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HEAVY METAL COMPOSITION OF COMMERCIAL FERTILIZERS FROM ZARIA, NORTHERN NIGERIA

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ABSTRACT

The heavy metal composition of some commercial fertilizers and soil supplements used in Zaria were analysed. The fertilizers analysed include Liquid Organic fertilizer, Palette Organic fertilizer, Urea, Super phosphate, NPK, some of the soil supplements analysed are cow dung and chicken droppings. Using Atomic Absorption Spectrophotometer (AAS) the following range of heavy metal concentrations were obtained: Cu 3.92-38.14mg/l, Mn 0.057-199.17mg/l, Cr 0.19-2.207mg/l, Zn 1.35-83.12mg/l, Fe 5.00-514.18mg/l, Ni 0.063-149mg/l, Pb 9.86-15.52mg/l, Co 0.26-2.87mg/l.. Super phosphate had the highest abundance of Iron (514.18mg/l). These values were compared to standards for heavy metals in fertilizers and supplements for other countries and were found to be below the limits. Like other countries, it will be important for Nigeria to have set standards for heavy metals levels for fertilizers used in the country.

KEYWORDS: fertilizer, Heavy metal, supplements, composition, AAS

INTRODUCTION

For many years commercial fertilizers have been regulated to ensure that label provides accurate information on essential plant nutrient content. In recent years, however, concerns about quality in some fertilizer and liming products have extended beyond nutrient content to the potential presence of non nutrient toxic substances, such as heavy metals (Cooke, 1982). Plants in contrast to animals have the ability to convert carbon dioxide from the atmosphere and inorganic components of the earth directly into high-energy carbohydrates, fat, and protein. These plant materials are absolutely essential to human nutrition as well as to the nutrition of other animal species (Kirk-Othmer, 1993).

There is increasing interest in recycling of by-products and waste materials for land application as fertilizers and supplements. The obvious benefits from this practice include the return of a number of nutrients to soil and improvement of soil physical conditions (Kirk-Othmer, 1993).

The benefits associated with the use of fertilizers must be balanced against the potential hazards, which the materials may present. They may contain significant levels of metals which can at high exposure levels adversely affect plants, animals or humans (Underwood, 1977; Nicholas and Egan, 1975; Goyer and Clarkson, 2001). In response to this concern, numerous regulatory agencies have enacted policies for by-product utilization. In 1979, under the authority of the fertilizer Act and Regulations, Agriculture and Agri-Food Canada (AAFC) introduce a series of standard for metals in fertilizer and supplements, which were re-evaluated in 1993 and 1995 in response to the standards developed elsewhere e.g United State Environmental Protection Agency (Canadian Food Inspection Agency, 1997).

In Nigeria, there are no such standards for metals concentrations in fertilizers and supplements. In Kano, Nigeria, it was reported by Ogbonna et al (1998) that sludge and effluent from tanneries are used as soil conditioners despite the high chromium content of the effluent as reported by Agunwa et al (2006) because of the in ability of most of the tanneries to treat their waste before discharge.

The worldwide use of fertilizers has an important, positive effect on the environment. Conservative estimate indicates that 30% of the world food production is directly attributable to fertilizer use (Kirk-Othmer, 1993). Possible negative effects of fertilizer use include; deterioration of food quality, destruction of natural soil fertility, and pollution of ground and surface water.

Prudent use of fertilizer does not contribute to this problem (Kirk-Othmer, 1993). The aim of this work is to determine the levels of heavy metals in commercial fertilizers and supplements and compare them with values from other countries.

MATERIALS AND METHODS

Five brand of commercial fertilizers where obtained from Sabon Gari Market in Zaria and a sample of chicken droppings and cow dung were collected from two farms in Zaria. These samples were collected in plastic bags and plastic bottles for the liquid samples.

The samples were grounded sufficiently to pass a sieve having mesh size about 1mm square. About 5g of each

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Table I: Standards for Mineral element levels for some other Countries

METAL	CHINA	CANADA		AUSTRALIA									JAPAN
	mg/kg Fertilizer	**kg/ha** Max. Acceptable Cumulative Additions to Soil over 45 years	**mg/kg dw** Maximum Acceptable Metal Conc.	**mg/kg P** Phosphorous fertilizers	**mg/kg product** Nonphosphorous fertilizers	**mg/kg** product Fertilizers wholly constituted by micro-nutrients	**mg/kg** product Phosphogypsum	**mg/kg** All fertilizers and micronutrients	**mg/kg** Major nutrient fertilizers & soil ameliorants	**mg/kg** Major nutrient fertilizer with micro-nutrients	**mg/kg** Micronutrient foliar app.	**mg/kg** Micro nutrient for soil app.	**mg/kg** in by product phosphate fertilizers
Arsenic	50	15	75	-	-	-	-	-	-	-	-	-	50
Cadmium	8	4	20	300	10	50	15	-	-	-	-	-	8
Cobalt	-	30	150	-	-	-	-	-	-	-	-	-	-
Mercury	5	1	5	-	-	-	-	-	-	-	-	-	5
Molybdenum	-	4	20	-	-	-	-	5	-	-	-	-	-
Nickel	-	30	180	-	-	-	-	-	-	-	-	-	-
Lead	100	100	200	-	-	-	-	-	100	500	500	2000	100
Selenium	-	2.8	14	-	-	-	-	-	-	-	-	-	-
Zinc	-	300	1850	-	-	-	-	-	-	-	-	-	-
Chromium	500	-	-	-	-	-	-	-	-	-	-	-	500

of the dried samples was placed into silica basin, covered with a silica clock glass, and placed in a muffle furnace, with the temperature raised to 450^{o}c for 6hrs. The samples were cooled, 10ml of HCl approx 6N was added and evaporated to dryness on a water bath. The soluble salts were extracted from the residue with two successive 10ml portion of boiling diluted HCl, approx 2N, decanting the solution each time through the same filter paper into a 50ml volumetric flask. 5ml of HCl and about 5ml of HNO_3 (6N) was added to the residue in the basin and the solution was filtered through the same filter paper into the flask. The extracts were made to the mark with distilled water, washing the filter paper in the process (Hanson, 1973). The heavy metals were determined by Atomic Absorption Spectrophotometer (Unicam 969) using hollow cathode lamps in default condition and flame absorption mode. For reproducibility this analysis was carried out tries.

RESULTS AND DISCUSSION

COPPER

From fig. I, super phosphate fertilizer had the highest copper value of 83.67mg/kg with NPK and chicken dung having values at 38.14mg/kg and 34.30mg/kg respectively. This high values in super phosphate could be due to the rock phosphate used, or from the sulphuric acid used to make the super, which might be a by-product of processing ore (Cooke, 1982). Limits for copper level in soil being 50 -140mg/kg (see table II). Copper is important for photosynthesis. Symptoms for copper deficiency include chlorosis (Barber 1984).

Table II: Sewage Sludge Metal Level Standards

METAL	Limit Values for Concentrations of Heavy Metals in Soil (Soil with pH of 6 -7) mg/kg	Limit Values for Heavy-Metal Concentrations in Sludge for Use in Agriculture mg/kg	Limit Values for Amounts of Heavy Metals which may be Added Annually to Agricultural Land (Based on 10-Year Avg.) kg/ha/yr
Cadmium	1 to 3	20 to 40	0.15
Copper	50 to 140	1000 to 1750	12
Nickel	30 to75	300 to 400	3
Lead	50 to 300	750 to 1200	15
Zinc	150 to 300	2500 to 4000	30
Mercury	1 to 1.5	16 to 25	0.1
Chromium	100 to 150	1000 to 1500	4

Source: World Fertilizer Metal Standard (2004). www.afpc.net

MANGANESE

From fig.1, Chicken dung has the highest value of 199.17mg/kg. Manganese is necessary for building the chloroplasts. Manganese deficiency may result in coloration abnormalities, such as discolored spots on the foliage (Simpson 1986).

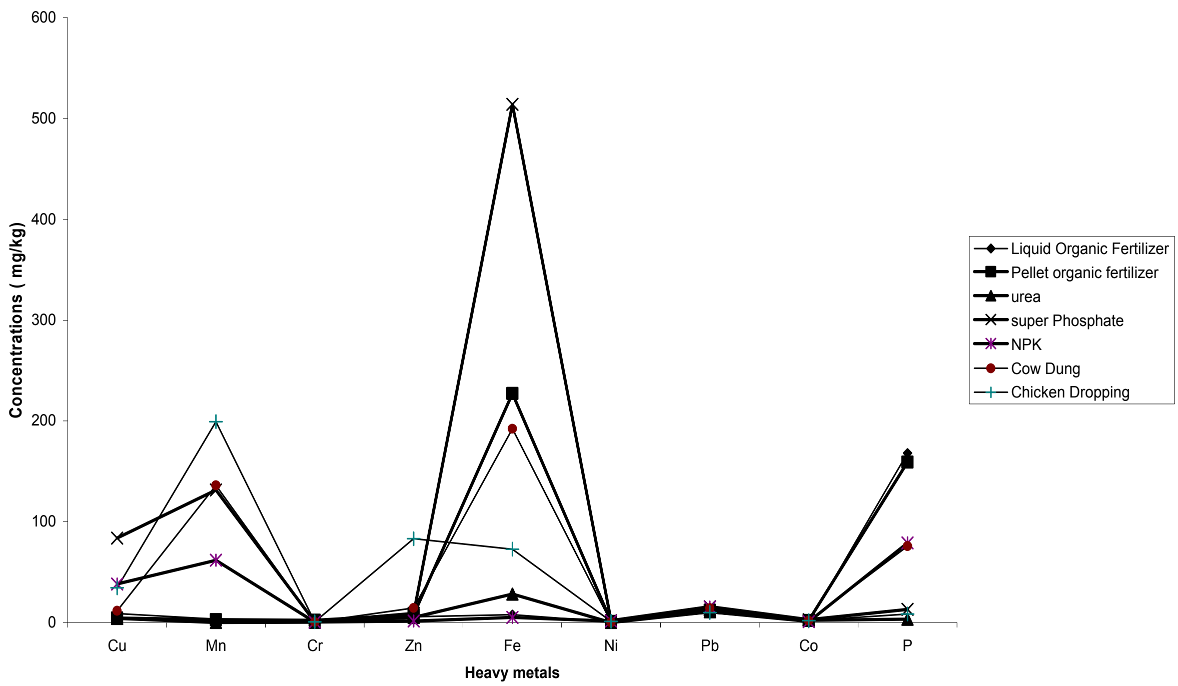

Fig. I: Heavy metal levels of some fertilizers and soil supplements

IRON
From fig.1, iron has the highest value of 514.18mg/kg in super phosphate Iron is necessary for photosynthesis and is present as an enzyme cofactor in plants. Iron deficiency can result in interveinal chlorosis and necrosis (Barber 1984).

ZINC
From fig.1, chicken dung had the highest value of 83.12mg/kg, with Canadian standards for Zinc being 1850mg/kg (see table I). Zinc is required in a large number of enzymes and play an essential role in DNA transcription. A typical symptom of zinc deficiency is the stunted growth of leaves, commonly known as “little leaf” and is caused by the oxidative degradation of the growth hormone auxin (Cooke 1982).

PHOSPHORUS
From fig.1, liquid fertilizer has the highest value of 168mg/kg. Phosphorus is important in plant bioenergetics. As a component of ATP, phosphorus is needed for the conversion of light energy to chemical energy (ATP) during photosynthesis. Phosphorus can also be used to modify the activity of various enzymes by phosphorylation, and can be used for cell signaling. Since ATP can be used for the biosynthesis of many plants bio-molecules, phosphorus is important for plant growth and flower/seed formation (Simpson 1986).

LEAD, NICKEL, COBALT, AND CHROMIUM
Some of the non-essential nutrient that were analysed include Pb, Ni, Co, and Cr. From fig. I, Pb has the highest value of 15.52mg/kg in super phosphate fertilizer; standard for lead in fertilizer are 100mg/kg for China and 500mg/kg for Canada (see table I). Lead is especially prone to accumulation in surface horizons of soil because its low water solubility within an environmentally relevant pH range results in very low mobility (Davies, 1995). Neurological problems, especially in children, are the principal concern for chronic lead exposure (Goyer and Clarkson, 2001). Past use of lead solder in food and beverage can lead to significant human exposures. Dietary intakes of 400 to 500μg/ day for Canada dropped to 20μg/ day with the elimination of this practice. Consumption of lead contaminated soil itself, rather than crop contamination , is a more likely exposure hazard.
Super phosphate fertilizer still has the highest Nickel value of 1.89mg/kg, limits been 180mg/kg for Canada. Super phosphate fertilizer still had the highest Cobalt value being 2.87mg/kg, limits for Canada is 150mg/kg (see table I). Nickel is moderately soluble in soil water and is typically true for metals, increases at low pH (McGrath, 1995). The predominant soluble species in most agricultural soil is Ni^{2+}. Nikel sulphides likely controls the Ni^{2+} concentrations in soil solution. The Nickel concentration in plant generally reflects that of their soils and plant transfer coefficients range from 0.1-1.0. Inhalation of nickel during refining of ore produces respiratory tract cancer, and allergic contact dermatitis to nickel alloy is common (Goyer and Clarkson, 2001). Aside from this problem Nickel toxicity appears quite low. It is a naturally essential metal for some plants, microbes, and invertebrates. There is no known biochemical function for Nickel in humans. Crop contamination with Nickel in fertilizers and related products seems an unlikely human health problem.

Organic fertilizer had the highest Chromium value of 2.21mg/kg, while the standard for chromium in fertilizer for China is 500mg/kg. Cr (IV) is a well epithelial irritant and human carcinogen (IARC, 1990). It is also toxic to many plants, aquatic animals and bacteria (USEPA, 1985). From the results in Table I, compared to standards from other parts of the world, the mineral elements present in these fertilizers are within the safe limits for addition to the soil.

CONCLUSION

Fertilizers made from naturally occurring raw material may contain appreciable quantities of micronutrients. Farm yard waste, like the cow dung and chicken dropping may contain varying amount of micronutrients based on their feed and the housing system used (Cooke 1982). Comparing the concentrations of heavy metals present in these fertilizers to set standards from other parts of the world, the levels are within safe limits for addition to soil. It will be important for the Nigerian Government to have her own standards for heavy metals in fertilizer; this will help in checking both essential and non-essential heavy metals that are added to the soil. Since use of fertilizers and related products is a repetitive practice, it is also necessary to consider cumulative changes in the soil over decades of applications.

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