



## Effect of fertilizer amendment on the levels of heavy and essential metals in the rice grains harvested from soils in Ishiagu, Ebonyi State

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### Abstract

Studies were carried out to evaluate the effect of fertilizer amendment on the heavy and essential metal levels in the rice grains harvested from the upland and lowland soils in Ishiagu, Ivo Local Government Area of Ebonyi State, using standard analytical procedures and instrumentation. The rice grain samples were digested in accordance with the standard procedures, hence, eight elements (Cr, Ni, Mn, Cd, Pb, Na, K and Mg) were assayed in the atomic absorption spectrophotometer to determine their concentrations.

Rice grain samples harvested from the lowland soils D<sub>1-4</sub> had mean range of 0.088-0.417, 0.225- 0.750, 0.270- 0.667, 2.025-3.696, 0.031- 0.073, 0.242 – 0.379, 0.508 -0.585 and 0.415 – 0.606 µg/g for Cr, Pb, Ni, Mn, Cd, Na, K and Mg respectively. Equally, rice grain samples harvested from the upland soils D<sub>1-4</sub> had mean range of 0.071- 0.102, 0.104 -0.273, 0.202 -0.261, 1.850–2.881, 0.028 -0.044, 0.323 -0.411, 0.967 – 1.117 and 0.950- 1.099 µg/g for Cr, Pb, Ni, Mn, Cd, Na, K and Mg respectively.

The result of the metal analysis of rice grain samples harvested from both the lowland and upland soils showed that the amendment with NPK at various weights significantly influenced the levels of the studied metals in the grain samples. In fact, it was observed that increase in the amendment of the soils with NPK increased the levels of the investigated metals in the harvested rice grain samples.

The studied metals were within their respective threshold limits in the harvested rice grain samples from both the upland and lowland soils, with the exception of Pb in the rice grain samples harvested from the lowland soil sample D<sub>4</sub> (with 150kg of NPK amendment).

Since this research has shown that both the essential and heavy metals increases their presence in harvested agricultural produce (in this case rice grains) with increase in amendment with inorganic fertilizer (NPK), the relevant authorities enforcing the implementation of integrated farming practices, should mount serious campaign in both the conventional and traditional media to discourage farmers from indiscriminate application of chemical fertilizers on the soil, in order to limit the dietary exposure to toxic heavy metals by food consumers of food crops produced through such practice.

**Keywords:** essential elements, heavy metals, upland soil, lowland soil, NPK fertilizer and soil amendment

### Introduction

Many soils especially in West Africa, show nutrient deficiency problem due to consistent farming and prevailing environmental factors (Padwick, 2013) [14]. Okeke *et al.*, (2019) [3], observed that farmers in a bid to improve yield sought to apply both organic and inorganic fertilizers to supplement the one supplied by the natural environment. Maintenance of the fertility status of the soil is a critical factor in ensuring a stable and sustainable agro-ecosystem. Kumar *et al.*, (2019) [7], stated that fertilizers can significantly enhance crop yield but also can damage the soil nutrient balance and cause environmental pollution. During fertilizer production, especially inorganic fertilizers, various amounts of heavy metals are present as impurities and when these fertilizers are applied to the soil affects the food chain.

Environmental pollution due to heavy metals have increased exponentially in recent times and have reached alarming levels in terms of effect on living creatures (Ezeh *et al.*,

2019) [3]. Metals such as Fe, Cu, Zn, Co, Na, K, Mg and Mn are nutritionally essential for a healthy life, however, where-as large amount of some of them like Fe, Cu, Zn and Mn may cause acute poisoning; similarly, heavy metals like As, Cd, Pb, Hg, Cr and Ni are of no human importance in human biochemistry and physiology and their consumption even at low concentrations can be toxic (Okeke *et al.*, 2019; Okeke *et al.*, 2020; Okeke *et al.*, 2020) [9]. Evidence of heavy metal contamination of agricultural soils and the uptake by living organisms through food chain and the eventual toxicity effects to body tissues and organs are well documented (Okeke *et al.*, 2020). Heavy metals are significant environmental pollutants and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons (Jaishanakar *et al.*, 2014) [6]. The presence of heavy metals in the environment poses a potential health risk because of their mutagenic, carcinogenic and reproductive toxicant effects (Naz *et al.*, 2022) [8].

Rice is an important annual crop and the most consumed staple food in Nigeria, with an average Nigerian consuming about 488kg of rice per year (Ihedioha *et al.*, 2013) [4]. According to Okeke *et al.*, (2020), due to environmental problems associated with rice farming in Ishiagu, Ivo Local Government Area of Ebonyi State, farmers resort to the use of inorganic fertility, particularly to increase yield and quality of the grains. These farmers apply fertilizers on the soils and negates the integrated farming practice of moderate application. Because metals are bio accumulative, their presence in the fertilizers as impurities enhances their loads in the soil and crops grown there-in. Farmers are concerned about yield but do not consider the effect of practices such as undue fertilizer application on the environment, nutrient status and the health safety of food crops harvested from such activity. Studies was therefore done to evaluate the effect of amendment with NPK on the levels of heavy and essential metals in rice grains harvested from upland and lowland soils in Ishiagu, Ebonyi State.

## Materials and Methods

### Sample collection and preparation

Harvested rice grain samples from the upland and lowland soils D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub> and D<sub>4</sub> were collected separately in well labeled sacs.

The samples were washed with distilled water to remove stuck soil particles on the husk. They were subsequently separated from the husk using pestle and mortar and winnowed with tray pan. The polished rice samples (without husk) were bagged separately in clean polyethylene bags and stored in a dry environment until metal analysis.

### Essential and heavy metals' determination

The rice grain samples were digested using 5ml of 65% HNO<sub>3</sub> and 70% HClO<sub>4</sub> in the ratio of 2:3 at a temperature of 70°C for 180min. The digest was diluted with de-ionized water and made up to mark with 50ml of standard volumetric flask and stored in labeled polyethylene containers until analysis. All samples were prepared identically in triplicates.

Blanks were prepared to check for background contamination from the reagents used. The heavy metals (Cr, Pb, Ni, Mn and Cd) were determined in the sample using atomic absorption spectrophotometer (AAS) (model Elico El- 194).

The essential elements (K, Na and Mg) were determined using flame photometer.

Statistical Analysis: The obtained data were represented in mean ± standard deviation and subjected to one way analysis of variance (ANOVA) at 5% confidence level using IBM SPSS 22.0.

## Results and discussion

**Table 1:** Mean essential and heavy metal levels in the rice grain samples harvested from the lowland soils

Metal(μg/g)	Metal concentration in the harvested rice grain samples from the lowland soils D <sub>1</sub> D <sub>2</sub> D <sub>3</sub> D <sub>4</sub>				WHO Standard (2014)	F test P value
	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>	D <sub>4</sub>		
Cr	0.086±0.010	0.145±0.026	0.145±0.030	0.417±0.116	100	0.02
Pb	0.225±0.040	0.334±0.070	0.325±0.070	0.750±0.187	0.5	0.01
Ni	0.270±0.011	0.370±0.069	0.370±0.050	0.667±0.106	50	0.02
Mn	2.025±0.321	3.842±0.459	3.976±0.100	3.696±0.500	500	0.02
Cd	0.030±0.000	0.054±0.001	0.067±0.001	0.073±0.020	0.5	0.01
Na	0.242±0.061	0.263±0.070	0.283±0.071	0.379±0.049	-	0.02
K	0.508±0.061	0.562±0.024	0.577±0.033	0.585±0.012	-	0.01
Mg	0.415±0.022	0.456±0.012	0.606±0.831	0.595±0.014	-	0.01

Where D<sub>1</sub>=control; D<sub>2</sub>= 50kg NPK amendment; D<sub>3</sub> = 100kg NPK amendment; D<sub>4</sub>= 150kg NPK amendment

**Table 2:** Mean essential and heavy metals in the rice grains harvested from the upland soils

Metal(μg/g)	Metal concentration in the harvested rice grain samples from the upland soils D <sub>1</sub> D <sub>2</sub> D <sub>3</sub> D <sub>4</sub>				WHO Standard (2011)	F test P value
	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>	D <sub>4</sub>		
Cr	0.071±0.010	0.093±0.010	0.145±0.030	0.101±0.021	100	0.01
Pb	0.104±0.031	0.221±0.011	0.242±0.022	0.273±0.010	0.5	0.02
Ni	0.202±0.031	0.261±0.044	0.251±0.022	0.211±0.033	50	0.01
Mn	1.850±0.212	2.571±0.360	2.881±0.244	2.280±0.030	500	0.02
Cd	0.028±0.000	0.033±0.012	0.042±0.011	0.044±0.010	0.5	0.01
Na	0.335±0.002	0.323±0.040	0.403±0.044	0.411±0.037	-	0.02
K	0.967±0.022	1.004±0.131	1.117±0.044	1.037±0.051	-	0.02
Mg	0.950±0.141	1.021±0.022	1.091±0.033	1.091±0.041	-	0.01

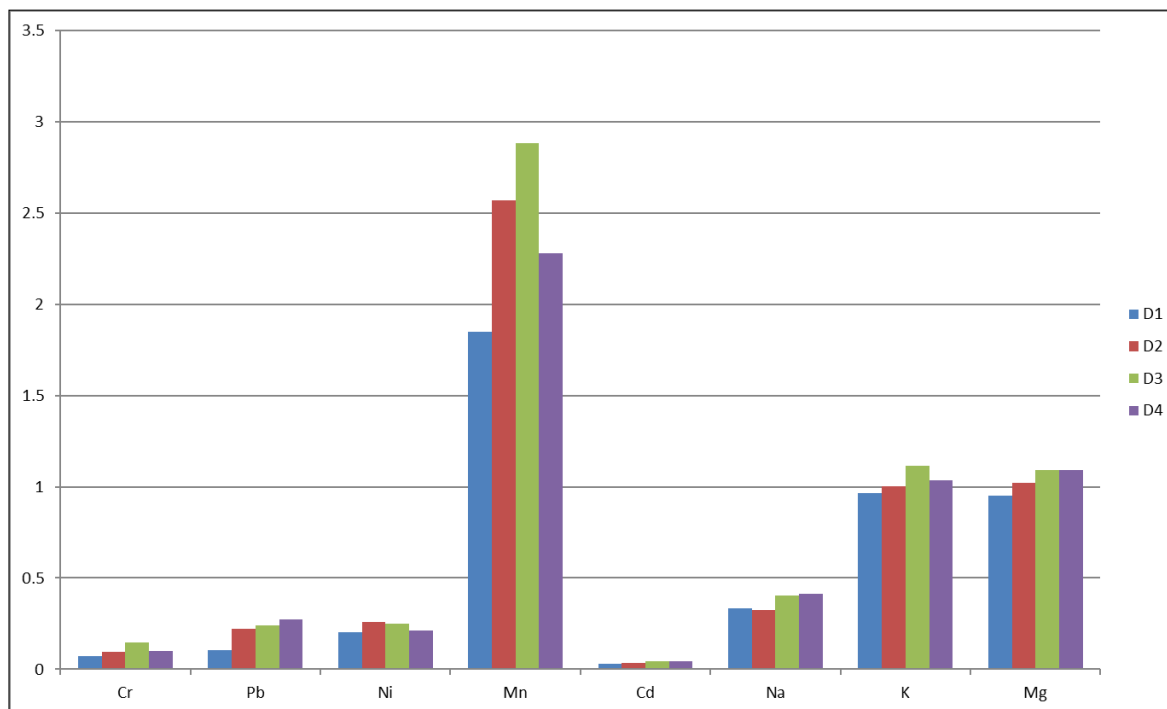
Where D<sub>1</sub>=control; D<sub>2</sub>= 50kg NPK amendment; D<sub>3</sub> = 100kg NPK amendment; D<sub>4</sub>= 150kg NPK amendment

### Chromium

Result of Table 1 shows that the mean Cr levels in the harvested grain samples from the lowland soils D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub> and D<sub>4</sub> were 0.086±0.010, 0.145±0.026, 0.145±0.030 and 0.417± 0.116 μg/g respectively. The result shows a significant (p<0.05) increase in the Cr levels in the grain samples as the amendment of lowland soils increased from 0 to 150kg of NPK. The mean Cr levels in the rice grain samples harvested from lowland soils were within the

metal's recommended threshold limits as shown in Table 1.

Result of Table 2 shows that the mean Cr levels in the rice grain samples harvested from the upland soils D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub> and D<sub>4</sub> were 0.071±0.010, 0.093±0.010, 0.101±0.021 and 0.102±0.023 μg/g respectively. Just as observed for Cr levels in the rice grain samples harvested from the lowland soils, the amendment of the upland soils significantly enhanced the Cr level in the harvested grain samples as shown in Figure 1.



**Fig 1:** Bar chart representation of the essential and heavy metal levels in the harvested rice grain samples from the upland soils

Hence, increase in the NPK amendment of the upland soils from 0 to 150 kg, increased the Cr availability in the soils for uptake. Also, the mean Cr levels of the rice grain samples harvested from the upland soils were within the permissible limits. Okeke *et al.*, (2018)<sup>[11]</sup>, reported a higher mean Cr level of  $0.285 \pm 0.07$  in the millet grains harvested in an inorganic fertilizer amended soil in Ayamelu Local Government Area of Anambra State, than what this study recorded for Cr in the harvested rice grain samples from the upland and lowland soils. Exposure to higher levels of chromium compounds in humans can lead to the inhibition of erythrocytes glutathione reductase, which in turn lowers the capacity to reduce methemoglobin (Jaishnakar *et al.*, 2014; Okeke *et al.*, 2020)

### Lead

Result of Table 1 shows that the mean Pb levels in the rice grains harvested from the lowland soils D1, D2, D3 and D4 were  $0.225 \pm 0.040$ ,  $0.334 \pm 0.070$ ,  $0.325 \pm 0.070$  and  $0.750 \pm 0.184$   $\mu\text{g/g}$  respectively. Rice grain samples harvested from lowland soil D4 had the highest mean Pb level, suggesting therefore a significant impact of increased amendment with NPK on the availability of heavy metals in the soils for uptake. This rice grain samples (from lowland soil D4) was therefore above Pb's permissible limits as against the rice grain samples harvested from the other studied upland soils that had mean Pb within the threshold limits. This result is significant in the sense that many farmers usually indulge in increased fertilizer application especially in less fertile soils to boost yield but are ignorant of the increased heavy metal exposure to food consumers, who consume food harvests from such practice.

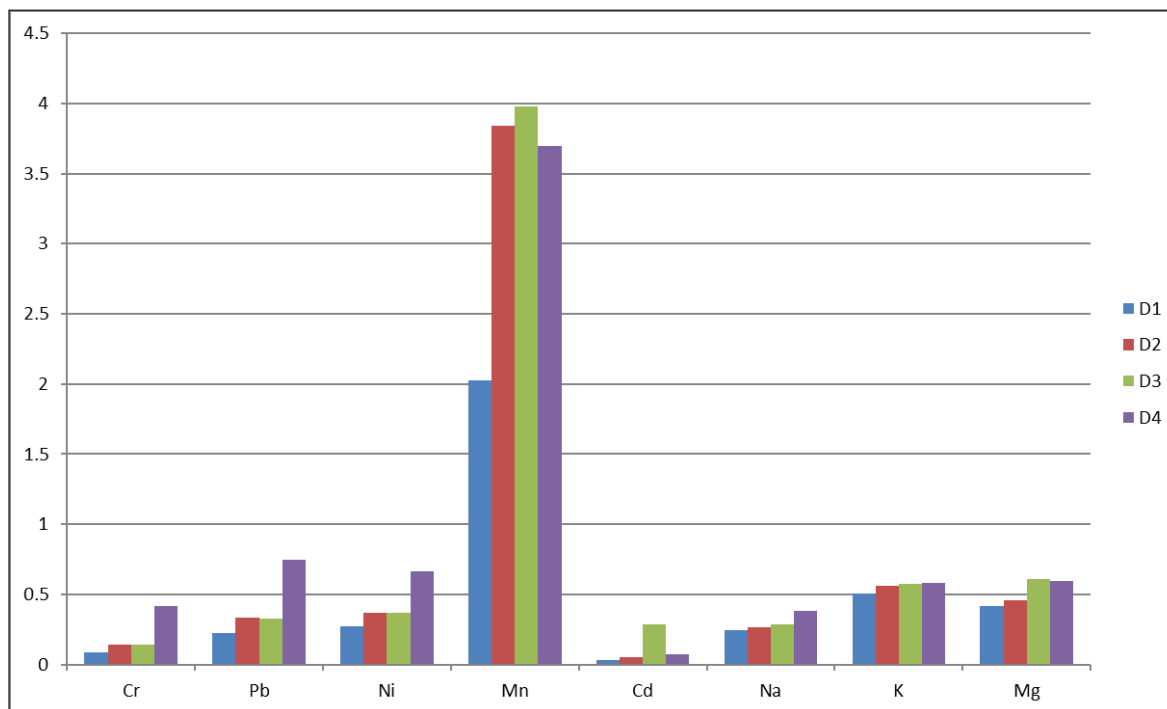
Result of Table 2 shows that the mean Pb levels in the rice grain samples harvested from the upland soils D1, D2, D3 and D4 were  $0.104 \pm 0.031$ ,  $0.221 \pm 0.011$ ,  $0.242 \pm 0.022$  and  $0.273 \pm 0.010$   $\mu\text{g/g}$  respectively. This result indicates a significant ( $p < 0.05$ ) increase in Pb levels in the rice grain

sample as the amendment of the upland soils were increased. The metal was within the permissible limits in the rice grain samples harvested from the upland soils. Comparing result of Tables 1 and 2 shows a significant higher mean Pb levels in the rice grain samples harvested from the lowland soils than the metal's level in the rice grain samples from the upland soils (as seen in Figures 1 and 2) and thus, this observation was supported by the findings of Aniobi *et al.*, (2022)<sup>[1]</sup>, who reported that the slow transport, mobility and consequently high retention of persistent pollutants such as Pb in the lowland soil areas accounted for the higher availability of such metals in crops harvested there-in than it can be found in crops harvested from upland soil areas. According to Oyareme *et al.*, (2021), Pb is a harmful body poison that can enter the human body system through air, water and food and cannot be eliminated by fruits and vegetable washing.

### Nickel

Result of Table 1 shows that the mean Ni levels in the rice grain samples harvested from the lowland soils D1, D2, D3 and D4 were  $0.270 \pm 0.011$ ,  $0.370 \pm 0.069$ ,  $0.375 \pm 0.050$  and  $0.667 \pm 0.106$   $\mu\text{g/g}$  respectively. The mean Ni levels in the grain samples were significantly ( $p < 0.05$ ) influenced by the various weight amendments with NPK on the lowland soils. Soil D4 with the highest weight amendment had a significantly higher mean Ni levels in the harvested rice grain samples than Ni levels in the rice grain samples harvested from the other studied lowland soils as shown in Figure 2.

Result of Table 2 shows that the mean Ni levels in the rice grain samples harvested from the upland soils D1, D2, D3 and D4 were  $0.202 \pm 0.031$ ,  $0.261 \pm 0.044$ ,  $0.251 \pm 0.022$  and  $0.211 \pm 0.033$   $\mu\text{g/g}$  respectively. It can be observed from this result that the amendment with NPK at upland soils D<sub>2-3</sub> significantly enhanced the mean Ni levels in the harvested rice grain samples from the soils as shown in Figure 1



**Fig 2:** Bar chart representation of the essential and heavy metal levels in the harvested rice grain samples from the lowland soils

Although increase in NPK application on the upland soils from 0 to 150kg led to an increase in the Ni levels in the harvested grain samples, it was however not even and regular, which could be due to leaching and run-off effects in the soils. The mean Ni levels in the grain samples harvested from both the upland and lowland soils were within the threshold limits.

### Manganese

Result of Table 2 shows that the mean Mn levels in the harvested rice grain samples from the lowland soils D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub> and D<sub>4</sub> were  $2.025 \pm 0.321$ ,  $3.842 \pm 0.459$ ,  $3.976 \pm 0.100$  and  $3.696 \pm 0.500 \mu\text{g/g}$  respectively. The above result showed a significant increase in the mean Mn values in the rice grain samples as the amendment with NPK was increased on the soils (D<sub>2</sub> → D<sub>4</sub>). Although Mn is not a major elemental composition of NPK fertilizer, its strong presence in the grain samples from the incremental application suggests its contamination of the production process as an impurity. The mean Mn levels in the rice grain samples harvested from the lowland soils were within the permissible limits. Result of Table 2 shows that the mean Mn levels in the rice grain samples harvested from the upland soils D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub> and D<sub>4</sub> were  $1.850 \pm 0.212$ ,  $2.571 \pm 0.360$ ,  $2.881 \pm 0.244$  and  $2.280 \pm 0.030 \mu\text{g/g}$  respectively. The weight amendments with NPK on the upland soils significantly increased the mean Mn levels in the harvested rice grain samples although without following a consistent trajectory, however, the metal's mean levels in the harvested grain samples were within the permissible limits. Undue exposure to manganese could result to a medical condition called manganism, which resemble Parkinson disease (Sitarz-Palezak and Kalemekiewicz, 2012; Okeke *et al.*, 2020).

### Cadmium

Result of Table 1 shows that the mean Cd levels in the rice grain samples harvested from the lowland soils D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub> and D<sub>4</sub> were  $0.030 \pm 0.000$ ,  $0.054 \pm 0.001$ ,  $0.067 \pm 0.001$  and

$0.073 \pm 0.002 \mu\text{g/g}$  respectively. The result of this study shows a significant ( $p < 0.05$ ) increase in Cd levels in the rice grain samples on increased amendment of the soils with NPK. Cd is a well-known impurity in inorganic fertilizer manufacture, therefore its strong showing in the harvested rice grain samples from the amended lowland soils was expected. Cadmium is a toxic heavy metal even at low concentrations, however, was within the permissible limits in the harvested rice grain samples from the lowland soils.

Result of Table 2 shows that the mean Cd levels in the harvested rice grain samples from the upland soils D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub> and D<sub>4</sub> were  $0.028 \pm 0.000$ ,  $0.033 \pm 0.010$ ,  $0.042 \pm 0.011$  and  $0.044 \pm 0.010 \mu\text{g/g}$  respectively. Just as observed for the Cd result in Table 1, increased amendment of the upland soils with NPK significantly ( $p < 0.05$ ) increased the Cd level in the harvested rice grain samples as seen in Figure 1. The mean Cd levels in the harvested rice grain samples from the upland soils were within the permissible limits. Although this observation is a cheering news to food consumers, the toxicity of Cd is such that at any concentration in a food substance exerts some toxicity effects over a long period of exposure. According to Irfan *et al.*, (2013)<sup>[5]</sup>; Aniobi *et al.*, (2021)<sup>[2]</sup>, Cd exerts adverse effects on the enzymatic system cells, induces oxidative stress and damages the kidney and liver.

### Sodium

Result of Table 1 shows that the mean Na levels in the rice grain samples harvested from the lowland soils D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub> and D<sub>4</sub> were  $0.242 \pm 0.061$ ,  $0.263 \pm 0.070$ ,  $0.283 \pm 0.071$  and  $0.379 \pm 0.049 \mu\text{g/g}$  respectively. This result indicates that the gradual increase in the amendment of the lowland soils with NPK significantly led to a higher mean Na levels observed in the harvested rice grain samples. This implies that increase in soil amendment with NPK increases the availability of Na in the soil for uptake and storage in vital plant parts. Result of Table 2 shows that the mean Na levels in the harvested rice grain samples from the upland soils D<sub>1</sub>,

D<sub>2</sub>, D<sub>3</sub> and D<sub>4</sub> were 0.335±0.002, 0.323±0.040, 0.403±0.044 and 0.411±0.037µg/g respectively. The result of Table 2 indicates that the increased amendment of the upland soils especially at D<sub>3</sub> and D<sub>4</sub> led to a significantly (p< 0.05) enhanced Na levels in the harvested rice grain samples as shown in Figure 1. Sodium is a macro-element, very essential for the body's biochemical and enzymatic optimum function and is therefore very welcoming that amendment of soils with NPK could increase its availability for plants uptake, optimum growth and yield.

### Potassium

Result of Table 1 shows that the mean K levels in the harvested rice grain samples from the lowland soils D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub> and D<sub>4</sub> were 0.508±0.061, 0.562±0.024, 0.577±0.033 and 0.585±0.012 µg/g respectively. It can be observed that increase in amendment of the lowland soils with NPK, significantly led to a steady increase in the mean K values in the harvested rice grain samples as shown in Figure 2. Potassium is an important element required by both plant and animals alike and it is of optimum biological and physiological importance. Result of Table 2 shows that the mean K values in the harvested rice grain samples from the upland soils D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub> and D<sub>4</sub> were 0.967±0.141, 1.004±0.131, 1.117±0.044 and 1.037±0.051µg/g respectively. It can be observed from the above result that the various weight amendment of the upland soils with NPK, significantly enhanced the availability of K in the soils for uptake and consequently more presence in the harvested grain samples.

### Magnesium

Result of Table 1 shows that the mean Mg levels in the harvested rice grain samples from the lowland soils D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub> and D<sub>4</sub> were 0.415±0.022, 0.456±0.012, 0.606±0.031 and 0.595±0.014µg/g respectively. Rice grain samples harvested from higher NPK amendment at soils D<sub>3</sub> and D<sub>4</sub> were significantly higher in mean Mg values than it was obtained for the element in the rice grain samples harvested at soils D<sub>1</sub> and D<sub>2</sub> as shown in Figure 2. Result of Table 2 shows that the mean Mg levels in the harvested rice grain samples from the upland soils D<sub>1</sub>, D<sub>2</sub>, D<sub>3</sub> and D<sub>4</sub> were 0.950±0.141, 1.021±0.022, 1.099±0.033 and 1.091±0.041 µg/g respectively. Just as observed for Mg in the rice grain samples harvested from the lowland soils, the result of Table 2 gave similar result trend because increased amendment with NPK on the upland soils led to a significantly higher presence of Mg in the harvested grain samples. Just as stated for Na and K; the essentiality of Mg to the healthy growth and development of plants as well as animals cannot be over emphasized.

### Conclusion

After the various weight amendments with NPK on both the upland and lowland soils, the harvested rice grain samples from the soils had the investigated metals (Cr, Pb, Ni, Mn, Cd, Na, K and Mg) within the detection limits. Increased amendment of the soils with NPK led to a significant increase in the mean levels of the investigated metals in the harvested rice grain samples.

For the heavy metals (Cr, Pb, Ni, Mn and Cd), increased amendment of the soils with NPK, significantly increased their levels in the harvested rice grain samples. With the exception of Pb in the rice grain samples harvested from the

highest amended lowland soil (soil D<sub>4</sub>), the mean levels of the studied heavy metals in the harvested rice grain samples from the upland and lowland soils were within their respective threshold limits. Because of the topography of the lowland soil surface, the studied metals were significantly more present in the rice grain samples harvested there-in than they were in the rice grains harvested from the upland soils.

Similar observations were made with the studied essential elements (Na, K and Mg) in the harvested rice grain samples from both the upland and lowland soils.

Therefore, in the quest to boost the fertility, growth and yield of staple crops such as rice in less fertile soils, undue application of chemical fertilizer should be discouraged and farmers should be educated on the right volume of fertilizer to apply on any soil so that while optimum yield would be sustained, the food risk of such agricultural produce due to excessive exposure to hazardous metals would be minimized.

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