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EFFECTS OF NPK FERTILIZERS ON TRACE METALS LOADS IN SOIL AND VEGETABLES, BIOAVAILABILITY IN VEGETABLES AND THE RELATED HEALTH RISK USING SIMULATION TECHNIQUES

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ABSTRACT

The impact of inorganic fertilizers on the accumulation of trace metals in surface soil, *Telfairia occidentalis, Talinum triangulare, Spinacia oleracea*, and *Amaranthus viridis* using Plot experiment was carried out in this study. Four experimental plots were prepared, the pre-fertilization soil samples were collected before the cultivation of these vegetables. Twelve weeks after, the pre-fertilization vegetable samples were also obtained. NPK fertilizers were applied to the different plots and six months after the post-fertilization soil and vegetable samples were obtained from each plot. The different plots were irrigated during the pre and post-fertilization periods with distilled water using the sprinkling method. The different fertilizers used and the samples obtained were treated using standard analytical techniques and analyzed for their Cd, Cu, Ni, Pb, Zn, and Cr content using Unicam 969 spectrophotometer. Results obtained showed the following mean concentrations ($mgkg^{-1}$) for Cd, Cu, Ni, Pb, Zn, and Cr in the fertilizers: 2.72±0.48, 6.56±0.61, 9.58±0.86, 7.88±0.55, 14.56±1.40, and 2.23±0.14, respectively. The results revealed relatively higher concentrations of these metals in the post-fertilization than in the pre-fertilization samples for both the soil and vegetables. The transfer factor of each of the trace metals was less than one. It was also realized that, the plots were heavily contaminated with trace metals using different environmental pollution models. *Telfairia occidentalis* and *Talinum triangulare* displayed very high potentials for absorbing these metals from the fertilizers-impacted soil. The principal component analysis identified two and three major factors for the accumulation of metals in soil and vegetables, respectively. Results of health risk analysis indicated that, Cd, Pb, and Ni levels in the vegetables were higher than their recommended oral reference limits. It was also observed that, the consumers of these vegetables may be affected by Cd and Pb toxicity and the children population was more vulnerable. Accordingly, the study has shown the effect of inorganic fertilizers on the buildup of trace metals in soil and vegetables. The pollution status of the fertilizers-impacted soil and the health risk associated with the exposure to the studied vegetables were also revealed.

Keyword: Bioaccumulation, inorganic fertilizer, *Telfairia occidentalis. Health risk, Talinum triangulare*

INTRODUCTION

The application of agrochemicals such as pesticides, herbicides, fungicides, fertilizers, and animal feeds to improve outputs by farmers is now a global practice. However, these chemicals have some negative impact on the quality of the soil and plants cultivated with regards to the accumulation of toxic substances (Benson *et al*., 2014; Orisakwe *et al*., 2017). These toxic substances are eventually transferred to human beings either through the consumption of plants cultivated on the polluted environment or exposure to soil particles (Kumar and Kothiyal, 2011; Orhuamen *et al*., 2012). According to Danjuma and Abdulkadir (2008) leafy vegetables have great potential for the accumulation of toxic metals from polluted environment into their tissues. Studies have shown that inorganic fertilizers have high levels of toxic metals such as cadmium cadmium, arsenic, lead, mercury etc (Oyedele *et al*., 2006; Ukpabi *et al*., 2012; Ebong *et al*., 2020).

Studies have shown that, the consumption of vegetables cultivated in polluted environment may result in serious health problems in the consumers irrespective of the age (Rai *et al*., 2019; Manwani *et al*., 2021). Trace metals are toxic at concentrations higher than their recommended limits and the toxic ones are not useful to living organisms including human even at very low concentrations (Jaishankar *et al*., 2014; Balali-Mood *et al*., 2021). The quantity of metals supplied by inorganic fertilizers to the soil and transferred to vegetables could be determined using the transfer factor (Taha *et al*., 2013). These leafy vegetables namely: *Telfairia occidentalis*, *Talinum triangulare*, *Spinacia oleracea*, and *Amaranthus viridis* were chosen because they are widely cultivated and consumed in Akwa Ibom State and Nigeria (Orhuamen, 2012; Uwah, 2017). Inorganic fertilizers (NPK) were also employed for this study due to their intensive applications in farms within the study area (Saweda *et al*., 2010).

Previous works concentrated mostly on the determination of trace and toxic metals in fertilizers used in Nigeria (Ogabiela *et al*., 2009; Ukpabi *et al*., 2012). Other Researchers concentrated on the concentration of trace metals in vegetables cultivated on fertilizers-impacted soils (Etuk *et al*., 2022). This study has investigated the levels of trace metals in soil and the studied vegetables during the pre and post-fertilization periods. The work has also evaluated the quantity of trace metals transferred from soil to the vegetables. Invariably, the work has estimated the amount of trace metals supplied to the soil and the studied vegetables.

The aim of this study was to evaluate the quantity of trace metals added to the soil by the different inorganic fertilizers and the amount absorbed by the studied vegetables. The study also aimed at assessing the potential of each of the studied vegetables for accumulating these metals for the purpose of bioremediation. It also aimed at assessing the associated health implications of these metals on the children and adults' consumers. The pollution status of the soil during the post- fertilization period and the metals was determined. Consequently, the study has closed the gaps created by the previous studies. The outcome of this study will useful to the Environmental Scientists, manufacturers of fertilizers, the farmers and the consumers of vegetables cultivated on fertilizer-impacted soil.

MATERIALS AND METHODS

Study Area

The plot experiment was conducted in Abak local government area of Akwa Ibom State, Nigeria between November, 2019 and April, 2020. The experiment was carried out during the dry season of the study area to avoid leaching of contaminants in the soil by rainwater during the wet season. Abak is the headquarters of Abak local government and it lies between latitude 5° 02ˡ N and longitude 7° 76ˡE of Nigeria. Abak is located in the humid tropics and has abundant rainfall with very high temperature. The average yearly temperature is between 25°C and 29°C, while the average yearly rainfall varies between 2000 mm to 3000 mm (Ekpenyong, 2012). The yearly evaporation rate of Abak varies from 1500 mm to 1800 mm (Afangideh *et al*., 2005).

Fertilizer collection, treatment, and analysis

Inorganic fertilizers with different NPK percentages by weight namely: NPK 20:10:10, NPK 15:15:15, NPK 20: 5: 10 and NPK 12:12:17 were purchased from Uyo main market (Akpan Andem). Two gram of each fertilizer was weighed into a beaker containing 20ml of Conc, HNO_3 and 10ml of Conc. $HClO_4$, and then digested on a hot plate. The mixture was later evaporated to dryness and the residue was mixed with 10ml 2M HCl, filtered into a 100ml flask and made to mark with deionized water. The concentration of Cd, Cu, Ni, Pb, Zn, and Cr were obtained from the filtrates using Unicam 969 spectrophotometer.

Soil Preparations, cultivation of vegetables, treatment and analysis

An experimental farmland was properly prepared in a natural soil environment and divided into four different plots at a size of 8×8 feet each. The pre-fertilization soil samples were obtained immediately after land preparation at a depth of 0-15 cm using soil Augar. Leafy vegetables namely: *Telfairia occidentalis* (Fluted pumpkin), *Talinum triangulare* (Water leaf), *Spinacia oleracea* (Spinach), *Amaranthus viridis* (Green amaranth) were cultivated in each of the plots. Twelve weeks after the pre-fertilization vegetable samples were obtained using stainless-steel knife. After which a mixture of the four different NPK fertilizers in the proportion of 5g each was applied to the various plots by the broadcasting method. The post-fertilization soil and vegetable samples were obtained six months after with the same methods used for the collection of pre-fertilization samples. These plots were irrigated with distilled water three times a week during the pre and post-fertilization periods using the sprinkling technique. Soil samples collected were dried under the sun for three days, homogenized and sieved. One gram of the sieved soil sample was digested with a mixture of 3:1 HCl and HNO_3 on a hot plate. Vegetables collected were washed first with tap water and later on with distilled water. The samples were air dried, reduced into smaller pieces, and dried at 60 ºC for a day in an oven. The dried sample (1g) was ground and homogenized then,, one gram of the sieved sample was digested with Aqua regia on a hot plate. Concentrations of analyzed metals in the soil and vegetables samples were obtained using Unicam 969 spectrophotometer.

Pollution status of the studied soil at the different locations

Metal pollution index (MPI)

Metal pollution index was employed to assess the relationship between trace metals in the soil during the pre and post fertilization periods (Lacatusu, 2000). MPI of the trace metals was calculated using Equation 1.

$$MPI = \frac{Concentration\ of\ metal\ in\ soil\ during\ the\ post-fertilization\ period}{Concentration\ of\ metal\ in\ soil\ during\ the\ pre-fertilization\ period} \quad (1)$$

Degree of contamination (Cdeg)

The Cdeg for each of the studied location was evaluated using Equation 2.

$$Cdeg = \Sigma MPI \quad (2)$$

Where ΣMPI represents the sum of metal pollution index for the entire metals determined at each location. The various degree of contamination and their environmental implications by Hakanson (1980) are: Cdeg< 8 = low degree of contamination; 8 <Cdeg< 16 = moderate degree of contamination; 16 <Cdeg< 32 = considerable degree of contamination; and 32 <Cdeg = very high degree of contamination.

Ecological risk factor (ERF)

Ecological risk factor was utilized to review the environmental problems associated with the buildup of trace metals in the soil using Equation 3.

$$ERF = Tr \times MPI \quad (3)$$

Where Tr = the toxic-response factor for the trace metals and MPI indicates the metal pollution index. The toxic response factors for the trace metals as proposed by Hakanson (1980) are as follows: Cd (30.0), Cu (5.00), Ni (5.00), Pb (5.00), Zn (1.00), and Cr (2.00). The various categories of ecological risk factor by Liu *et al*. (2012) are ERF < 40 = Low ecological risk, 40 < ERF ≤ 80 = Moderate ecological risk, 80 ≤ ERF < 160 = Considerable ecological risk, and ERF ≥160 = Very high ecological risk.

Potential ecological risk index (RI)
The potential ecological index was used to appraise the effects of trace metals determined on the quality of soil at the various locations examined.

$$RI = \Sigma(ERF)- \quad (4)$$

Where $\Sigma(ERF)$ = the sum of all the trace metals determined at each location. The several classes of potential ecological risk by Liu *et al*. (2012) are as follows: RI < 94 = Low ecological risk, 94 ≤ RI < 188 = Moderate ecological risk, 188 ≤ RI < 376 = Considerable ecological risk and RI ≥ 376 = Very high ecological risk.

Transfer factor (TF) of trace metals
The transfer factor was used to assess the quantity of each of the trace metals available in soil for uptake by the studied vegetables. The transfer factor of trace metals from soil to vegetables was determined using Equation 5.

$$TF = \frac{Cplant}{Csoil} \quad (5)$$

Where TF is the transfer factor, Cplant = the concentration of individual trace metal in the vegetable, and Csoil indicates the concentration of trace metal in soil.

Table 1: The units, values, and sources of the parameters used for computing risks associated with the consumption of the studied vegetables

S/N	Parameter	Numerical value	Source
1.	Body weight (kg)	15 kg – child, 70 kg – adult	USEPA (1989) and (2000)
2.	Estimated consumption rate of studied vegetables (kg/person/day)	0.118 – child 0.182 – adult	Nabulo *et al.* (2010)
3.	Exposure frequency (E_f)	350 days / year	Wang *et al*. (2012)
4.	Exposure duration	6 yrs – child, 30 years – adult	Grzetic and Ghariani (2008)
5.	Oral reference doses of toxic metals ($mgkg^{-1}day^{-1}$)	Cd - 0.001, Cu – 0.040, Ni - 0.02, Pb – 0.0035, Zn- 0.300; Cr – 1.5	USEPA (2010)
6.	Average time for non-carcinogens (day / year)	365 days/yr^d	USEPA (2000)

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The estimated daily intake rate of trace metals was evaluated using Equation (1)

$$ECDI = \frac{MI \times MC}{BW} \quad (1)$$

Where MI represents the estimated quantity of vegetables consumed in kg/person/day. MC = the average concentration of each trace metal in the studied vegetables expressed in $mgkg^{-1}$, BW = the average body weight for children and adults in kg. The numerical values of these parameters and the sources are shown in Table 1.

The hazard quotient (HQ) of each trace metal was obtained using Equation (2).

$$HQ = \frac{Ef \times EDtotal \times EDI}{RfDo \times BW \times AT} \times 10\,E - 03 \quad (2)$$

Where EF = exposure frequency; ED_{total} indicates the total exposure duration; EDI signifies the estimated daily intake of each metal; RfDo = the oral reference dose; BW is the average body weight for the children and adults' populations, and; AT = average time for non-carcinogens. The values, units, and sources for the parameters are shown in Table 1.

The values for total hazard index (THI) of the trace metals were computed by Equation (3).

$$THI = \Sigma HQ = HQCd + HQCu + HQNi + HQPb + HQZn + H \quad (3)$$

Where ΣHQ signifies the sum of all the hazard quotients (HQ) of the trace metals determined.

Statistical analysis
The statistical analysis of values obtained was done with IBM SPSS Statistics 20 (IBM USA) model to obtain the mean, minimum, maximum, and standard deviation. Principal component analysis was performed with Varimax Factor analysis on six (6) parameters and values from 0.622 and above was considered significant.

RESULTS AND DISCUSSION
The results for the total concentrations of trace metals in the various inorganic fertilizers used are shown in Table 1.

Cd varied between 2.11 and 3.26 $mgkg^{-1}$ with a mean value of 2.72±0.48 $mgkg^{-1}$ in the studied inorganic fertilizers. This is within the range (1.85 – 316 $mgkg^{-1}$) reported by Benson *et al.* (2014) but lower than 3.17 – 19.09 $mgkg^{-1}$ obtained by Gambuoe and Wieczorek (2012) in inorganic fertilizers. Cu in the studied fertilizers ranged from 5.72 to 7.14mgkg-1 with an average value of 6.56±0.61 $mgkg^{-1}$. The range obtained is below 3.92-38.14 $mgkg^{-1}$ reported by Ogabiela *et al.* (2009). Ni ranged between 8.78 and 10.75 $mgkg^{-1}$ in the studied fertilizers with a mean concentration of 9.58±0.86 $mgkg^{-1}$

Table 1: Concentration (mgkg^{-1}) of trace metals in the different fertilizers applied

	Cd	Cu	Ni	Pb	Zn	Cr
NPK 20:10:10	2.84	7.14	10.75	8.29	16.41	2.38
NPK 15:15:15	3.26	6.85	9.13	8.42	13.74	2.05
NPK 20:5:10	2.11	6.53	9.66	7.50	14.83	2.21
NPK 12:12:17	2.68	5.72	8.78	7.32	13.25	2.26
MIN	2.11	5.72	8.78	7.32	13.25	2.05
MAX	3.26	7.14	10.75	8.42	16.41	2.38
MEAN	2.72	6.56	9.58	7.88	14.56	2.23
SD	0.48	0.61	0.86	0.55	1.40	0.14

These values are lower than 14.4 – 17.4 mgkg-1 obtained by Ukpabi *et al*. (2012) but higher than 4.85 – 5.95 mgkg^{-1} reported by Benson *et al*. (2014) in inorganic fertilizers. A range and mean concentration of 7.32 – 8.42 mgkg^{-1} and 7.88±0.55 mgkg^{-1}, respectively were recorded for Pb in the fertilizers applied. The obtained range is consistent with 7.43 – 9.02 mgkg^{-1} obtained by Ukpabi *et al*. (2012) but lower than 3.80 – 103.30 mgkg^{-1} reported by Guilherme *et al.* (2019). Zn varied between 13.25 and 16.41 mgkg^{-1} with a mean value of 14.56±1.40 mgkg^{-1}. The reported range is lower than 4.11–1748.01mgkg^{-1} obtained by Gong *et al.* (2019). Cr contents in the fertilizers varied from 2.05 to 2.38mgkg^{-1}with an average concentration of 2.23±0.14 mgkg^{-1}. The reported range is within the 0.19-2.207 mgkg^{-1} obtained by Ogabiela *et al*. (2009) but below 38.7 – 274.7 mgkg^{-1} recorded for Cr in inorganic fertilizers by Gambuce and Wieczorek (2012). Despite the high levels of metal contaminants in the inorganic fertilizers applied, the concentration of all the metals were within their acceptable limits specified by different countries by Westfall *et al*. (2005) in Table 3. The levels of Cu and Zn in the applied inorganic fertilizers should be supplemented since they are essential elements for normal plant growth and fertility.

Table 2: Concentration (mgkg^{-1}) of trace metals in soil during the Pre and Post-fertilization periods

	Pre-fertilization period					
	Cd	Cu	Ni	Pb	Zn	Cr
SITE						
1	0.08	1.84	4.72	1.29	6.07	0.56
2	0.07	1.79	4.25	1.03	5.88	0.61
3	0.06	1.96	4.50	1.12	6.04	0.58
4	0.06	1.82	4.61	1.06	5.85	0.60
MIN	0.06	1.79	4.25	1.03	5.85	0.56
MAX	0.08	1.96	4.72	1.29	6.07	0.61
MEAN	0.07	1.85	4.52	1.13	5.96	0.59
SD	0.01	0.08	0.20	0.12	0.11	0.02
	Post-fertilization period					
1	1.96	2.38	5.73	3.11	10.06	1.26
2	2.14	2.40	5.81	2.89	9.45	1.18
3	1.95	2.58	5.78	2.83	8.92	1.20
4	1.97	2.45	5.80	2.91	9.75	1.21
MIN	1.95	2.38	5.73	2.83	8.92	1.18
MAX	2.14	2.58	5.81	3.11	10.06	1.26
MEAN	2.01	2.45	5.78	2.94	9.55	1.21
SD	0.09	0.09	0.04	0.12	0.49	0.03
FEPA (1999)	0.80	10.1	35.0	85.0	140.0	100.0
WHO (2008)	1.0	2.0	20.0	10.0	250.0	50.0

The total concentrations of the metals determined in soil during the pre-fertilization period are shown in Table 2. The results obtained revealed that, Cd varied between 0.06 and 0.08 mgkg^{-1} with a mean value of 0.07±0.01 mgkg^{-1}. The range and mean concentration of Cu are 1.79 – 1.96mgkg^{-1} and 1.85±0.08 mgkg^{-1}, respectively. Ni ranged from 4.25 to 4.72mgkg^{-1} with average concentration of 4.52±0.20mgkg^{-1}. Total Pb varied between1.03 and 1.29mgkg^{-1} with an average value of 1.13±0.12 mgkg^{-1}. The range and mean value of total Zn are 5.85 – 6.07 mgkg^{-1}and 5.96±0.11 mgkg^{-1}, respectively. Total Cr ranged between 0.56 and 0.61 mgkg^{-1}with average concentration of 0.59±0.02 mgkg^{-1}. The mean results of all the metals were within the Nigerian (FEPA, 1999) and world health organization (WHO, 2008) standards in Table 2. Consequently, the natural status of the studied soil may not interfere with agricultural activities negatively.

The mean values (mgkg^{-1}) of total metals in soil from the studied locations as shown in Table 2 are as follows: 2.01±0.09, 2.45±0.09, 5.78±0.04, 2.94±0.12, 9.55±0.49, and 1.21±0.03 for Cd, Cu, Ni, Pb, Zn, and Cr, respectively. The mean concentrations of the metals reported are much higher than the values obtained in soil during the pre-fertilization period. This is similar to the previous studies on the effects of inorganic fertilizers on soil quality (Atafar *et al*., 2010; Munir *et al*., 2019; Izuagie *et al*. 2022; Orluchukwu and Amadi, 2022). Consequently, the inorganic fertilizers applied might have contributed substantial quantity of these metals to the host soil environment. However, the mean concentrations of the metals are within the permissible limits by FEPA (1999) and WHO (2008) except for Cd and Cu. Hence, this might result in the bioaccumulation of Cd and Cu and the associated health problems to their toxicities along the food chain as reported by ATSDR (2012) and Taylor *et al*. (2020). The study has shown that, the application of inorganic fertilizers has the potentials of affecting the quality of the soil environment negatively as reported by Etuk *et al*. (2022).

Table 3: Average concentration (mgkg^{-1}) of trace metals allowable in inorganic fertilizers by different countries of the world.

	Cd	Cu	Ni	Pb	Zn	Cr
China	8.0	-	-	100.0	-	500.0
Canada	20.0	-	180.0	200.0	1850.0	-
USA	11.0	280.0	37.0	12.0	-	109.0
North Africa	60.0	-	33.0	6.0	-	105.0

Source: Westfall *et al*. (2005)

Pollution Assessment of trace metals in soil

Table 4: Results for the metal pollution index (MPI) and potential ecological risk (RI) during the post-fertilization period

	Cd	Cu	Ni	Pb	Zn	Cr
Metal Pollution Index of Trace Metals						
S1	24.50	1.29	1.21	2.41	1.66	2.25
S2	30.57	1.34	1.37	2.81	1.61	1.93
S3	32.50	1.32	1.28	2.53	1.48	2.07
S4	32.83	1.35	1.26	2.75	1.67	2.02
Min	24.50	1.29	1.21	2.41	1.48	1.93
Max	32.83	1.35	1.37	2.81	1.67	2.25
Mean	30.10	1.33	1.28	2.63	1.61	2.07
Potential Ecological Risk of Trace Metals						
S1	735.0	6.45	6.05	12.05	1.66	4.50
S2	917.1	6.70	6.85	14.05	1.61	3.86
S3	975.0	6.60	6.40	12.65	1.48	4.14
S4	984.9	6.75	6.30	13.75	1.67	4.04
Min	735.0	6.45	6.05	12.05	1.48	3.86
Max	984.9	6.75	6.85	14.05	1.67	4.50
Mean	903.0	6.63	6.40	13.13	1.61	4.14

The values recorded for metal pollution index (MPI) of trace metals at the different locations investigated are shown in Table 4. The range of MPI for Cd, Cu, Ni, and Pb as indicated in Table xxx are 24.50 – 32.83, 1.29 – 1.35, 1.21 – 1.37, and 2.41 – 2.81, respectively. While the MPI values for Zn and Cr varied from 1.48 to 1.67 and 1.93 to 2.25, respectively. Based on the MPI classifications by Lacatusu (2000), Cd belongs to the excessive pollution class; Cu and Ni are in the slight pollution category while Pb belongs to the moderate pollution class. Zn belongs to the slight pollution class while Cr varies between the slight and moderate pollution classes. The levels of all the trace metals determined are above the contamination class hence, they belong to the pollution category. Consequently, the metals may pose serious negative effect on the soil, plant, and the environment (Lacatusu, 2000). Obviously, the application of inorganic fertilizers to the studied plots may have elevated the levels of these metals in soil (Benson *et al*., 2014; Orisakwe *et al*., 2017). The mean MPI of the trace metals followed the order: Cd > Pb > Cr > Zn > Cu > Ni. This indicates the low availability of the essential Zn and Cu at the different locations investigated; hence this may lead to the deficiency symptoms on the vegetables cultivated over time. Consequently, this could be the result of the low levels of Zn and Cu in the inorganic fertilizers applied and as earlier suggested supplementary sources may be required.

The ecological risk factor (ERF) for the trace metals in the soil during the post-fertilization period are indicated in Table 4. The mean ERF values for Cd, Cu, and Ni are 903.0, 6.63, and 6.40, respectively. While Zn and Cr showed mean ERF values of 1.61 and 4.14, respectively. Accordingly, Cd belongs to the very high ecological risk class whereas; Cu, Ni, Pb, Zn, and Cr are in the low ecological risk category

(Liu *et al*., 2012). This is an indication that, those expose to these soil particles after the application of inorganic fertilizers either directly or indirectly are susceptible to risks associated with high Cd. The mean ERF values of the trace metals are in the following order: Cd >> Pb > Cu > Ni > Cr > Zn. This exposes the high levels of toxic Cd and Pb in the studied plots during the post-fertilization period, and this is very risky for the food chain.

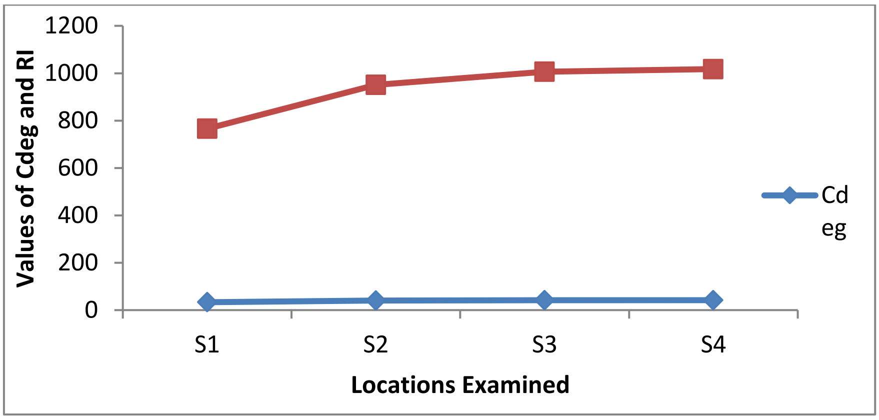

Figure 1: Results of degree of contamination (C_{deg}) and potential ecological risk index (RI).

The extent of soil contamination by trace metals at the different plots examined was assessed by the use of degree of contamination (Cdeg). The Cdeg for the different plots are illustrated in Figure 1. The values of Cdeg varied between 33.3 at Plot 1 and 41.9 at Plot 4. The Cdeg values for Plots 2 and 3 are 40.0 and 41.2, respectively. The Cdeg values of all the plots are in the very high degree of contamination category according Hakanson (1980) classifications. This corroborates the findings that, the application of inorganic fertilizers in soil to improve soil fertility may increase the levels of these trace metals in the environment (Singh *et al*., 1997).

Results for the potential ecological risk factor (RI) are demonstrated in Figure 1. The RI values for trace metals in the various plots varied from 765.71 to 1017.41. The highest RI value was obtained at plot 4 while the lowest was recorded in plot 1. The RI values for plots 2 and 3 are 950.17 and 950.17, respectively. The RI values of all the plots belong to the very high ecological risk class following the classifications of Liu *et al*. (2012). The high RI values reported should be closely monitored as these values are directly proportional to human health (Etuk *et al*., 2022). This also confirms the negative impact of inorganic fertilizers on the quality of the environment applied.

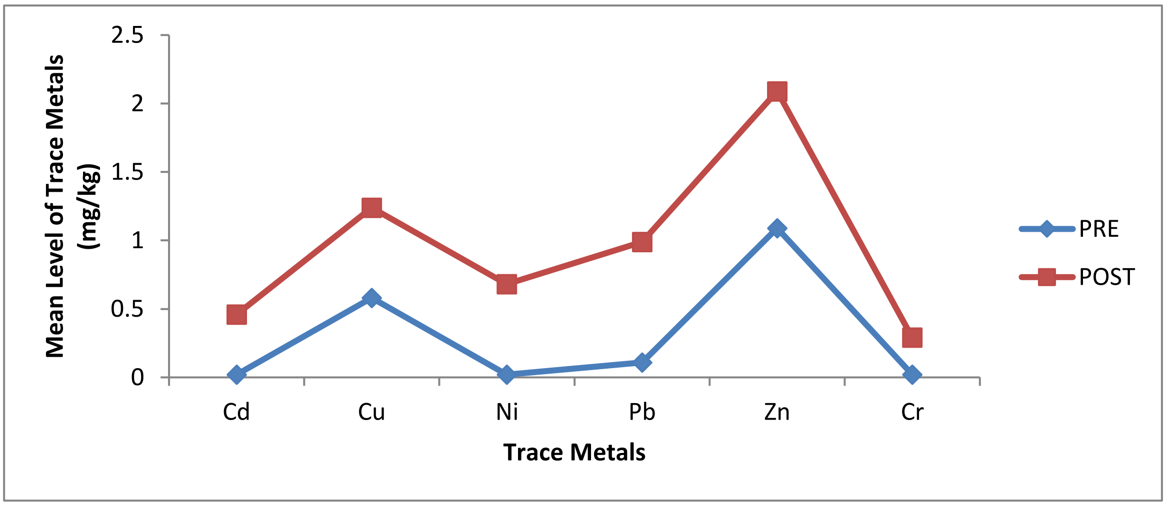

Figure 2: Concentration of trace metals in the studied vegetables during the pre and post- fertilization periods

Results for the concentration of trace metals in the studied vegetables during the pre and post- fertilization periods are illustrated in Figure 2. During the pre-fertilization period, the mean concentrations ($mgkg^{-1}$) of the metals were as follows: 0.02±0.01, 0.58±0.06, 0.02±0.01, 0.11±0.02, 1.09±0.07, and 0.02±0.01 were recorded for Cd, Cu, Ni, Pb, Zn, and Cr, respectively. These mean concentrations are within the limits of 0.2$mgkg^{-1}$, 10.0 $mgkg^{-1}$, 10.0 $mgkg^{-1}$, 2.0 $mgkg^{-1}$, 99.4 $mgkg^{-1}$, and 0.10 $mgkg^{-1}$ stipulated for Cd, Cu, Ni, Pb, Zn, and Cr, respectively in leafy vegetables by FAO/WHO (2014). Consequently, the consumption of these vegetables cultivated on the natural soil may not pose serious health problems to the consumers. However, during the post-fertilization period, higher mean concentrations (mgkg^{-1}) were reported for the metals as follows: 0.46±0.05, 1.24±0.39, 0.68±0.08, 0.99±0.45, 2.09±1.68, and 0.29±0.02 for Cd, Cu, Ni, Pb, Zn, and Cr, respectively. Hence, the mean levels of Cd, Ni, Pb, and Cr were higher than their recommended limits for leafy vegetables by FAO/WHO (2014). Accordingly, the consumption of these vegetables after the application of inorganic fertilizers may results in the toxicity of these metals and their attendants' health problems. The higher levels of trace metals in the studied vegetable during the post-fertilization period are in agreement with the report by Atafar *et al.* (2010). Generally, *Telferia occidentalis* and *Talinum triangulare* showed very high potentials for accumulating these metals from the soil; this corroborates the findings by Vahter *et al.* (2007) and Agbogidi and Erhenhi (2013). Nevertheless, Spinacia *oleracea* showed very strong capacity to absorb Zn from the fertilizer impacted soils. Thus, *T. occidentalis*, *T. triangulare*, and *S. oleracea* could be used as excluders and for phytostabilization since the transfer factors of the metals are less than one (Bahemuka and Mubofu, 1999).

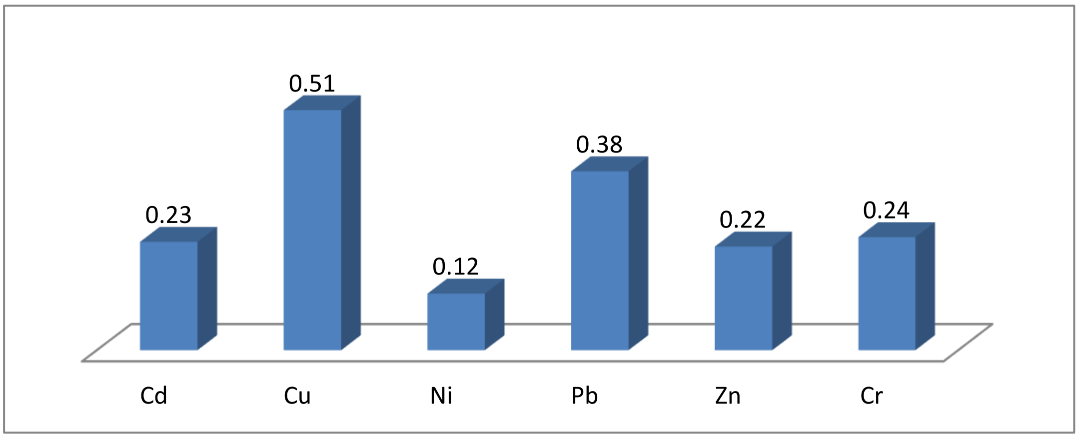

Figure 3: Transfer factor of trace metals from soil to vegetables during post-fertilization period.

Transfer factor of trace metals from soil to vegetables

Results for the transfer factor (TF) of metals from soil to vegetables during post-fertilization period are demonstrated in Figure 3. Transfer factor indicates the amount of available trace metals in soil for plant uptake (McEldowney *et al.*, 1994; Haynes and Toohey, 1998). The mean TF values of the metals were as follows: 0.23, 0.51, 0.12, 0.38, 0.22, and 0.24 for Cd, Cu, Ni, Pb, Zn, and Cr, respectively. The highest mean TF value was recorded for Cu in *Telferia occidentalis* and *Talinum triangulare* while the lowest was recorded for Ni in *Telferia occidentalis.*

Multivariate analysis

Table 4: Result of Factor analysis indicating comparative loading from metals during the post-fertilization period

	SOIL		VEGETABLES		
	PC1	PC2	PC1	PC2	PC3
Variable					
Cd	-0.377	0.878	0.402	0.851	-0.339
Cu	-0.677	-0.779	-0.299	0.954	-0.135
Ni	-0.850	0.408	0.937	0.075	-0.340
Pb	0.985	0.135	0.923	0.230	0.307
Zn	0.866	0.398	0.189	0.389	0.902
Cr	0.953	-0.303	0.853	-0.520	-0.041
% Total Variance	64.8	30.2	45.5	35.3	19.3
Cumulative %	64.8	95.0	45.5	80.7	100.0
Eigen value	3.9	1.8	2.7	2.1	1.2

PC: Principal component

Principal component analysis (PCA) was used to identify the actual factors responsible for the accumulation of trace metals determined in the studied soil during the post-fertilization period (Kahangwa, 2022). The results obtained revealed two main factors that are responsible for the accumulation of trace metals in the studied soils (Table 4). The factors responsible for the buildup of metal in soil have Eigen values greater than one with 95.0% of the total variance. The first factor (PC1) added 64.8% to the total variance with significant positive loadings on Pb, Zn, and Cr but, with strong negative loadings on Cu and Ni (Table 4). This represents the impact of natural and anthropogenic (fertilizer application) on the quality of the soil (Yin *et al*., 2010). The second factor (PC2) contributed 30.2% to the total variance with strong positive loading on Cd and significant negative loading on Cu (Table 4). This indicates clearly the influence of inorganic fertilizers on the quality of the studied soil (Olabanji *et al*., 2015; Rodriguesa *et al*., 2017).

The results of PCA of trace metals in the studied vegetables are shown in Table 4. Table 4 indicates three major factors that are responsible for the availability of trace metals in the studied vegetables with total variance of 100%. Factor one donated 45.5% to the total variance with strong positive loadings on Ni, Pb, and Zn. This signifies the negative impact of inorganic fertilizers on the quality of the studied vegetables as reported by Singh *et al*. (2010) and Etuk *et al*. (2022). Factor two contributed 35.3% to the total variance with strong positive loadings on Cd and Cu. This indicates the effects of natural factor and inorganic fertilizers on the quality of the vegetables (Ebong *et al*., 2020). The third factor added 19.3% to the total variance with significant positive loading on Zn only. This could be the negative impact of natural factor such as aerial deposition on the quality of the studied vegetables (Azeez *et al*., 2011).

Health risk evaluation

Results for the evaluation of health risk associated with the consumption of the studied vegetables on both the children and adult populations are shown in Tables 5 and 6.

Table 5: Estimated chronic daily intake of trace metals via the studied vegetables during post-fertilization period

	T. occidentalis		*T. triangulare*		*S. oleracea*		*A. viridis*		Mean	
	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult
Cd	3.70E-03	1.22E-03	3.54E-03	1.17E-03	3.54E-03	1.17E-03	3.78E-03	1.25E-03	1.46E-02	4.81E-03
Cu	9.76E-05	3.22E-03	9.60E-03	3.17E-03	9.76E-03	3.22E-03	9.83E-03	3.25E-03	2.93E-02	1.29E-02
Ni	5.35E-03	1.77E-03	5.35E-03	1.77E-03	5.27E-03	1.74E-03	5.35E-03	1.77E-03	2.13E-02	7.05E-03
Pb	9.76E-03	3.22E-03	8.81E-03	2.91E-03	7.87E-03	2.60E-03	8.65E-03	2.86E-03	3.51E-02	1.16E-02
Zn	1.68E-02	5.56E-03	1.63E-02	5.38E-03	1.65E-02	5.46E-03	1.63E-02	5.38E-03	6.59E-02	2.18E-02
Cr	2.36E-03	7.80E-04	2.44E-03	8.06E-04	2.20E-03	7.28E-04	2.28E-03	7.54E-04	9.28E-02	3.07E-03

Table 6: Hazard quotient and total hazard index of trace metals in the studied vegetables during post-fertilization period

	T. occidentalis		*T. triangulare*		*S. oleracea*		*A. viridis*	
	Children	Adult	Children	Adult	Children	Adult	Children	Adult
Cd	1.42E-03	5.00E-04	1.36E-03	4.80E-04	1.36E-03	4.80E-04	1.45E-03	5.13E-04
Cu	9.36E-05	3.31E-05	9.21E-05	3.26E-05	9.36E-05	3.31E-05	9.43E-05	3.34E-05
Ni	1.03E-04	3.64E-05	1.03E-04	3.64E-05	1.01E-04	3.58E-05	1.03E-04	3.64E-05
Pb	1.07E-03	3.78E-04	9.66E-04	3.42E-04	8.62E-04	3.05E-04	9.48E-04	3.36E-04
Zn	2.15E-05	7.62E-06	2.08E-05	7.37E-06	2.11E-05	7.48E-06	2.08E-05	7.37E-06
Cr	6.03E-07	2.14E-07	6.24E-07	2.21E-07	5.63E-07	2.00E-07	5.83E-07	2.07E-07
THI	2.71E-03	9.55E-04	2.54E-03	8.99E-04	2.44E-03	8.62E-04	2.62E-03	9.26E-04

Results for the estimated daily intake rate of trace metals

The estimated rate at which human beings (children and adult populations) could be exposed to these trace metals via the studied vegetables was assessed using the estimated daily intake rate (Orisakwe *et al*., 2012). Results for estimated daily intake of trace metals through the consumption of studied vegetables are shown in Table 5. Results recorded revealed that, the levels of Cd and Pb in both populations and Ni in the children population were higher than their Rfd values by USEPA (2010). Consequently, the consumption of these vegetables may result in higher levels of Cd, Pb, and Ni in the consumers and the associated health problems. The sequences for EDI rate for the children and adult populations are Cr > Zn > Pb > Cu > Ni > Cd and Zn > Cu > Pb > Ni > Cd > Cr. Notwithstanding the high EDI values of Cr and Zn, their levels are still within their Rfd limits thus, may not pose any health risk.

Results for the non-carcinogenic risk

Results for the hazard quotients (HQ) of the metals via the consumption of the studied metals are indicated in Table 6. The HQ for individual trace metal is below one hence, the consumption of these vegetables may not pose serious health hazards to the consumers (Children and adult populations). The HQ for the trace metals via the consumption of *T. occidentalis* by both populations is in the following order: Cd > Pb > Ni > Cu > Zn > Cr. While the HQ of the metals via the consumption *T. triangulare*, *S. oleracea* and *A. viridis* is in the order Cd > Pb > Ni = Cu> Zn > Cr. Although, the HQ values of the metals is less than one, the high values of the toxic Cd, Pb, and Ni is risky as these metals are very toxic even at their very low concentrations. The HQ values also revealed that, the children are more vulnerable to health problems associated with high levels of these metals than the adult population. Notwithstanding the low HQ values reported, those exposed to these metals are still vulnerable to the non-carcinogenic health problems since these problems have strong correlation with the total THI value (Ebong *et al*., 2019).

Results for the total hazard index of trace metals

Results for the total hazard index (THI) of oral exposure to trace metals via the consumption of the studied vegetables for both the children and adult populations are shown in Table 6. The THI values ranged as follows: 2.44E-03 – 2.71E-03 and 8.62E-04 – 9.55E-04 for the children and adult populations, respectively. Consequently, higher THI values were recorded for the children than the adult population. Accordingly, the children exposed to these metals via these vegetables may be more vulnerable to metal toxicity and related health problems that the adult. The higher THI values for the children reported are consistent with the findings by Singh *et al*. (2010). The results also indicated that, Cd and Pb contributed 52 and 40 %, respectively to the total THI value obtained in *T. occidentalis* for both the children and adult populations. However, in *T. triangulare* Cd and Pb contributed 53 and 38%, respectively to the THI for both populations. In *S. oleracea,* Cd and Pb added 56 and 35%, respectively to the overall THI for both populations while 55 and 36% were donated by Cd and Pb, respectively to the total THI in *A. viridis* for the children and adult populations. Generally, Cd and Pb contributed 80% of the entire THI value for all the vegetables and populations.

CONCLUSION

The study revealed the impact of inorganic fertilizers widely utilized by farmers for the improvement of plant yield on the quality of soil and vegetables cultivated. It showed unambiguously that, inorganic fertilizers have the potential of contaminating the environment with toxic metals. The pollution status of these metals in soil depicted higher levels of Cd and Cu, but the mean concentrations of Ni, Pb, Zn, and Cr were within their permissible limits. The key factors responsible for the accumulation of these metals in both the studied soil and vegetables were natural, fertilizers and as aerial deposition. *T. occidentalis* and *T. triangulare* exhibited very high tendency for the absorption of metals from the fertilizers-impacted soil. The quantity of Cd, Cu, Ni, Pb, Zn, and Cr contributed by fertilizers to the soil and vegetables examined has been determined. The consumption of vegetables cultivated on a fertilizer-impacted soil potentially predisposes the consumers to health problems associated with Cd and Pb toxicity. The results of this study indicated that, the children population were the more vulnerable class to high Ni. However, subsequent works should study the effects of these fertilizers individually to ascertain the one with higher environmental potential.

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