International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Impact Factor (2012): 3.358

Characterization of Selected Inorganic Fertilizers by Atomic Absorption Spectroscopy: Possible Carryover of Heavy Metals from Phosphate Rock

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Abstract: ***Fertilizers are important in increasing and sustaining soil fertility resulting in increased productivity and hunger reduction. The excessive use of inorganic fertilizers on croplands may contaminate the soil with heavy metals and naturally occurring radioactive materials. Seven elements (Cd, Cu, Fe, Ni, Mn, Pb, and Zn) in six randomly selected Nitrogen- Phosphorous- Potassium fertilizers, two Single Super Phosphate and one Diammonium Phosphate fertilizers purchased from Zaria, Kaduna State, Nigeria and two Phosphate rock samples obtained from Institute for Agricultural Research , Ahmadu Bello University, Zaria were characterized using Atomic Absorption Spectroscopic technique. The results showed that, the highest concentration of Cd 15.9mg/kg recorded by DAP fertilizer sample was lower than in Sokoto and Togo Phosphate rock samples but was higher than the concentration in agricultural soils.. The concentration of Copper in Sambuka four corner vital NPK (15-15-15) and DAP was 13.0 mg/kg and 32.0 mg/kg respectively these were higher than the copper concentration in Sokoto rock phosphate sample, 11.2mg/kg. The NPK fertilizers have a range of Fe concentrations 12,63mg/kg-99.24mg/kg which is lower than the concentration in Sokoto rock phosphate sample160,28mg/kg.The fertilizers(crp6,crp8and crp9) have Fe concentration one and half times higher than Togo rock phosphate sample. However, CRP4, CRP5 and CRP6 of the NPK fertilizer samples had Fe concentration three times higher than Togo Phosphate rock. Diammonium phosphate fertilizer has the highest concentrations 3900mg/kg of Zinc. The average concentration of the seven elements analyzed was within the ranges in agricultural soils. The samples showed appreciable concentration of Mn, and Zn which are beneficial to plant growth.of lead is insignificant.***

Keywords: AAS, characterization, heavy metals, Inorganic fertilizers

1. Introduction

Fertilizers are very important in agriculture as a means of sustaining soil fertility and increasing the productivity of our croplands for hunger reduction. Among these fertilizers, phosphate fertilizers are the most important in sustaining soil fertility and fighting hunger [1]. Phosphorous, one of the key components of inorganic fertilizers occurs in nature almost entirely as phosphate rock deposits containing many types of minerals [2], [3] Phosphate fertilizers contain Nitrogen-Phosphorous-Potassium (NPK) as major components and heavy metals in association with naturally occurring radioactive materials (Uranium-234, Thorium-232, and Potassium-40) transferred from the Phosphate rock during fertilizer production, these elements emit alpha, beta, or gamma radiation when they decay. The addition of phosphate fertilizers to our croplands affects the environment by contaminating it with heavy metals and naturally occurring radioactive materials [4], this could be harmful to organisms and damaging to soil [5). 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 soft tissues and cause h challenges. For example the accumulation of Pb is associated with developmental problems in children. The presence of heavy metals in the soil can runoff into water bodies or percolates into the underground water, thus affecting food, microorganisms and plant growth [6]. Elements analyzed include Cd, Cu, Fe, Pb, Mn. Ni, and Zn. These elements get into the human body when they accumulate in plant parts and eventually are taken in by humans from the food chain. These elements above threshold level not only affect humans but plants as well. For instance Cd which is highly persistent in the soil can affect the growing conditions of plants which may result to its accumulation in the soil above its threshold level and so affect soil acidity and the solubility of beneficial elements such as Zn . Besides Cd is easily absorbed from the soil by corn and wheat which means that our food supply is at risk of contamination by toxic substances that threaten human life.

2. Materials and Methods

Five hundred grams of six different brands of Nitrogen-Phosphorous- Potassium (NPK), two, Simple Super Phosphate (SSP), and one Diammonium Phosphate (DAP) were purchased from Samaru market, Sabon Gari Local Government Council, Kaduna State. The samples were transferred into polythene bags and labelled. Togo and Sokoto Phosphate rock samples were obtained from Institute for Agricultural Research (IAR) Ahmadu Bello University Zaria for comparison. The samples were crushed using agate mortar and pestle until homogenous. One gram aliquot was separately weighed into 100 ml glass-boiling tube, to this was added de-ionized water and digested at 80^{o} C in concentrated Hydrochloric acid and Nitric acid. The samples were gradually brought to boil for four hours, cooled, filtered and diluted to 100ml volume with de-ionized water. The pre pared samples were taken to the Multiuser laboratory, Ahmadu Bello University Zaria for analysis using Variant AA240FS (Fast Sequential Atomic Absorption Spectrometer) and the results were acquired by use of spectra AA software.

3. Results and Discussion

Table 1: Elemental Composition of Inorganic Fertilizer Samples in mg/kg by AAS

S/N	*Code*	*Cd*	*Cu*	*Fe*	*Ni*	*Mn*	*Pb*	*Zn*
1	CPRI	10.7	13.0	549.0	127.3	299.2	1.0	153.9
2	CPR2	1.0	5.6	1,263.0	8.7	258.6	1.0	32.1
3	CPR3	5.0	12.1	4,247.0	5.8	335.8	5.0	20.7
4	CPR4	3.0	7.2	6,515.0	15.3	206.6	BDL	25.7
5	CPR5	5.0	5.3	5,992.0	10.3	177.2	0.012	15.8
6	CPR6	4.0	6.7	7,412.0	12.2	246.2	BDL	19.2
7	CPR7	15.9	32.0	6,440.0	62.2	475.3	BDL	3900
8	CPR8	3.0	8.6	8,713.0	16.7	282.3	2.0	20.5
9	CPR9	3.7	8.9	9,924.0	20.9	170.2	3.2	106.5
Mean		3.6	11.20	6,228.0	31.0	442.4	1.2	474.9
Range		1.0-15.9	5.3-32.0	1,263.0-9,924.0	5.8-127.3	177.2-1,702.0	BDL 5.0	15.8-3900.0

Key:
CRP1=Sambuka 15-15-15 NPK
CRP2= Golden 15-15-15 NPK
CRP3=AFCUTT 15-15-15 NPK
CRP4= Tak 20-10-10 NPK
RP5= Maishaho 20-10-10 NPK
CRP6= Golden 20-10-10 NPK
CRP7= Diammonium Phosphate (DAP)
CRP8=Tak Agro SSP 18%
CRP9= FSFC SSP 18%

Table 2: Elemental composition of phosphate rocks of Togo and Sokoto origin

S/N	CODE	Cd	Cu	Fe	Ni	Mn	Pb	Zn
1	CPRI0	63.3	13.0	549.0	127.3	299.2	1.0	153.9
2	CPR11	62.1	5.6	1,263.0	8.7	258.6	1.0	32.1
MEAN		62.7	12.1	4,247.0	5.8	335.8	5.0	20.7

Key:
CRS 10= Sokoto Phosphate rock
CRS I1= Togo Phosphate rock

Table1 presents the results of the seven heavy metals analyzed in the fertilizer samples using AAS. Pb was not detected in Tak (20-10-10) NPK, Golden (20-10-10) NPK and DAP. The concentration of Pb in the other samples ranged from 0.1 mg/kg -5.0 mg/kg with a mean of 1.16mg/kg. The highest concentration of 5.0 mg/kg was recorded for AFCUTT (15-15-15) NPK. This value falls below 10-30mg/kg range in soil [7] and within the range 3-5 mg/kg found in sedimentary rocks [8] The presence of Cadmium in the fertilizers is of great importance because of its toxicity and its ability to accumulate in soil and bio-accumulate in plants and animals [9]. It accumulates in the kidney [10 and it is considered a carcinogen [11].

The range of Cd concentration in the inorganic fertilizers was 0.1 mg/kg -15.9 mg/kg with a mean of 3.6 mg/kg, this value falls within the range of uncontaminated soil [9]. Sambuka (15-15-15) NPK and DAP recorded higher Cd concentration of 10.7 mg/kg and 15.9 mg/kg than all other inorganic fertilizers whose Cd concentration is not significantly different from one another.

The higher Cd concentrations observed in the two fertilizers could be due to the origin of the raw material from which they were produced and the process of production which may have allowed the transfer of Cadmium into the fertilizer as noted by[12]. Note that, Cd concentration of the phosphate rock samples CRC12 and CRC13 as in Table1 above is high and that fertilizers use phosphate rock as raw material in their manufacture and these could easily pass into the fertilizers during production.

The DAP fertilizer showed the highest Cd concentration of 15.9 mg/kg which is above the tentative critical phytotoxic level of total Cd which is in the range of 3-8 mg/kg as reported by Kabata-Pendias &Pendias , [13]. The range of Cu concentration in the inorganic fertilizers was 5.3 mg/kg -32.0 mg/kg with a mean of 11.20 mg/kg. DAP fertilizer recorded the highest Cu concentration of 32.0 mg/kg followed by Sambuka (15-15-15) NPK and AFCUTT (15-15-15) NPK with concentrations of 13.0 and 12.1mg/kg respectively. However, Golden 15-15-15, Golden 20-10-10,Maishaho 20-10-10, Tak 20-10-10 NPK, Tak Agro ssp 18% and FSFC SSP 18 % fertilizers analyzed showed no significant difference in the copper concentration. Copper is an essential micronutrient, but it is a potential pollutant when it accumulates in the soil above its threshold level 2-100mg/kg as reported by Munkholm, [8]. The difference in copper concentrations within the fertilizer samples could be due to the amount allowed or added to the fertilizer by the manufacturers as an essential micronutrient for plants, Soil Microorganisms and animals.

The Fe concentration in the inorganic fertilizers ranged from 12.63 mg/kg- 99.24mg/kg and it had the mean of 62.28 mg/kg. The highest concentration of 99.24 mg/kg Fe was recorded by FSFC SSP 18% followed by Tak Agro SSP 18%. The DAP and Tak (20-10-10) NPK showed no significant difference in their Fe concentrations. Iron is recognized as beneficial to the growth of plants and crops and to quality of soil [14]

Ni had a range of concentrations from 5.8 mg/kg to 127.3 mg/kg with mean concentration of 31.0 mg/kg. The highest Ni concentration 127.3 mg/kg is recorded in Sambuka (15-15-15) NPK followed by DAP at 62.2mg/kg. Ni is not a micronutrient, and at high concentration, it could be a pollutant. The abundance of Nickel in rocks and soils is 5 mg/kg to 20 mg/kg and 2 mg/kg to750 mg/kg respectively. The maximum value for Nickel obtained from the inorganic fertilizers analyzed is far below its minimum in soils as reported by [8]. Kabata- Pendias &Pendias, [13] estimated the phytotoxic level of total Nickel in surface soils to be 100 mg/kg.

Mn is also recognized as beneficial to plant growth and crops and to the quality of soil. The range of 177.2 mg/kg to 1702.0 mg/kg and a mean of 442.4mg/kg respectively were recorded for Mn in the inorganic fertilizers analyzed. FSFC SSP 18% fertilizer recorded the highest concentration of Mn followed by DAP fertilizer which recorded a concentration of 475. 3mg/kg.

The range of concentrations of Zn in the inorganic fertilizers was 0.0158 to 39.0mg/kg and a mean concentration of 474.9 mg/kg .DAP fertilizer recorded the highest value of 3900 .0 mg/kg followed by Sambuka (15-15-15) NPK1.539mg/kg and by FSFC super phosphate 18% fertilizer 1.07mg/kg. Ogunyele *et al*., [2] quoted Reilly (1980) as stating the

maximum permissible concentration in food stuff as 40-50 mg/kg and the concentration in uncultivated soil of north Guinea Savannah as 31.5 to 402 mg/kg. Note that maximum concentration recorded by DAP fertilizer falls within the values obtained in the soils of North Guinea Savannah.

4. Conclusion

This study has revealed that, the nine inorganic fertilizers analyzed using AAS technique, except Diammonium Phosphate brand of fertilizer, which contained higher concentration of Cd than found in agricultural soils have in them heavy metals like Cd, Ni and Pb whose concentrations are lower than those in phosphate rock and are within the concentration in agricultural soils and they also contain Cu, Fe, Mn, and Zn elements in quantities that are beneficial to plant growth. Further work should be carried out to find out the intake of these nutrients by different plants.

5. Recommendation

The use of these nine inorganic fertilizers presents no immediate hazard to users and to the environment; however, Diammonium Phosphate brand of the fertilizers needs to be monitored because of possible cumulative effects of Cd in agricultural soil.

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