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Trace Metals Levels in Inorganic Fertilizers Commercially Available in Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Author NUB designed the study, wrote the protocol and wrote the first draft of the manuscript. Author NUB managed the literature searches. Author UME performed the extraction and managed the experimental and elemental analyses. Author WUA revised the first draft of the manuscript. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

Aims: To investigate the concentrations of arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), vanadium (V) and zinc (Zn) in commercially available inorganic fertilizers (calcium superphosphate and urea).

Place and Duration of Study: Urea and superphosphate fertilizers were purchased from a local market in Uyo, Southern Nigeria.

Methodology: A total of twenty seven fertilizer samples were randomly taken representing triplicate samples from three urea and six superphosphate original fertilizer bags. Each sample were digested and extracted using the ethylenediamine tetraacetic acid (EDTA) extraction technique. The elemental analysis was performed using an inductively coupled plasma atomic emission spectrophotometer (ICP-AES) (Optima 3000 – Perkin Elmer).

Results: The analyses indicated the presence of trace metals in commercially available fertilizers sold in Nigeria. Cadmium was found in comparatively high concentrations. Zinc was found present in relatively high concentrations in both urea and phosphate fertilizer samples but As was found in low concentration. By comparison, the superphosphate

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fertilizer contained higher concentrations of Cu, V and Zn as impurities while urea fertilizer recorded slightly elevated concentrations of Ni, Pb and Cd. The levels of some trace metals in the urea and superphosphate fertilizers analyzed were within the allowable limits.

Conclusion: This study led to the conclusion that urea and superphosphate fertilizers sold in Nigeria could act as sources of trace metal enrichment of agricultural farmlands. Enhanced trace metals in inorganic fertilizers could constitute a threat to human health and the sustainability of farming practices. This study provided a new data for the agriculture and health authorities in Nigeria. Relevant government agency (ies) should regularly monitor trace metals impurity levels in imported fertilizers.

Keywords: Trace metals; inorganic fertilizers; soil pollution; nutrient amendments.

1. INTRODUCTION

In recent years, there have been heightened concerns about human health, the environment and the sustainability of farming practices arising from the use of commercial fertilizers that contain elevated amounts of toxic trace metals. Recent developments of trace metal research in the area of soil contamination has indicated that toxic trace metals in soil are capable of being incorporated into plant edible tissues through primary uptake as nutrients. Some trace metals could be toxic to food crops and plants themselves. However, food crops ingested by humans represent a potentially proficient pathway of exposure to toxic and nutritionally important minor and trace elements [1-3].

The presence of enhanced trace metals in inorganic fertilizers and other soil inputs are indicative of the presence of prohibited sources and ingredients. However, trace metals presence and contamination of fertilizers and other soil nutrient amendments is becoming an increasingly serious threat, which has drawn the attention of agricultural and environmental stakeholders, public policymakers, health experts, consumers and farmers because of the attendant health risks and environmental problems. There are proven evidences that excessive fertilizer use can cause deterioration in the integrity of water quality, exceed natural abundances in soils with potential hazards to human health and the environment [1-3]. The application of commercial fertilizers that has elevated concentrations of trace metals could result in accumulation in soils, as well as responsible for much of the soil metal pollution [1,4,5]. This increases the potential exposure of crops, animals, and humans to toxic trace elements. Both organic and chemical fertilizer products may be at risk for trace metal contamination.

Generally, the most serious cause of heavy metal contamination results when industrial byproducts are recycled into fertilizers. Micronutrient fertilizers, for example, are frequently derived from recycled industrial wastes. Increasing concentrations of trace metals in fertilizers have also been attributed to production process. Superphosphate fertilizers derived mainly from phosphate ores can contain significant amounts of a wide range of impurities, including trace metals [5].

Fertilizers are presently one of the primary anthropogenic sources of trace metals. The application of fertilizers containing these metals to the soil could have substantial capability for both bioaccumulation and food web accumulation. This development can pose a threat to crop yield and quality as well as undesirable consequences to human and animal health [6-9]. The toxicity, potential environmental and human health effects of some of these metals could occur even at very low concentrations [9-10]. However, studies have revealed that the extent of soil metal contamination and subsequent uptake by crops depends on several chemical and physical factors such as ionic strength of soil solution, pH, soil type, Eh, organic matter level, among others [2,11,12]. Studies have indicated the presence of trace metals in commercially available fertilizers [2,3,13-15]. Moreover, of the trace metals found in inorganic fertilizers, the detection and presence of enhanced levels of cadmium is of greatest concern, taking into consideration its toxicity, potential for bioaccumulation and food web accumulation [5,9]. Cadmium is a known human carcinogen and has no nutritional or biochemical relevance [7,9,16].

In recent years, there has been increasing awareness of the environmental and health impacts that are associated with trace metal toxicity, however there is dearth of information regarding the concentrations of several trace metals in commercial fertilizers available for agricultural purposes in Nigeria. This study was carried out to establish the concentrations of arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), vanadium (V) and zinc (Zn) in calcium superphosphate and urea fertilizers commonly used in Nigeria.

2. MATERIALS AND METHODS

2.1 Sampling Chemical Digestion and Elemental Analysis

Two commercially available brands of urea and superphosphate fertilizers were purchased from a local market in Uyo, Southern Nigeria. Eighteen (18) composite samples representing triplicates of SPP fertilizer of the same brand were randomly taken from six original tamper proof bags. Triplicate samples of URE fertilizer were also taken from each of the original bags marked urea fertilizer. From the representative quantities taken, approximately 0.5g was weighed into pre-cleaned 250 mL beakers, digested and extracted using the ethylenediamine - tetraacetic acid (EDTA) extraction technique [17]. The concentrations of each trace metal were released via digestion of the fertilizer samples carried out in a microwave oven after addition of hydrofluoric acid [18,19]. The digestion procedure was completed by removing the fluoride via heating of the sample with nitric acid (HNO_3). The extent of digestion of trace metals in the 27 fertilizer samples was verified by using EDTA as extractant with extractant to fertilizer ratio of 2.5 [2]. Chemicals used were of analytical grade. The concentrations of arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), vanadium (V) and zinc (Zn) in extracts were determined using an inductively coupled plasma spectrophotometer (ICP-AES).

2.2 Preparation of Standards

In order to reduce the detrimental effects of overlapping spectral interferences on element quantitation during metal analyses, an interelement correction standard was prepared by using standardized solution of metal ions prepared from their salts. A mixture of commercially available 100mg kg^{-1} stock solutions (Analar Grade) of As^{6+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+} and Zn^{2+} were prepared as interelement working standard solution to verify that the overlapping lines do not cause the detection of elements at concentration above methods detection limits (MDLs) [20].

2.3 Statistical Analysis

Multiple-variable analyses and comparative summary descriptives of data were performed using Statgraphics Centurion VI Statistical Software, with level of significance maintained at 95% for each test.

3. RESULTS AND DISCUSSION

Table 1. shows the summary statistics for each of the quantitative trace metal data obtained from analyzed superphosphate (SPP) and urea (URE) fertilizer samples. It includes measures of central tendency and measures of variability.

Table 1. Summary statistics of trace metal levels in superphosphate and urea fertilizers commercially available in Nigeria

Trace metals	As	Cd	Cu	Ni	Pb	V	Zn
Superphosphate fertilizer							
Average (mg/kg)	0.0012	2.59	7.80	5.26	6.65	1.92	15.81
Standard deviation	0.0004	0.58	5.31	0.44	3.57	0.26	3.49
Coeff. of variation %	34.99	22.26	68.07	8.28	53.70	13.81	22.09
Minimum	0.001	1.85	2.45	4.85	4.3	1.39	11.30
Maximum	0.002	3.16	13.1	5.95	13.75	2.09	19.35
Range	0.001	1.31	10.65	1.10	9.45	0.70	8.05
Urea fertilizer							
Average (mg/kg)	0.0013	2.67	3.49	5.87	7.46	1.53	3.90
Standard deviation	0.0006	0.24	0.72	0.62	0.42	1.24	1.70
Coeff. of variation %	43.30	8.98	20.64	10.59	5.64	81.47	43.68
Minimum	0.001	2.52	2.96	5.15	7.10	0.73	2.70
Maximum	0.002	2.95	4.31	6.25	7.92	2.96	5.85
Range	0.001	0.43	1.35	1.1	0.82	2.23	3.15

The concentration of As, Cd, Cu, Ni, Pb, V and Zn in superphosphate and urea fertilizer samples obtained from triplicate measurements are presented in Figs. 1 and 2 respectively. In general, the concentrations of all trace metals analyzed appear to be considerably higher in the superphosphate fertilizer samples than the urea fertilizer samples. This confirms the report that phosphorus fertilizers usually contain trace metals at concentrations above levels found in other fertilizers [21]. The results obtained indicated that superphosphate fertilizer contains higher concentrations of Cu, V and Zn as impurities with mean levels of 7.80, 1.92 and 15.81 mg/kg respectively, while urea recorded slightly elevated concentrations of Ni, Pb and Cd. However, zinc exhibited a remarkable presence in superphosphate fertilizer with an overall mean concentration of 15.81 mg/kg. Zinc is an essential trace element that can be toxic to plants at an enhanced level. Many zinc bearing fertilizers are highly insoluble and crops amended with these materials can show noticeable zinc deficiencies [22,27].

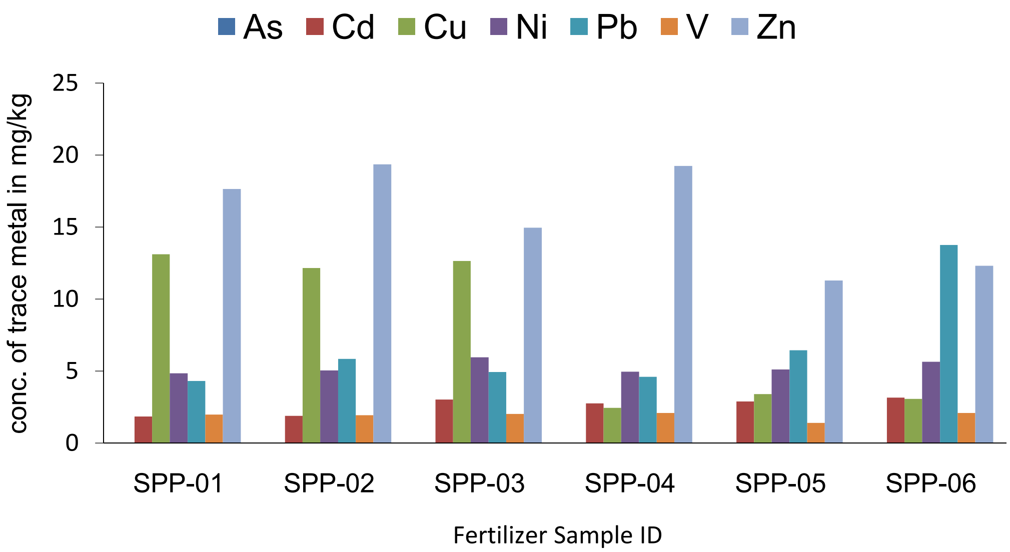

Fig. 1. Trace metal levels (mg/kg) in commercially available superphosphate fertilizer used in Nigeria

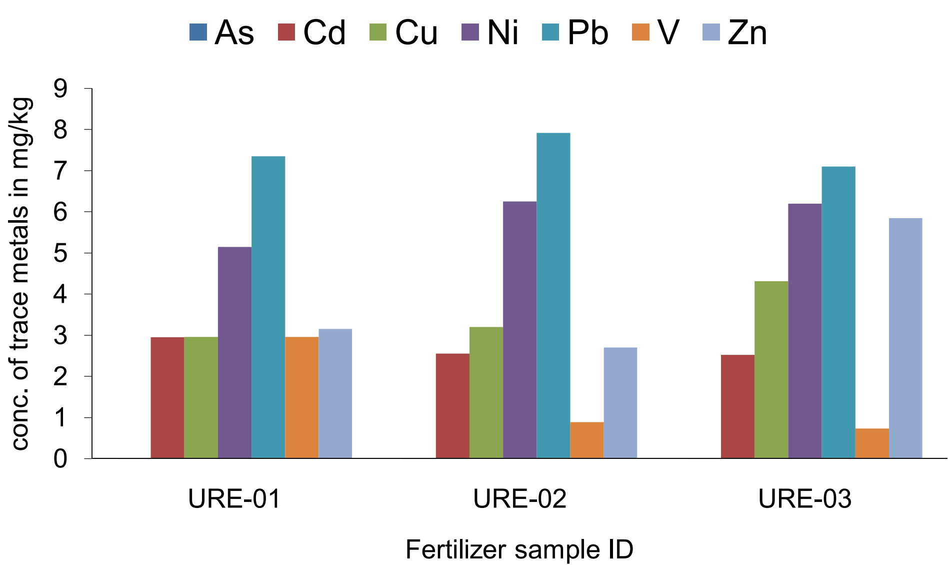

Fig. 2. Trace metal levels (mg/kg) in urea fertilizer used in Nigeria

Although, some trace elements such as Cu and Zn are essential to plant growth (micronutrients), they could be toxic to plants at high concentrations [23,27]. Trace elements such as Cd, Pb, Ni, As also have toxic effects on living organisms and are often considered as contaminants. In recent times, large-scale soil-trace metals pollution occurs primarily from repeated use of metal-enriched chemicals, fertilizers, and organic amendments such as sewage sludge as well as wastewater [3,14,15,23,24]. Most toxic metals are stored in the soil, usually attached to organic matter and clay. Once in the soil water, heavy metals may move within the soil profile are available to plants and can be leached into groundwater.

The potential risks originating from trace metals especially As and Cd accumulations in cropland soils through fertilizer applications and subsequent food-web accumulation have been of public concern [25]. Model simulation studies to evaluate the long-term fate and transport of As and Cd soils have shown that normal cropping practices do not have a significant effect on the total As content of the receiving soils [26], but the application of Cd-containing P fertilizers could, over time, cause Cd to accumulate in agrosystems and therefore increases the risk of its transfer through the food chain. The simulation outcomes indicated that some of the existing fertilizer regulations are not strict enough to prevent significant accumulation of Cd in cropland soils. Aside fears of ecotoxicity arising from application of trace metal-prone commercially available fertilizers, excessive salt and enhanced nutrient concentrations may accumulate and cropland soil quality may deteriorate [24].

Tables 2-3 show the Pearson product moment correlations between each pair of trace metal concentrations. These correlation coefficients ranged between -1 and +1 and measure the strength of the linear relationship between the variables. Each table highlights the associated *p*-value, which tests the statistical significance of the estimated correlations. More so, *p*-values below 0.05 indicate statistically significant non-zero correlations at the 95.0% confidence level.

Table 2. Correlation coefficients and their *p*-values (in parenthesis) between trace metals in

	Superphosphate fertilizer						
	As	**Cd**	**Cu**	**Ni**	**Pb**	**V**	**Zn**
As		0.13 (0.80)	-0.49 (0.32)	-0.34 (0.51)	-0.28 (0.59)	0.32 (0.54)	0.48 (0.33)
Cd			-0.64 (0.17)	0.69 (0.12)	0.51 (0.31)	-0.06 (0.90)	-0.69 (0.12)
Cu				0.05 (0.92)	-0.49 (0.33)	0.22 (0.67)	0.42 (0.41)
Ni					0.43 (0.39)	0.24 (0.65)	-0.51 (0.31)
Pb						0.12 (0.82)	-0.59 (0.22)
V							0.54 (0.27)
Zn							

Correlation (p-value)

Table 3. Correlation coefficients and their *p*-values (in parenthesis) between trace metals in

	Urea fertilizer						
	As	**Cd**	**Cu**	**Ni**	**Pb**	**V**	**Zn**
As		-0.44 (0.71)	-0.35 (0.77)	0.53 (0.64)	0.95 (0.19)	-0.44 (0.71)	-0.61 (0.58)
Cd			-0.68 (0.52)	-0.99 (0.07)	-0.16 (0.89)	1.00 (0.001)	-0.44 (0.71)
Cu				0.61 (0.59)	-0.61 (0.58)	-0.69 (0.52)	0.96 (0.19)
Ni					0.26 (0.83)	-0.99 (0.07)	0.34 (0.78)
Pb						-0.16 (0.89)	-0.82 (0.39)
V							-0.44 (0.71)
Zn							

Correlation (p-value)

A pair-wise linear correlations between trace metals in superphosphate fertilizer samples indicated positive but statistically insignificant (p = 0.05) relations between As and Cd (r = 0.13); As and V (r = 0.32); As and Zn (r = 0.48); Cd and Ni (r = 0.69); Cd and Pb (r = 0.51); Cu and Ni (r = 0.05); Cu and V (r = 0.22); Cu and Zn (r = 0.42); Ni and Pb (r = 0.43); Ni and V (r = 0.24); Pb and V (r = 0.12); V and Zn (r = 0.54); and negatively insignificant (p = 0.05) correlations between As and Cu (r = -0.49); As and Ni (r = -0.34); As and Pb (r = -0.28); Cd and Cu (r = -0.64); Cd and V (r = -0.06); Cd and Zn (r = -0.69); Cu and Pb (r = -0.49); Ni and Zn (r = -0.51); Pb and Zn (r = -0.59) (Table 2). In general, the pair-wise correlation analyses showed that there were no pairs of variables that recorded p-value below 0.05 in superphosphate fertilizer samples. Therefore, there were statistically insignificant correlations at the 95.0% confidence level between pairs of trace metals levels.

However, in urea fertilizer samples, the correlation coefficients ranged mostly between -0.99 and 1.00 (Table 3). Statistically insignificant (p = 0.05) but positive correlations were found between As and Ni (r = 0.53); As and Pb (r = 0.95); Cu and Ni (r=0.61); Cu and Zn (r=0.96); Ni and Pb (r = 0.26); and, Ni and Zn (r=0.34). More so, negatively insignificant relations were obtained for As and Cd (r = -0.44); As and Cu (r = -0.35); As and V (r = -0.44); As and Zn (r = -0.61); Cd and Cu (r = -0.68); Cd and V (r = -0.99); Cd and Pb (r = -0.16); Cd and Zn (r = -0.44); Cu and Pb (r = -0.61); Cu and V (r=-0.69); Ni and V (r=-0.99); Pb and V (r = -0.16); Pb and Zn (r = -0.82); V and Zn (r=-0.44) (Table 3). Comparatively, the pair-wise correlations were generally negative, implying inverse relations between pairs of trace metals. However, there was a perfect relationship between Cd and V in urea samples. The result highlighted that Cd and V had p-value (p=0.001) below 0.05, indicating statistically significant correlation (r=1.00) at 95.0% confidence level.

the trace metals in imported inorganic fertilizers commercially available for farming in Nigeria has confirmed that fertilizer is a notable source of toxic trace metal impurities, and most importantly a source of exposure to the general population through ingestion of farm produce and contaminated soil.

Table 4. Fertilizer trace metal standards applicable in some countries in the world

Metal	China	Canada	Australia					Japan
	mg/kg Fertilizer	mg/kg dw Maximum acceptable metal concentration	mg/kg P P fertilizers	mg/kg product Non-P fertilizers	mg/kg product Fertilizers wholly constituted by micro-nutrients	mg/kg All fertilizers and micro-nutrients	mg/kg Major nutrient fertilizer with micro- nutrients	mg/kg in by-product phosphate fertilizers
As	50	75	-	-	-	-	-	50
Cd	8	20	300	10	50	-	-	8
Cu	-	-	-	-	-	-	-	-
Ni	-	180	-	-	-	-	-	-
Pb	100	500	-	-	-	-	500	100
V	-	-	-	-	-	-	-	-
Zn	-	1850	-	-	-	-	-	-

4. CONCLUSION

This study provided a new data for the agriculture and health authorities in Nigeria such as the Ministry of Agriculture, Ministry of Environment and the Ministry of Health. The results of In Nigeria, there are no federal or state limits on trace metal contaminants that are generally applied to imported and locally manufactured inorganic fertilizers. However, the trace metal concentrations in commercially available urea and superphosphate fertilizers marketed in Nigeria were within the allowable limits based on the Chinese, Canadian, Australian and Japanese standards (Table 4). Zinc was found present in extremely high concentration in both urea and phosphate fertilizer samples. Arsenic on the other hand, was found in relatively low concentrations in all analyzed fertilizers. The present research has revealed that superphosphate fertilizer marketed in Nigeria has high concentrations of Cu, V and Zn as impurities while urea fertilizer recorded slightly significant concentrations of Ni, Pb and Cd. However, elevated levels of toxic metals in inorganic fertilizers demand continuous evaluation and monitoring from an environmental and public health standpoint.

Mineral fertilizers could act as sources of diffuse metal enrichment of agricultural soils especially from phosphate fertilizers. Enhanced trace metals in inorganic fertilizers and other agrosystem inputs may constitute potential threat to the sustainability of farming practices. Therefore, regulations should be enacted to set the maximum contaminant levels for trace elements in fertilizers imported and locally produced in Nigeria. In addition, reduction of trace metals inputs to agricultural soils should be a strategic aim of soil protection policies.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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