlorophyll which aids in photosynthesis(5). Excessive levels can however, be damaging to the organism by causing phytotoxicity by forming reactive oxygen radicals that damage cells. Other heavy metals such as Mercury, Plutonium, and Lead are toxic metals which have no known beneficial effects on the organisms, while Vanadium, Tungsten and Cadmium are normally toxic however, for some organisms, they can be beneficial under certain conditions [6].

The supply of these plant nutrients that improve the properties of soil for good harvest of crops is limited and depleted with every harvest, through leaching and runoff water thus, causing further reduction in quality and yield of plants. Much as we need fertilizers to sustain soil fertility and productivity; possible negative effects of excessive phosphate fertilizer application to crop lands are the contaminations of cultivated lands by heavy metals and naturally occurring radioactive materials (NORM) [7]. It has been noted by Rossler, Smith, Bolch, & Prince [8] and IAEA [9] that, generally Uranium (^{238} U) in phosphate rocks has concentrations ranging from 3–400 mg/kg which is equivalent to 37–4900 Bq/kg ^{238}U in terms of radioactivity measurement and for Radium (^{226}Ra) whose activity concentration is measured in place of Uranium activity concentration has a range of 100–10,000 Bq/kg for the different phosphate rock deposits.

The United Nations Scientific Committee on the Effects of Atomic Radiation noted that, the concentration of ^{238}U and its decay products tend to be higher in phosphate rock deposits of sedimentary origin where ^{238}U series have typical concentrations of about 1500 Bq/kg [10]. Phosphate rock can be of sedimentary, volcanic or biological origin. It is the raw material for the production of all phosphate products including phosphate fertilizers. The presence of radionuclides in the environment through the excessive use of phosphate fertilizers increases the level of naturally occurring radioactive materials (NORM) in the environment. The increase of heavy metals and naturally occurring radioactive materials in the environment above threshold limits poses some health problems to humans, problems like cancer and genetic aberrations caused by gamma radiation emitted by elements like Uranium, Thorium and Potassium - 40.Therefore, the concentrations of these materials in the environment must be monitored to safeguard human health [11], since excesses could be harmful to organisms and damaging to the soil [12]. They accumulate in the body especially in vital organs such as the kidney and the liver. For example, the accumulation of lead in human body is associated with developmental problem in children. Exposure to high levels of Lead, Gold and Mercury has been associated with autoimmune disease [13]. Heavy metals in the soil become problem when they runoff into water bodies and cause algal bloom and they can also percolate into underground water to affect food, microorganisms and plant growth [14]. Cadmium is highly persistent in the soil and can affect plant growing conditions and result in accumulation in the soil. Cadmium is easily absorbed from the soil by corn and wheat which means, our food supply is at risk of contamination by toxic substances that threaten human life [15].

The presence of heavy metals in the soil can affect soil acidity and the solubility of beneficial elements like Zinc. In Nigeria, just in other parts of the world, NPK fertilizers are annually used to improve the productivity of the croplands, thus exposing them to the danger of contamination by heavy metals and radioactive materials. The objective of this work was to determine:

(i) The presence and concentrations of heavy metals, other elements and

(ii) The activity concentrations of naturally occurring radioactive materials (^{226}Ra, ^{232}Th, and ^{40}K) found in inorganic fertilizers.

Radium equivalent activity is used as a common index which takes into account the radiation hazard associated with ^{226}Ra, ^{232}Th, and ^{40}K. Radium equivalent activity provides a useful guideline in regulating safety standards on radiation protection for the public. It is defined based on the assumption that 10BqKg^{-1} of ^{226}Ra, 7 BqKg^{-1} of ^{232}Th and 130Bqkg^{-1} [16] ^{40}K produce the same gamma dose rate. It is calculated by use of the following equation;

$$Raeq = A_{Ra} + 1.43A_{Th} + 0.077A_{K.} \quad (1)$$

The letters A_{Ra}, A_{Th} and A_K are activity concentrations of Radium, Thorium and Potassium respectively. The recommended value of radium equivalent in the environment is 370Bq kg-1[16]. Table 1 shows the radium equivalent activities in Bq kg^{-1} for different brands of inorganic fertilizers. The radium equivalent of 370Bq kg-^{1} corresponds to the dose rate limit of 1 mSv of radiation for the public [17].The decay of naturally occurring radionuclides in the soils produces a radiation field that transcends the soil-air interface to produce significant human exposure. The quantification of this exposure factor is done by external hazard index, Hex which is given by the expression:

$$Hex = \frac{ARa}{370} + \frac{ATh}{259} + \frac{AK}{4810} \leq 1 \quad (2)$$

Taking into consideration the hazardous effects of Radon a progeny of Radium to the respiratory organs, its internal exposure is quantified by the internal hazard index which is given by the expression;

$$Hin = \frac{ARa}{185} + \frac{ATh}{259} + \frac{AK}{4810} \leq 1 \quad (3)$$

2. Experimental

Nine different brands of fertilizers comprising six NPK fertilizers, two brands of Single Super phosphate and one Diammonium phosphate fertilizers were purchased from Samaru Zaria, Sabon Gari Local Government Area Kaduna State, Nigeria. The samples were transferred into polythene bags, labelled and taken to the Centre for Energy Research and Training, Ahmadu Bello University, Zaria for analysis.

Elemental analysis was carried out by the use of Mini Pal 4 version, PW 4030 X-ray spectrometer in the Centre for Energy Research and Training, Ahmadu Bello University Zaria. The Mini pal 4 is an energy dispersive spectrometer designed for elemental analysis of a wide range of samples (solids, powders, and liquids). The system is controlled by a PC running the dedicated Mini Pal analytical software microprocessor designed for the detection and the measurement of elements in samples of different matrices. The samples for analysis were weighed and ground in agate mortar and a binder (PVC dissolved in Toluene) was added to the samples, carefully mixed and pressed in a hydraulic press into a 100mg /cm^2 pellet. The pellet was loaded in the sample chamber of the spectrometer and a voltage (30KV maximum) and a current (1mA maximum) were applied to produce the X-rays that excited the sample for a preset time (10minutes in this case). The spectrum from the sample was then analyzed to determine the concentration of the elements in the sample.

The nine fertilizer samples were crushed into fine powder by use of an agate mortar and pestle for Gamma –Ray analysis. Three hundred grams (300g) were weighed and packaged into Radon-impermeable cylindrical plastic containers and sealed by a triple-stage sealing system to avoid Radon-222 from escaping. The inner rims of each container lid were smeared with Vaseline wax; the lid was filled with candle wax to block the gap between lid and container, and finally tight –sealing lid container with a masking adhesive tape. The prepared samples were left alone for thirty days to enable Radon and its progenies to reach radioactive equilibrium prior to the laboratory analysis for more details on this method of analysis refer to [18].

3. Results and Discussions

The elemental composition of inorganic fertilizers by X-Ray fluorescence method is shown in Table1 below. Silicon recorded a mean of 8,148 mg/kg with the highest value of 20,400 mg/kg recorded for Tak Agro SSP18%. However, Silicon was not detected in Golden (15-15-15) NPK. Vanadium with a mean of 29.0 mg/kg has the highest concentration recorded for Tak Agro SSP 18% at 58 mg/kg. Vanadium was not detected in FSFC SSP18% and AFCUTT (15-15-15) NPK. Chromium was not detected in FSFC SSP18%. The mean concentration of Chromium was 34.0 mg/kg with the highest mean concentration recorded by Sambuka (15-15-15) NPK at 72.0 mg/kg. Titanium was also detected in all the inorganic fertilizer samples at a mean concentration of 631 mg/kg. Table 2 shows the statistical comparison of selected toxic elements determined by XRF method of analysis. The Cr concentration in Sambuka and in Tak Agro ssp 18% is significantly different at $P > 0.05$ but Cr concentrations of Sambuka 15-15-15, AFCUTT 15-15-15, Tak 20-10-10, Maishaho20-10-10 and DAP are not significantly different from each other but, significantly different from the concentration of Sambuka and Tak Agro at $P > 0.5$.

The concentration of Si in all the inorganic fertilizers is not significantly different at $P > 0.05$.The Ti concentration in Tak Agro ssp 18% is significantly different at $P > 0.05$ from the other fertilizers. The concentration of V in DAP fertilizer is significantly different at $P > 0.05$ from the activity concentrations of the other inorganic fertilizers which are not significantly different at $P > 0.5$. Table 3 shows the recommended XRF sources and the minimum detectable limits of the elements as measured by the Mini Pal 4 spectrometer.

Table 4 shows the activity concentration of $^{40}K > ^{232}Th > ^{226}Ra$. The ^{40}K has a mean activity concentration of 566.32±0.36Bqkg-^{1} ranging from 101.45 Bq/kg to 1033.60 Bqkg^{-1}. The ^{226}Ra activity concentration ranges from 22.99 Bq/kg to 34.48Bqkg^{-1} with a mean activity concentration of 28.36±1.96 Bqkg^{-1}. ^{232}Th has mean activity concentration of 57.33 ± 0.74Bqkg^{-1} ranging from 40.71Bq/kg to 77.10Bqkg-^{1}. The Raeq (Radium equivalent) ranged from 113.06Bq/kg to 207.69Bqkg^{-1} with a mean activity concentration of 134.84±3.13Bqkg^{-1}. Table 5 shows the result of statistical comparison of activity concentrations of inorganic fertilizer samples analyzed by gamma ray spectrometry using Na (I) Tl detector. Means with the same letters are not significantly different at 0.05; this is exemplified by the mean activity concentration of ^{40} K of Sambuka 15-15-159 (CPR1) and Maishaho 20-10-10 (CPR5) are not significantly different at $P > 0.05$. The ^{40} K activity concentrations of the remaining fertilizers are significantly different at 0.05.

The mean Radium -226 activity concentration of AFCUTT (15-15-15) NPK and Tak (20-10-10) NPK are not significantly different at 24.467±0.713d and 24.953±0.180cd Bq/kg. The ^{226} Ra mean activity concentration of Sambuka 15-15-15 (CPR1), and Maishaho 20-10-10 (CPR5) at 31.64±1.37abc Bq/kg and 31.64±1.37abc Bq/kg are not significantly different at $P > 0.05$. However, the ^{226} Ra activity concentration of DAP (CPR7) at 36.739±1.737a Bq/kg is significantly different at $P > 0.05$ from the mean activity concentration of the other fertilizers.

The activity concentration of ^{226} Ra in the DAP fertilizer is not significantly different from the concentration of Maishaho (CPR5) and Sambuka (CPR1).The mean activity concentrations of ^{232} Th in Sambuka, Golden 15-15-15(CPR1) and Maishaho (CPR5) at of 51.6±0.59e Bq/kg , 50.63±1.03e Bq/kg and 51.6±0.59e Bq/k are not significantly different at $P > 0.05$; also, its concentrations in Tak 20-10-10(CPR4) and FSFC SSP18% (CPR9) at 54.18±0.28d Bq/kg and 59.02±0.98c Bq/kg are significantly different at $P > 0.05$. Furthermore, the results show that the ^{232} Th activity concentration in AFCUTT 15-15-15 at 41.45±0.70f Bq/kg, Maishaho 51.6±0.59e Bq/kg and Golden 20-10-10 at 70. 07±1.20 b Bq/kg is significantly different at $P > 0.05$.

Table 6 is the Summary of inorganic fertilizer radiation hazard indices. The inorganic fertilizers have mean air absorbed dose rate of 72.31 nGy/h. Golden (15-15-15) recorded the highest air absorbed dose rate at 144.9 nGy/h. The lowest air absorbed dose rate 49.5 nGy/h was recorded by AFCUTT (15-15-15) NPK. The inorganic fertilizers recorded mean annual effective dose rates 88.37 μSv/y. AFCUTT has the highest value 178.23 μSv/y; the lowest value 60.51 μSv/y was recorded by Tak Agro SSP 18%. The inorganic fertilizers have Raeq mean 134.83 μSv/y. Golden (15-15-15) NPK have the value of 207.67 μSv/y which is the highest value though this value is below the Benchmark.

Table 1: Elemental composition of inorganic fertilizer samples mg/kg by XRF method

Sample Code	Al	Ca	Cr	Cu	Fe	K	Mn	Ni	Si	Ti	V	Zn
CRP1	BDL	BDL	72	5	3,930	114,678	66	142	288	62	24	49
CRP2	BDL	BDL	32	7	853	133,814	34	72	BDL	113	2	BDL
CRP3	110,400	9,401	31	5	438	85,698	BDL	64	9,630	335	BDL	BDL
CRP4	79,580	BDL	24	2	9,676	34,776	118	48	17,640	1,773	33	BDL
CRP5	65,320	2,761	26	4	11,441	40,940	140	52	15,840	1,773	45	BDL
CRP6	59,800	BDL	0.040	8	7,874	142,462	10	64	7,110	1,327	51	BDL
CRP7	BDL	6,378.4	0.047	5	4,076	1,104	139	54	816	119	52	98
CRP8	77,280	1,426	0.037	7	12,209	13,110	439	60	20,400	1,897	58	20
CRP9	5.520	84,799	BDL	BDL	3,770	BDL	220	BDL	1,608	55	BDL	23
Mean	44,211	1,.641	0.034	5	6,467	62,954	129	126	8,148	631	29	21
Range	BDL-11,.400	BDL-84,799	BDL-72	BDL-7	853-12,209	BDL-142,462	BDL-439	BDL-142	BDL-20,400	55-1,897	BDL-58	BDL-98

BDL=Bellow detectable limit
KEY:
CPR1=Sambuka
CRP2= Golden (15-15-15) = NPK
CRP3= AFCUTT (15-15-15) NPK
CRP4= Tak (20-10-10) NPK
CRP5= Maishaho (20-10-10) NPK
CRP6= Golden (20-10-10) NPK
CRP7= DAP (Diammonium phosphate)
CRP8= Tak Agro (Single superphosphate 18%)
CRP9= FSFC (Single superphosphate 18%)

Table 2: Statistical comparison of selected toxic elements in inorganic fertilizers determined by XRF method

	Cr	Si	Ti	V
NAME	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E
Sambuka15-15-15	27.4±17.5ab	1157.376±11a	273±260.86b	11.546±7.77bc
Golden15-15-15	14.199±9.4abc	1061.376±11a	290±268.07b	4.836±4.04bc
AFCUTT15-15-15	21.466±8.1abc	4271.376±28a	364±302.02b	13.396±6.18bc
Tak20-10-10 NPK	11.633±7.9abc	6941.376±45a	843±568.15b	14.393±9.48bc
Maishaho20-10-10 NPK	19.366±7.3abc	6341.376±41a	843±568.15b	23.606±9.92bc
Golden20-10-10 NPK	16.949±11.1abc	3431.376±23a	695±480.88b	20.493±13.2bc
DAP	23.378±11.5abc	1333.376±12a	292±268.97b	89.650±38.70a
TAK_Agrossp18%	33.033±10.8a	7861.376±50a	2441±878.87a	38.963±13.10b
FSFCssp_18%	BDL	536.00±34a	18.19±11.5b	BDL

Note: Means with the same letter are not significantly different at 0.05

Table 3: XRF Standard Sources and Minimum detectable limits

	X-ray	*Recommended sources*	*Possible sources*	*Minimum detectable limit %*
Ca,Sc,Ti,V	K	Fe55(20mCi)		0.2
Cr	K	Fe55(20mCi)	Pu-8(30mCi)	0.2
Mn, Fe ,Co ,Ni	K	Pu-38(30mCi)		0.2
Cu,Zn,Ga,Ge,As,Se	K	Pu-38(30mCi)	Cd-09(1mCi)	0.1
Br,Rb,Sr,Y,Zr,Nb,Mo,Ru	K	Cd-109(1mCi)		0.05
Rh,Pd,Ag,Cd,In,Sn,Sb,Te,I,Cs,Ba,La,Tm	K	Am-41(3mCi)		0.05
Yb,Lu,Hf,Ta,W,Re,Os,Ir,Pt,Au,	K	Co-57(1mCi)	Gd-1mCi)(Yb to Bi)	0.3
	L	Pu-83(30mCi)(Yb to U	Cd	0.2

Table 4: Specific activity concentration of radionuclides in inorganic fertilizers

Inorganic Fertilizer.	K-40	error ±	Ra-226	error±	Th-232	error ±	Raeq Bq/kg
CRP1	198.590	0.129	30.269	2.734	50.966	1.178	118.442±4.04
CRP2	2,481.60	1.594	22.987	10.094	49.601	2.057	113.059±13.7
CRP3	317.850	0.204	23.754	1.425	40.707	1.482	106.440±3.112
CRP4	356.140	0.229	24.773	0.359	60.905	0.551	139.290±1.755
CRP5	198.590	0.128	30.269	2.734	50.966	1.178	118.442±4.04
CRP6	1,033.62	0.665	26.187	0.226	71.266	0.063	207.686±0.95
CRP7	101.450	0.065	38.476	0.033	77.101	0.068	156.540±0.166
CRP8	227.010	0.149	23.335	0.020	54.457	0.048	118.690±0.217
CRP9	179.440	0.115	35.226	0.030	60.000	0.053	134.840±0.198
Mean	566.032	0.364	28.364	1.962	57.329	0.742	134.826±3.130
Range	101.450-2,481.60	0.065-1.596	22.990-38.480	0.020-10.10	40.710-77.100	0.040-1.482	113.060-207.690

Key:
CRP1= Sambuka four corner vital (15-15-15) NPK
CRP2 Golden (15-15-15) = NPK
CRP3= AFCUTT (15-15-15) NPK
CRP4= Tak (20-10-10) NPK
CRP5= Maishaho (20-10-10) NPK
CRP6= Golden (20-10-10) NPK
CRP7= DAP (Diammonium phosphate)
CRP8= Tak Agro (Single superphosphate 18%)
CRP9= FSFC (Single superphosphate 18%)

Table 5: The Results of Statistical Comparison of Activity Concentration of Inorganic Fertilizer Samples

Types of Fertilizers	K-40	$Bqkg^{-1}$	Ra-226	$Bqkg^{-1}$	Th-232	$Bqkg^{-1}$
	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E	Mean±S.E
CRP1	0.128±0.0003f	199.050±0.457f	0.027±0.001abc	31.640±1.37abc	0.0452±0.001e	51.600±0.59e
CRP2	1.598±0.0018a	2,488.400±6.838a	0.024±0.004bcd	28.034±5.05bcd	0.0444±0.001e	50.630±1.03e
CRP3	0.207±0.002d	321.120±3.266d	0.021±0.001d	24.467±0.713d	0.0364±0.007e	41.450±0.74f
CRP4	0.231±0.002c	358.850±2.708c	0.022±0.0002cd	24.953±0.180cd	0.0537±0.0003c	61.180±0.28c
CRP5	0.128±0.0003f	199.050±0.457f	0.027±0.0012abc	31.640±1.37abc	0.0452±0.0005e	51.60±0.59e
CRP6	0.662±0.0025b	1,029.800±3.810b	0.022±0.0011cd	24.971±1.217cd	0.062±0.001b	70.070±1.20b
CRP7	0.064±0.001h	99.305±2.145h	0.032±0.0015a	36.739±1.737a	0.0674±0.0002a	76.870±0.23a
CRP8	0.148±0.0015e	227.210±0.241	0.019±0.0005d	22.836±0.50d	0.048±0.0003d	54.180±0.28d
CRP9	0.115±0.0008g	178.280±1.166g	0.029±0.0011ab	34.010±1.22ab	0.0518±0.0009c	59.020±0.98c
Mean	0.364±0.113	566.790±176.5	0.025±0.0011	28.809±1.217	0.0503±0.0022	57.390±2.48

Note: Means with the same letter are not significantly different at 0.05

Key:
CRP1= Sambuka four corner vital (15-15-15) NPK
CRP2 Golden (15-15-15) NPK
CRP3= AFCUTT (15-15-15) NPK
CRP4= Tak (20-10-10) NPK
CRP5= Maishaho (20-10-10) NPK
CRP6= Golden (20-10-10) NPK
CRP7= DAP (Diammonium phosphate)
CRP8= Tak Agro (Single superphosphate 18%)
CRP9= FSFC (Single superphosphate 18%)

Table 6: The summary of inorganic fertilizer dose rates and radiation hazard indices

S/N	*Sample Code*	*Air absorbed Dose rate nGy/h*	*Annual effective dose μSv/y*	*Raeq*	*Hex*	*Hin*
1	Sambuka 15-15-15	53.91	66.15	118.442	0.398	0.316
2	Golden 15-15-15	144.9	178.23	113.059	0.832	0.77
3	AFCUTT 15-15-15	49.5	60.89	106.44	0.542	0.287
4	Tak 20-10-10	64.12	79.87	139.29	0.443	0.29
5	Maishaho 20-10-10	53.91	66.31	118.442	0.398	0.316
6	Golden 20-10-10	99.46	122.34	207.686	0.549	0.478
7	DAP	69.89	85.96	156.54	0.527	0.423
8	Tak Agro ssp 18%	54.07	60.51	118.69	0.384	0.321
9	FSFC ssp 18%	61.01	75.04	134.84	0.459	0.364
	Mean	72..31	88.37	134.83	0.504	0.396

4. Discussions

Table1 shows the result of nine inorganic fertilizer samples analyzed by XRF for twelve elements. Al was not detected in Sambuka (15-15-15) NPK, Golden (15-15-15) NPK and DAP. The range was BDL to 110,400 mg/kg. The mean concentration of Al in the inorganic fertilizer samples was 44, 2213 mg/kg. The AFCUTT (15-15-15) NPK recorded the highest Al concentration of 110,400 mg/kg. Though Al is the most abundant element in the earth crust it however, is not an essential element needed for plant growth. Al toxicity in human is associated with loss of memory and dementias, which is why Al concentration in fertilizers should be monitored so that its concentration in agricultural soils should not exceed the threshold in soil. The high value of Al recorded by AFCUTT (15-15-15) makes this fertilizer candidate for monitoring because; concentrations above threshold levels may reduce the availability of other nutrient cations such as Mg through competitive interactions.

The range of BDL-84,799 mg/kg Ca was recorded by the inorganic fertilizer samples. Calcium is essential for animal and plant nutrition; it participates in many biological functions mainly skeletal building and moderating muscle action. The levels found in the fertilizers analyzed are adequate; therefore pose no immediate concerns to humans, plants and to agricultural soils. Silicon recorded its highest value of 20,400 mg/kg in Tak Agro SSP18%. It was not detected in Golden (15-15-15) NPK. Its range was BDL-20, 400 mg/kg and the mean was 8, 1148 mg/kg. Silicon in dust form can cause silicosis which is a disease that affects human lungs. Care should be taken by farmers when applying Tak Agro ssp 18% by keeping upwind to avoid inhaling silicon dust during fertilizer application. Silicon concentrations in fertilizers should be monitored because it can easily be added to fertilizers to increase volume by unscrupulous marketers. Vanadium recorded a mean of 29 mg/kg with the highest concentration recorded by Tak Agro SSP 18% at 58mg/kg. The lowest concentration was recorded by Golden (15-15-15) NPK. Vanadium was not detected in FSFC SSP18% and AFCUTT (15-15-15) NPK. The Vanadium concentration ranged from BDL to 58 mg/kg with a mean of 29 mg/kg. The highest Vanadium concentration was recorded by Tak Agro ssp18% fertilizer sample. Chromium was also detected in all the fertilizer samples except in FSFC SSP18%. The mean concentration was 34 mg/kg with the highest concentration recorded for Sambuka (15-15-15) NPK at 72 mg/kg the remaining samples recorded concentrations below 50 mg/kg.

Moreover, the recorded concentration of chromium in the soil is 2-60 mg/kg [15]. It is not known if it is an essential element to plants or not but, all plants contain it up to 0.19ppm [19]). The Cr concentration in Sambuka was 72 mg/kg is higher than the maximum concentration in soils [15]. This fertilizer should not be chosen for soils recording maximum Cr concentration to avoid its build up in the soil and subsequent uptake by plants and passed on to humans through the food chain. Titanium was also detected in all the inorganic sample fertilizer at a mean of 631 mg/kg. The highest concentration was recorded for Tak Agro SSP 18% at 1,897mg/kg. Inorganic fertilizers analyzed contain sufficient nutrients like Fe, Zn, Mg and Cu which are needed by both animal and plant nutrition and metabolism. Most heavy metals contained therein are within concentrations found in agricultural soils. The activity concentrations of the naturally occurring radionuclides in the inorganic fertilizer samples were determined by gamma spectrometry using Thallium doped Sodium Iodide, NaI (Tl) detector. The results are presented in Table 4.

The ^{40}K has a mean activity of 566.322±0.3643Bq kg^{-1} ranging from 101.45 to 2,481Bq kg^{-1}. Potassium is a macronutrient that is needed by both plants and animals for biochemical processes. The high concentration of Potassium in the fertilizers analyzed is expected due to the composition of this element in the earth crust this is due to the fact that potassium is the most abundant element in the soil [19]. Even though all fertilizers show abundance of ^{40}K activity the lowest activity concentration was recorded for DAP fertilizer at 101.45±0.0653 Bqkg^{-1}. All fertilizers show ^{40} K activity concentrations within the world average in soil 140.0 to 850.0Bqkg-^{1} [10] in excess in the soil Potassium decreases the vitamin and carotene content of vegetables and fruits for that reason its concentration in agricultural soils should be monitored. The ^{226}Ra activity concentration ranges from 22.99 to 34.48Bqkg^{-1} with a mean activity of 28.3641±1.9619 Bqkg-^{1}. ^{226}Ra was detected in all the fertilizers at >22.987±10.094Bq kg$^{-1.}$ The highest activity was recorded for DAP fertilizer at 38.4765±0.033BqKg^{-1} followed by FSFC SSP 18% at 35.269±.2264±0.0304Bq/kg. The ^{226}Ra activity concentration is within the world average in soil 17.0-60BqKg-1[11]. ^{232}Th has mean activity concentration of 57.3298 ± 0.7418Bq kg^{-1} ranging from 40.71 to 77.10Bq kg-1. Where Th -232 concentration is high in the environment DAP fertilizer may not be recommended to avoid Thorium build up in the soil.

The Raeq ranges from 113.06 to 207.69Bq kg^{-1} with a mean activity of 134.826±3.130Bq kg-^{1} which implies that the gamma dose rate from these fertilizers is not harmful to both plants and animals. Thorium (^{232}Th) was detected in all the fertilizers at >50Bqkg^{-1} Table 5. The highest ^{232}Th activity was recorded for DAP fertilizer at 77.101 ±0.0676 Bqkg^{-1} followed by the activity concentration of Golden (20-10-10) NPK at 71.2655±0.0625Bq/kg. ^{232} Th in DAP and Golden (20-10-10) NPK exceeded the world average in soil 11.0 - 64.0 Bq kg^{-1} [10]. The higher than world values of ^{232} Th displayed by DAP and Golden (20-210-10) NPK fertilizers means that the raw material from which this fertilizers were produced had high concentration of ^{232}Th that was transferred to the fertilizers during the production process. The absorption of this radionuclide by plants through the food chain and finally transferred to humans and animal could be a serious health risk.

For radiation hazard to be negligible, the Hex and Hin values must be less or equal to unity [11]. The Hex and Hin values for inorganic fertilizers range from 0.398 to 0.832 with a mean of 0.482 for Hex and 0.29 to 0.77 with a mean of 0.395 for Hin. The Hex and Hin represent values associated with externally absorbed and internally absorbed radiation respectively, see Table 6. The Hin and Hex values for inorganic fertilizers are less than unity, signifying that the use of these fertilizers may constitute no radiological hazard to both plants and animals.

The absorbed dose rate is the energy impacted by ionizing radiation per unit mass of irradiated material; it has the units of Gray or Rad. The air absorbed dose rate (D) due to gamma radiation in air at 1m above the ground surface for uniform distribution of naturally occurring radionuclide was calculated for inorganic fertilizers by use of the expression:
$D\ (nGyh^{-1}) = 0.0461A_{Ra} + 0.623A_{Th} + 0.0417A_K$ **4** The mean of the air absorbed dose rate of the fertilizers was 72 nGy/h .This average is above the world average value of 51 n Gy/h; which means that farmers could be exposed to gamma radiation in the process of applying inorganic fertilizers to their farms with the consequences of compromising their health.

5. Conclusion

- It is now known that the mean specific activity concentration of K-40 in the selected inorganic fertilizers in Nigeria is 566 Bq/kg is high as compared to that obtained in Pakistan 221Bq/kg.
- The specific activity concentrations of ^{40} K are within regulatory benchmark of 140-850Bq/kg [10].
- Ra-226 values of the fertilizers are higher than that obtained in Italy at 120 Bq/kg, but are within the world benchmark 17.0-60.0Bq/kg.
- Th-232 mean specific activity for the fertilizers is 57.39Bq/kg is higher than in Pakistan at 50Bq/kg, but within word benchmark 11.0-60Bq/kg.
- The Raeq is 134Bq/kg is far below the minimum value of 370 Bq/kg world average.
- The low concentrations of radionuclides imply that our croplands face no immediate contamination by radionuclides from the application of inorganic fertilizers.
- It is now known that inorganic fertilizers contain up to sixteen elements in their composition.
- These elements are made up of micronutrients and heavy metals whose concentrations are within those in agricultural soils, except for Sambuka 15-15-15 which showed Cr concentrations higher than those in agricultural soils.
- However, due to the mean absorbed air-dose rate of inorganic fertilizers which was 72.31nGyh^{-1} is slightly higher than the world average 51nGyh^{-1} and the annual effective dose rate which averaged 88.37µSv/y, implies that farmers could be exposed to radiation hazards from excessive use of phosphate base fertilizers; for that reason regular monitoring of both the fertilizers and of agricultural soils is necessary

- The true picture of what elements and radionuclides these fertilizers contained may be achieved by widening the scope by combining the X-ray fluorescence method with Instrumental Neutron Activation Analysis.

6. Recommendations

Farmers are hereby advice to take extra precautions when applying fertilizers to their farmlands. Such precautions could be in the form of wearing protective clothing, hand gloves and by keeping upwind when applying fertilizer to their farms. Furthermore, soils should be tested before fertilizer application to ascertain which fertilizer is appropriate for which soil type and the soils should also be monitored from time to time to ascertain any heavy metal build up in the soil.

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