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SHORT-TERM APPRAISAL OF HEAVY METAL CONTENTS IN COMMERCIAL INORGANIC FERTILIZERS BLENDED AND MARKETED IN NIGERIA

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ABSTRACT

Human food chain toxicity has been shown to be influenced by application of inorganic fertilizers. This research was conducted to appraise heavy metal contents of three (3) commercial NPK fertilizers blended and marketed in Nigeria in a short-term experiment. The different NPK fertilizers analysed were $N_{15}P_{15}K_{15}$, $N_{20}P_{10}K_{10}$ and $N_{27}P_{13}K_{13}$ using Atomic Absorption Spectrophotometer (AAS). Three batches of each of these samples were analysed in 2008, 2011, and 2014. In 2008, the results showed varied concentrations of toxic non-nutritious metals (Cd and Pd) and trace elements (Fe, Zn, Mn, Co, Cu, Mo, Ni and Cr) while V, As, Hg and Ag were below detection level. The heavy metal assessment in 2011 showed significant reduction ($p>0.05$) in some toxic metals and trace elements. Follow-up evaluation in 2013 showed further significant reduction ($p>0.05$) in addition to V, As, Hg and Ag that were below detection level. Only Pb was indicated as toxic non-nutritious metal with values (mg/kg) of 0.20±0.01, 0.27±0.08 and 0.12±0.01 in $N_{15}P_{15}K_{15}$, $N_{20}P_{10}K_{10}$ and $N_{27}P_{13}K_{13}$ fertilizers respectively. Though the concentrations of these heavy metals were within the recommended levels, however a slight increase could be expected from other possible inputs especially in mining areas. This should raise the need to monitor changes that could occur in soils in view of their health implications.

Keywords: Human food chain, inorganic fertilizers and heavy metal toxicity.

INTRODUCTION

Human food chain toxicity has been shown to be influenced by application of inorganic fertilizers (Ukpabi *et al.,* 2012). Historical cases of catastrophic and endermic exposures of heavy metals abound in literature. Iraq mercury poisoning [Harrison, 1990], Minamata diseases [Harada, 1994], the Pink disease [Jacob et al., 2011], the Itai-ita disease [Lister and Renshaw, 1991], and Alexander Litvinenko Poisoning [Jacob et al., 2011] are all associated with heavy metal poisoning. The worst heavy metal poisoning in Nigeria history was recorded in Zamfara State in 2010 were at least 460 children died and about 2000 were poisoned (Tsafe, 2013).

Heavy metals are thus commonly defined as metals having specific density of more than $5g/cm^3$ and are associated with toxicity. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury, and arsenic which are classified as toxic non-nutritious metals. These toxic metals have no known function in human biochemistry or physiology and do not occur naturally in living organisms (Duruibe et al., 2007) Food is the most important source of heavy metal exposure in the general population in most countries (WHO, 1992). Heavy metals are present in most foodstuffs but concentrations as well as individual intake vary considerably due to differences in terrestrial habits.

Heavy metals become toxic when they are not metabolized by the body and accumulate in the tissues. Some people cannot excrete them efficiently enough and build up occurs (Ukpabi et al., 2012). Godfrey *et al.*, 2002 revealed that those who cannot excrete heavy metal efficiently appear to be genetically predisposed to this condition. Although several adverse health effects of heavy metals have been known for a long time, exposure to heavy metal continues and is even increasing in some parts of the world, especially in some developing countries (Jerup, 2003).

Schroeder and Balassa [1963] were the first to identify that fertilizers were implicated in raising some heavy metal concentrations in food crops and that the main source of fertilizer derived heavy metals in soils was phosphate fertilizer manufactured from phosphate rocks. Some decade ago analysis of fertilizers commercially marketed in India, USA, Australia, Sardi-Arabia and Sweden indicated that phosphate fertilizers contained significant and varied amount of heavy metals (Charter et al., 1993). In recent years, commercial fertilizers have been regulated to ensure that the fertilizer products labels or websites provide accurate information on essential plant nutrient contents and the potential presence of toxic non-nutritious metals such as Cd, Pb, Ag, Hg, As.

This policy has significantly reduced the presence of these potential toxic substances especially in developed countries. Random sampling survey, showed that in Nigeria, these toxic non-nutritious metals and trace elements are not indicated on the product labels, hence farmers do not find helpful information for selecting fertilizer products with the lowest heavy metal concentrations. Fertilizer manufacturing companies in Nigeria have been out of serious production for nearly 10 years now, while Nigeria has all the necessary resources locally to produce all the needed fertilizers. However, 70% of the technology has to be imported while about 30% is locally available Ahmed (2007). The most common type of fertilizer in Nigeria is the inorganic type in different NPK composition. A study conducted by the Agricultural Project Monitoring and Evaluation Unit (APMEU) of Ministry of Agriculture in 2006 estimated NPK fertilizer use at 697,000 metric tons.

Since regular monitoring of heavy metal in fertilizers is essential for preventing continuous building up of the metals in food chain? The present study assesses the heavy metal concentrations of three inorganic fertilizers ($N_{15}P_{15}K_{15}$, $N_{20}P_{10}K_{10}$ and $N_{27}P_{13}K_{13}$) blended and marketed in Nigeria from 2008 to 2014 and compares them with international standards established for fertilizers.

MATERIALS AND METHODS

Chemicals and equipment

All chemicals and reagents used were from reliable sources and of high analytical grade. Heavy metal analyses were carried out using atomic absorption spectrophotometer (UNICAM 969), Japan. Optical densities were measured using digital flame photometer (ESIPO, model 1381) and digital spectrophotometer (Model 390, Tuner® USA).

Sampling

Three inorganic fertilizers (Federal and Chemical Company Limited, Kaduna, Diamond fertilizer Company Limited, Abakaliki and Golden Fertilizer Company Limited, Kaduna) were purchased in full bags from various markets in Aba metropolis. The mineral NPK

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percentages by weight of these fertilizers were $N_{15}P_{15}K_{15}$, $N_{20}P_{10}K_{10}$ and $N_{27}P_{13}K_{13}$ respectively.

Fertilizer Analysis
Total Nitrogen

The total nitrogen in the each fertilizer sample was determined using a regular macro-Kjeldahl method ASTM (1999). The fertilizer sample (2g) was weighed and transferred into a Kjehdahl digestion flask. Few bumping chips, 4 tablets of the digestion catalyst (each contains 1g sodium tetraoxosulphate (VI) (Na_2S0_4)) and 0.5g selenium and 25ml of the conc. tetraoxosulphate (VI) acid (H_2SO_4) were added. The flask was placed on an electrothermal heater and held on a slanting position with the clamp on the retort-stand. The flask was gently heated until frothing ceased. The digestion temperature was intensified until the digest cleared. The flask was cooled and 100ml of distilled water added slowly. Boric acid (2%, 50ml) was measured into a 250ml conical flask and 4 drops of 1% double indicator (methyl red-methylene blue combination) was added into the boric acid solution. Diluted digest (20ml) was measured into 250ml round-bottomed distillation flask. The steel head carrying the Liebig condenser was connected to the flask and the distillation flask was held in position with a retort stand. The conical flask was placed at the tip of the receiver adaptor connected to the Liebig condenser and 40ml of 50% sodium hydroxide (NaOH) was injected into the distillation flask through a syringe. The distillation flask was heated until 150ml of ammonia (NH_3) was collected in the receiving flask over boric acid. The content of the receiving flask was allowed to cool and titrated with 0.1M Hydrochloric acid (HCL) until a pink colour appeared. The reading was noted and recorded while the blank underwent the same treatment.

Potassium Content

Flame emission spectrometry using flame photometer was used for the measurement of potassium ASTM (1999). Fertilizer sample (20g) was weighed into a beaker and digested with 10ml of conc. Trioxonitrate (V) acid (HNO_3) and 5ml of conc. perchloric acid ($HClO_4$) on a hot plate with gentle boiling. The digested sample was evaporated to dryness and the residue mixed with 5ml of 2.0M hydrochloric acid (HCl) and then, filtered into a 100ml standard flask using Whatman No 1 filter paper. The resultants digest was aspirated into the flame photometer and the intensity of the radiation recorded. A standard solution of potassium chloride (KCl) (0.5mg/l) was prepared and aspirated into the flame photometer. The intensity of the radiation was recorded while the blank underwent the same treatment using distilled water

Phosphate

This method was based on the formation of heterophosphomolybdate compound when an acid molybdate was added to a solution containing orthophosphate APHA (1998). Fertilizer sample (20g) was digested using concentrated tetraoxosulphate (vi) acid (H_2SO_4) and trioxonitrate (v) acid (HNO_3), mixed acid solution, in the presence of a pinch of (0.3g) copper sulphate and potassium sulphate. The colourless solution was treated with 2ml ammonium molybdate and stannous chloride solution and was allowed to stand for 5minutes.A blue colour was developed which was measured at a wavelength of 690nm. A standard solution was prepared using a phosphate compound (0.2mg/l) and was treated as the test sample. The absorbance was also measured at 690nm and recorded.

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Heavy Metal Contents

Atomic absorption spectrophotometry (AAS) is an analytical method for the determination of elements in small quantities in test samples including fertilizers ASTM (1999). Fertilizer sample (2g) was weighed into a beaker and digested with 20ml of conc. HNO_3 and 10ml of conc. $HClO_4$ on a hot plate with gentle boiling. The digested sample was evaporated to dryness and the residue mixed with 10ml of 2.0M HCl, filtered into a 100ml standard flask using Whatman No1 filter paper. Several digested samples were analysed for the heavy metals of interest – Mn, Bo, Cu, Fe, Mo, Ni, Zn, Mg, Ca, V, As, Cd, Hg, Pb, Co, Cr, Ag using an atomic absorption spectrophotometer equipped with a computer printout. The samples were analyzed in triplicates. The effectiveness of the methods used was tested by using spiked samples that were later used as reference samples.

Statistical Analysis: The confidence limits of the data were based on one way analysis of variance by ANOVA.

RESULTS

Table 1: HEAVY METAL COMPOSITION OF $N_{15}P_{15}K_{15}$ FERTILIZERS USED IN THE STUDY

Parameter Mg/kg	Canadian Standard mg/kg	2008	2011	2014
Fe	NI	91.0±1.73	67.18±1.27	11.12±0.83
Zn	1850	12.57±0.38	11.48±0.16	<0.01
Ni	100	17.4±1.96	10.70±1.91	<0.01
Mn	NI	7.80±0.95	5.50±0.18	1.14±0.10
Mo	20	1.80±0.50	0.44±0.02	<0.01
Cd	20	11.32±1.12	6.18±1.07	<0.01
Pd	500	7.45±0.80	5.28±0.42	0.20±0.01
Cr	NI	1.58±0.40	<0.01	<0.01
Co	NI	4.70±0.26	3.71±0.18	0.18±0.01
Cu	NI	8.26±0.27	4.06±0.12	2.56±0.09
Hg	NI	<0.01	<0.01	<0.01
Ag	NI	<0.01	<0.01	<0.01
V	NI	<0.01	<0.01	<0.01
As	75	<0.01	<0.01	<0.01

Values are mean ± standard deviation of triplicate determinations.

Table 2: HEAVY METAL COMPOSITION OF $N_{20}P_{10}K_{10}$ FERTILIZERS USED IN THE STUDY

Parameter Mg/kg	Canadian Standard mg/kg	2008	2011	2014
Fe	NI	35.00±1.78	24.79±3.81	19.4±1.61
Zn	1850	14.48±0.79	6.88±1.81	<0.01
Ni	100	17.10±1.81	8.35±1.30	<0.01
Mn	NI	19.30±1.57	4.21±0.56	1.58±0.12
Mo	20	2.30±3.60	1.89±0.51	<0.01
Cd	20	2.84±0.28	1.01±0.11	<0.01
Pd	500	8.57±0.69	2.21±0.10	0.27±0.08

Cr	NI	6.11±0.31	3.12±0.38	<0.01
Co	NI	5.10±1.40	2.29±0.15	0.14±0.10
Cu	NI	9.01±1.07	8.64±0.26	<0.01
Hg	NI	<0.01	<0.01	<0.01
Ag	NI	<0.01	<0.01	<0.01
V	NI	<0.01	<0.01	<0.01
As	75	<0.01	<0.01	<0.01

Values are mean ± standard deviation of triplicate determinations.

Table 3: HEAVY METAL COMPOSITION OF $N_{27}P_{13}K_{13}$ FERTILIZERS USED IN THE STUDY

Parameter Mg/kg	**Canadian Standard mg/kg**	**2008**	**2011**	**2014**
Fe	NI	40.00±1.70	36.50±2.19	22.41±3.12
Zn	1850	17.02±1.65	8.52±3.60	1.12±0.01
Ni	100	14.4±1.41	1.90±0.01	<0.01
Mn	NI	0.50±0.10	<0.01	<0.01
Mo	20	1.34±2.64	0.80±0.01	<0.01
Cd	20	6.13±0.96	2.13±0.01	<0.01
Pd	500	4.02±1.08	1.31±0.02	0.12±0.01
Cr	NI	4.70±0.72	2.70±0.01	0.17±0.02
Co	150	4.30±0.81	0.38±0.01	0.22±0.01
Cu	NI	0.27±0.10	0.79±0.02	0.12±0.01
Hg	NI	<0.01	<0.01	<0.01
Ag	NI	<0.01	<0.01	<0.01
V	NI	<0.01	<0.01	<0.01
As	75	<0.01	<0.01	<0.01

Values are mean ± standard deviation of triplicate determinations.

DISCUSSION

The heavy metal composition of the three (3) inorganic fertilizers- $N_{15}P_{15}K_{15}$, $N_{20}P_{10}K_{10}$ and $N_{27}P_{13}K_{13}$ were represented in Tables 1, 2 and 3 respectively. The data showed that the concentrations of heavy metals varied considerably among the three fertilizers and there were significant reduction ($p>0.05$) in their heavy metal concentrations from 2008 to 2014.

Fe concentrations were the highest whereas V, As, Hg and Ag were not detected by our analytical method. The concentrations of Fe, Zn, Ni and Mn were significantly higher ($p<0.05$) than the other trace elements (Mo, Cr, Co, Cu) examined in all the fertilizer samples especially in the 2008 analysis. The results also indicated significant reduction ($p<0.05$) in some concentrations from 2008 to 2011 and subsequently to 2014, as, Zn, Ni, Mo and Cr were below the detection limit. These trace elements are involved in electrolyte balance, metabolic process and components of essential parts of living systems. The most important information reported on the poisoning effects of these metals are due to their interference with the normal body biochemistry in the metabolic processes and toxicities associated with their oxidation state. Example is Zn whose interferes with Cu metabolism causes, vascular shock, dyspeptic nausea, vomiting and diarrhea, (Gyorffy and Chan, 1992; Islam et al., 2007). The health effect of Cr depends largely on its oxidation state; Cr (III) in severe acute effects

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results in gastrointestinal disorder and possible convulsion while Cr (VI) has been found to be carcinogenic.

Values of the toxic non-nutrition metals content in the fertilizer samples showed the highest variation with Cd content (11.32±1.12mg/kg) in $N_{15}P_{15}K_{15}$ fertilizer while Pb highest content (8.57±0.69mg/kg) was indicated in $N_{20}P_{10}K_{10}$ fertilizer. Similarly there were significant reduction ($p>0.05$) in concentrations especially from 2008 to 2011 Cd mean concentrations followed significantly ($p<0.05$) the phosphate percentage by weight of the fertilizers in 2007 analysis as shown in table 1 that is $N_{15}P_{15}K_{15}$ (11.32±1.12mg/kg) > $N_{27}P_{13}K_{13}$ (6.13mg/kg) > $N_{20}P_{10}K_{10}$ (2.84mg/kg). Only Pb was indicated in 2014 fertilizer analysis with values (mg/kg) of 0.20±0.01, 0.27±0.08 and 0.12±0.01 in $N_{15}P_{15}K_{15,}$ $N_{27}P_{13}K_{13}$ and $N_{20}P_{10}K_{10}$ fertilizers respectively, as Cd was below detection level. This agrees with the reports of Kongshong *et al* (1992) and Finck (1992) that inorganic fertilizer manufactured from phosphate rocks contains various metals as minor constituents in the ores. The significant reduction may be attributed to the fact that feritilizer plants now use imported Diammonium Phosphate (DAP) and Monoammonium Phosphate (MAP) as major raw materials rather than ground phosphate rocks.

Pb, a serious soil and environmental pollutant has attracted the most attention due to its potential toxicity of low concentrations. Pb has been reported not to have any known function in human biochemistry or physiology and does not occur naturally in living organism hence continuous low Pb intake may results in serious illnesses of the lungs, liver and kidney Recent literature review has indicated that there may be toxicological effects of Pb at low level of exposure than previously anticipated especially in genetically predisposed persons

CONCLUSION

The mean concentration of heavy metals contents of the three inorganic fertilizers marketed in Nigeria within the period studied were within to limits as established by Canadian standard. However, a slight annual increase could be expected. This increase compiled with other possible inputs (especially mining) of heavy metals to agricultural soil, should raise the need to monitor changes that could occur in soils.

RECOMMENDATION

It is important to encourage manufacturers to indicate heavy metals concentrations on the fertilizer labels in view of their health implication.

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