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Elemental Composition of Selected Inorganic Fertilizers in Zaria by XRF Method: A Source of Possible Environmental Contamination

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Abstract: *Elemental composition of nine randomly selected inorganic fertilizers purchased from Samaru Zaria, were analyzed using X-ray fluorescence spectrometric techniques. The analytical results show that the average concentrations of some toxic elements (Cr, Ni, Si, V, and Zn) were within the ranges in agricultural soils, except for Sambuka fertilizer which recorded average Cr concentration higher than found in agricultural soils.*
Key words: *Elemental composition, Environmental Contamination, Inorganic Fertilizers, XRF*

I. Introduction

Fertilizers are very important in agriculture for sustaining soil fertility and productivity. They however, may constitute one source of heavy metals to the environment in addition to other sources of anthropogenic activities such as mining, smelting, steel, iron and chemical industries (Susie *et al*., 2001). Among these fertilizers, NPK (Nitrogen- Phosphorous-Potassium) are the major components in association with natural radioactive materials (Uranium-234, Thorium-232, and Potassium-40) transferred from phosphate ore during production. These could emit alpha, beta or gamma radiation. The addition of these plant nutrients may affect the environment by contaminating it with heavy metals and radioactive materials (Santos *et al.,* 1975), and this could be harmful to organisms and damaging to the soil (GRPC, 1977). The exposure to heavy metals and radioactive materials has been associated with some health problems because of their toxicity when they are not metabolized by the body. They accumulate in the body especially in vital organs. 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 autoimmunity, a condition in which the immune system destroys its cells, mistaking them for foreign invaders (Janet Glover-Kervliet, 1995)

Heavy metals in the soil can runoff into water bodies and also percolate into underground water thus affecting food, microorganisms and plant growth (Popescu *et al.,* 2009). Heavy metals get into the body through food when plants take them from the soil. They may accumulate in plant parts and eventually be taken in by humans through the food chain. Chromium is highly persistent in the soil and can affect plant growing conditions and result in accumulation in the soil. The presence of heavy metals in the soil can increase soil acidity and decrease the solubility of beneficial elements like Zinc. Chromium 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. In Nigeria, just as in other parts of the world, NPK fertilizers are annually used to improve the productivity of the croplands, thus exposing our croplands to the danger of contamination by heavy metals and radioactive materials. The objective of this study was to determine the presence and concentrations of heavy metals and other elements added to our croplands from excessive use of NPK fertilizers by the use of X-Ray Fluorescence Spectrometry.

II. Experimental

2.1Sample Materials

Six brands of NPK fertilizers (Sambuka 15-15-15-15, Golden 15-15-15, AFCUTT 15-15-15, Tak 20-10-10, Maishaho 20-10-10 and Golden 20-10-10), two brands of Single Super Phosphate (Tak Agro SSP 18% and FSFC SSP18%) 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 Centre for Energy Research and Training, Ahmadu Bello University, Zaria laboratory for analysis.

2.2 Procedure for sample analysis

2.2.1 X-Ray Fluorescence (XRF)

The PW 4030 X-ray Spectrometer (Mini Pal 4 version) in the Centre for Energy Research and Training, Zaria was used. It is an energy dispersive microprocessor controlled analytical instrument designed for the detection and the measurement of elements in samples (solids, powders, and liquids). The samples 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 to excite 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 analysis of variance was used in comparing the concentration of the metals in the fertilizers; the mean levels of concentration of the metals in the different fertilizers are compared. Letters along the means indicate classes of significant differences.

III. Results and discussions

The elemental composition of nine inorganic fertilizers determined by X-Ray Fluorescence method is shown in Table 1. Silicon recorded a mean of 8,148 mg/kg with the highest value of 20,400 mg/kg recorded for Tak Agro 18% SSP. It was not detected in Golden 15-15-15 NPK. The high concentration of Si in the Tak Agro18% SSP could be due to adulteration, while the FSFC 18% SSP that might not have been adulterated recorded the absence of Si in its composition. Vanadium recorded a mean of 29.0 mg/kg the highest concentration was recorded for Tak Agro SSP 18% at 58 mg/kg. 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.

The lowest concentration was recorded for Golden 15-15-15 NPK. Vanadium was not detected in FSFC SSP18% and AFCUTT 15-15-15 NPK which could have been eliminated when the phosphate ore was processed. Chromium was not detected in FSFC SSP18%. The mean concentration was 34.0 mg/kg with the highest concentration recorded for Sambuka 15-15-15 NPK at 72.0 mg/kg the remaining inorganic fertilizers recorded concentrations below 50.0 mg/kg.

The concentration of chromium in the soil is 2-60 mg/kg (Kabata- Pendias & Pendias, 1984). The concentration found in Sambuka 72mg/kg is higher than the maximum concentration in soils. This fertilizer should not be chosen for soils recording maximum 60 mg/kg concentrations of Chromium to avoid Chromium build up in the soil.

Titanium was also detected in all the inorganic sample fertilizers at a mean of 631 mg/kg. Aluminium was not detected in Sambuka 15-15-15 NPK, Golden 15-15-15 NPK and in DAP. The range was BDL to 110,400 mg/kg. The mean concentration of Aluminium in the inorganic fertilizer samples was 44,221mg/kg. The AFCUTT 15-15-15 NPK recorded the highest Aluminium concentration of 110,400 mg/kg.

The danger of high concentrations of Aluminium in the soil is not only its toxicity but its ability to replaced strontium which can then replace calcium. When plants absorb Strontium instead of calcium and animals eat these plants, there will be poor bone formation in the animals. The range of BBL-84,799 mg/kg Ca was recorded by the inorganic fertilizer samples.

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	11,641	0.034	5	6,467	62,954	129	126	8,148	631	29	21
Range	BDL-110,400	0-84,799	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:

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

NAME	Cr Mean±S.E	Si Mean±S.E	Ti Mean±S.E	V Mean±S.E
Sambuka15-15-15	27.4±17.5ab	1157.376±1101a	273±260.86b	11.546±7.766bc
Golden15-15-15	14.199±9.4abc	1061.376±1061a	290±268.07b	4.836±4.043bc
AFCUTT15-15-15	21.466±8.1abc	4271.376±2824a	364±302.02b	13.396±6.180bc
Tak20-10-10 NPK	11.633±7.9abc	6941.376±4466a	843±568.15b	14.393±9.479bc
Maishaho20-10-10 NPK	19.366±7.3abc	6341.376±4094a	843±568.15b	23.606±9.915bc
Golden20-10-10 NPK	16.949±11.1abc	3431.376±2321a	695±480.88b	20.493±13.228bc
DAP	23.378±11.5abc	1333.376±1178a	292±268.97b	89.650±38.703a
TAK_Agrossp_18	33.033±10.8a	7861.376±5039a	2441±878.87a	38.963±13.102b
FSFCssp_18	BDL	536.00±339a	18.19±11.5b	BDL

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

IV. Conclusion

The inorganic fertilizers analysed by XRF method have in them twelve different elements like Cu, Fe , Ca and Zn which are beneficial to plant health and growth and are considered safe for use on our croplands . However, Sambuka 15-15-15 had higher concentration of Cr than found in agricultural soils.

V. Recommendations

As much as it is recommended to monitor the environment for heavy metals to avoid land degradation and contamination, it is also important to monitor it for beneficial elemental depletion. From this study therefore, it is recommended that before Sambuka 15-15-15 is used, the land on which it is to be applied should first be tested for Cr to avoid Cr build up in the soil.

Recommended Sources and Minimum detectable limits

Element	X-ray	Sources		Minimum *detectable limit wt %
		Recommended	Possible	
Ca,Sc,Ti,V	K	Fe55(20mCi)		0.2
Cr	K	Fe55(20mCi)	Pu-238(30mCi)	0.2
Mn, Fe ,Co ,Ni	K	Pu-238(30mCi)		0.2
Cu,Zn,Ga,Ge,As,Se	K	Pu-238(30mCi)	Cd-109(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-241(3mCi)		0.05
Yb,Lu,Hf,Ta,W,Re,Os, Ir,Pt,Au,	K	Co-57(1mCi)	Gd-153(1mCi)(Yb to Bi)	0.3
	L	Pu-283(30mCi)(Yb to U	Cd	0.2
*2 sigma counting statistics, 10 seconds measuring time.				

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