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ASSESSMENT OF HEALTH RISKSFROM CONSUMPTION OF FOOD CROPS FUMIGATED WITH METAL BASED PESTICIDES IN GWADAM, GOMBE STATE, NIGERIA

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ABSTRACT
Intensive use of agrochemicals has led to build of heavy metals in the soil ecosystem and their transfer to edible parts of crops. This study was aimed to determine the heavy metals (Cd, Pb, Cr, Cu and Zn) concentrations in some twenty commonly used pesticides in northern Nigeria, and health risk associated from the consumption of food crops fumigated with these pesticides as the only source of metal contamination. Heavy metals content in pesticides, food crops and soils were analyzed after acid digestion using atomic absorption spectrometry. Traces of heavy metals (Cd, Pb, Cr, Cu and Zn) were detected in most of the pesticides. The concentrations of heavy metals in crops fumigated with pesticides ranged from 0.33-4.68, 1.75-38.08, 0.67-16.83, 9.01-436.75, 0.17-20.80 mg/kg for Cd, Pb, Cr, Cu, and Zn respectively. The mean concentrations of Cd, Pb, and Cr in all the crops were above WHO, (2019) permissible limit. Heavy metals in soils of corresponding crops were below the permissible limits by UNEP, (2013) and NESREA, (2011). Bioaccumulation factor BAF showed high BAF>1 for Cu and Pb in all the studied crops, while pollution index value revealed contamination for Cd and Pb in all the studied crops. Hazard quotient showed potential health risk from the consumption of only Capsicumannuum for Pb. However, consumers may experience advance health risk through the consumption of Oryza sativa, Zea mays, Solanumlycopersicum, Capsicumfrustescens for all metals (Hazard index). Hence, there is the need for screening of heavy metals in pesticides and monitoring of metals contents in food crops.
Keywords: Bioaccumulation, Heavy metals, Hazard Quotient, Pesticides

INTRODUCTION

The increase of agricultural practices in the world and in particular developing nations has led to an increasing use of pesticides over the past decades (Daam and Van den Brink, 2010; Lewis *et al*, 2016). There has been a surge of 134% in global pesticides sale from 2000 to 2014 (Bombardi, 2017). Pesticides have been shown to contain compounds and traces of metal that are environmentally persistent and highly toxic and are mostly banned from agriculture use in developed nations, but are still use in developing countries like Nigeria (Carvalho, 2006). In northern Nigeria there is a proliferation of new pesticides into the markets whose chemical contents for trace metals and other toxic constituents are not well labelled or conceal by the manufactures (Barau *et al*, 2018), even though a survey report on pesticides utilization in northern Nigeria has revealed that none of chemical pesticides investigated from the merchants was banned by the regulatory agency (NAFDAC) (Sule *et al.*, 2020). However, recent studies have identified traces of heavy metals in pesticides at the recommended farmer's dilution rate in Nigeria and even in developed nations (Yuguda *et al.,* 2015;Defarge*et al*, 2018; Oguh *et al*, 2019).Some heavy metals such as cadmium, mercury, lead, chromium, arsenic are non-biodegradable, persistent and toxic even at low concentration (Yang *et al.*, 2018).

There are few studies by Yuguda *et al.*(2015;Barau*et al.*(2018) on screening of heavy metals contents in pesticides use in agricultural farms and health risk associated from the consumption of food crops fumigated with metal based pesticides in northern Nigeria. Therefore, this study was designed with aim of determining the concentrations of heavy metals (Cd, Pb, Cr, Cu, Zn) in commonly used pesticides and the health risk associated from the consumption of food crops fumigated with these pesticides.

MATERIALS AND METHODS

Samples of leaves, stems, roots and fruits of seven selected matured plants were collected by randomly picking from two farm lands. Five (5) replicates from each of the seven plants were collected from Kwadam Farm (A) in Gombe State at coordinates of 32P N 0749836, 32 P E11366869 and Kwadam Farm (B) at coordinates of N0749941, E 1134986. At each sampling site, 20g each of the seven crops namely *Spinaciaoleracea, Capsiumcerasiforme, Solanumlycopersium, Lactuca sativa, Allium cepa, Zea mays, Oryza sativa* were collected from three different locations in each farm land to provide replicate samples of each crop. Soil samples were collected from corresponding soil of each plant. Control soil samples were collected from adjacent farm land which were not fumigated with pesticides. All the samples were collected from agricultural farms fumigated with pesticides and feed with bore hole water.Twenty commonly used pesticides by farmers were identified and purchased directly from the merchants with trade mark insecticide (Goodbye, Sharpshooter, Abatin, Rocket, DD force, Prime Force, Bakmethrin, Chemthrin, Perfect Killer, Vibrant, Storm Force, Power Insect), Fungicide (Clot, Z-force, Mancozebe), Herbicide (Vinash, Force up, Finish 68, Sunsate, Star combi).

Heavy Metal Analysis

The non-edible portions of the plants were separated from edible portion and chopped into small pieces. The soil and plant samples were oven dried at 80^{o}C and 1g each was digested separately with a mixture of (Nitric acid) HNO_3, 65% (Per chloric acid) $HClO_4$ and 70% (Sulfuric) H_2SO_4 in 5:1:1 ratio). The samples were analyzed for heavy metals using an Atomic Absorption Spectrophotometer model 210 VGP as described by (Zhong *et al*., 2018). 1.4 g sample of each herbicides, fungicides and 1ml for insecticides were digested with 10ml of concentrated HNO_3, 2ml of concentrated H_2SO_4 and analyzed for heavy metals using an atomic absorption spectrophotometer model 210 VGP as described by (Dafarge *et al*., 2018; Gimeno-Gracia, *et al.,* 1996)

Health Risk Assessment

Daily intake of metal

The daily intake of metals(DIM) was calculated to determine the health risk from consuming vegetables, with trace of heavy metals concentration using the formula below as described by (Zhong *et al.,* 2017).DIM=$\frac{M\times K\times I}{W}$

Hazard Quotient

The health risks to the local inhabitants from the consumption of vegetables were evaluated based on the Hazard Quotient, which is the ratio between exposure and oral reference dose (R_fD) as described (US-EPA, 2013).Given as;HQ=$\frac{\mathrm{Dim}}{RfD}$

Hazard Index

Potential risk to human health due to more than one heavy metal known as the Hazard index (HI) was calculated as described by US-EPA, (2013), which is the total sum of all the Hazard Quotients as shown in the equation below:

$HI=\sum HQ=HQ_{Cd}+HQ_{Pb}+HQ_{Cr}+HQ_{Cu}+HQ_{Zn}$

Estimated daily Intake (EDI)

The degree of toxicity of heavy metals to human upon their daily intake (mg/kg/day) known as the estimated daily intake was computed for each element as described by US-EPA, (2013).

EDI=$\frac{\mathrm{Cmetal}\times Averagedailyintake}{BA}$ mg/kg/day

Pollution Index (PI)

Pollution index (PI) is the ratio of metal concentration in a biotic or abiotic medium to that of the regulatory Standard of international bodies such as United states Environmental Protection Agency (USEPA) was computed as described by (Chukwuma, 1994).

Mathematically, PI was computed as PI=$C^{plant/CUS\text{-}EPA\text{-}STANDARD}$

Statistical Analysis

Analysis of variance ANOVA was used to analyze data using statistical software "R" 2014 version as described by Dytham, (2011).

RESULTS

Heavy metals concentrations in Pesticides

The mean concentrations of heavy metals (Cd, Pb, Cr,Cu and Zn) detected in twenty commonly used pesticides in the study areas are given in (Table 1).

The result revealed that the concentrations of heavy metals in pesticides ranged from 0.10-6.05, 2.33-46.44, 3.98-18.10, 0.62-5.69, and 0.34-34.11 for Cd, Pb, Cr, Cu, and Zn respectively (Table 1). Copper was only detected in insecticides and was not detected in all the studied fungicide and herbicide (Table 1).

Heavy metals concentration in crops

The concentration of heavy metals in different parts of crops (root, stem, leaf, and fruit) grown in 2018 season are given (Table 2a, 2b).The result showed that the concentration of heavy metals in the studied crops grown in 2018 dry season ranged from0.33-4.68, 1.75-38.08, 0.67-16.83, 9.01-436.75, 0.17-20.80 mg/kg for Cd, Pb, Cr, Cu, and Zn respectively (Table 2a, 2b).The concentrations of heavy metals varied significantly ($p<0.05$) in different parts of most of the investigated crops with no specific pattern (Table 2a, 2b). The concentrations of Cd, Pb, Cr in the all the studied crops in 2018 season were above the permissible limits by FAO/WHO (FAO/WHO, 2019) except in *Capsicum annuum* (root, stem, fruit) for Cr, while the concentrations of Cu, Zn in most of the investigated crops were below the FAO/WHO (FAO/WHO, 2011) (Table 2a, 2b).

Table 1. Concentration of Heavy Metals (Mg/Kg) in Pesticides Used in the Study

S/N		Heavy metals				
	Pesticides Trade Mark	Cd mg/kg	Pb mg/kg	Cr mg/kg	Cu mg/kg	Zn mg/kg
	Insecticide	Mean±SD	Mean±SD	Mean±SD	Mean±SD	Mean±SD
1.	*Goodbye*	4.25±0.52	19.63±2	4.68±0.4	ND	1.37±0.0
2.	*Sharpshooter*	6.05±0.21	28.87±1	7.72±0.5	1.35±0.7	0.34±0.0
3.	*Abatin*	4.13±0.33	2.33±3	3.98±0.1	1.44±0.2	2.86±0.0
4	*Rocket*	3.68±0.2	6.32±1	4.95±0.8	1.49±0.6	3.19±0.4
5.	*DD force*	3.40±0.26	9.84±1	10.45±0.5	1.66±0.0	1.05±0.1
6.	*Prime force*	2.63±0.5	13.59±1	12.98±1.5	5.69±0.5	0.50±0.1
7.	*Bakmethrin*	0.56±0.2	16.87±7	7.85±0.4	0.90±01	0.43±0.4
8.	*Chemthrin*	0.44±0.4	21.30±4	8.12±0.7	0.62±0.3	ND
9.	*Perfect Killer*	0.84±0.1	27.09±3	10.03±0.7	0.97±0.4	0.61±0.7
10	*Vibrant*	0.81±0.5	28.37±4	8.82±0.8	0.79±0.4	2.49±2.1
11.	*Storm force*	0.39±0.4	2.16±2	13.35±0.6	ND	5.39±1.1
12.	*Power insect*	0.45±0.8	8.73±2	18.10±0.9	ND	4.58±1.2
	Fungicide					
13	*Clot*	0.64±0.14	22.76±4	7.84±3	ND	0.91±0.2
14	*Z-force*	0.83±0.6	26.10±3	7.56±0.4	ND	ND
15	*Mancozebe*	0.49±0.7	6.31±4	10.31±0.6	ND	11.99±1.1
	Herbicide					
16	*Vinash*	1.01±0.3	27.81±5	12.41±1	ND	8.01±1.4
17	*Force up*	0.10±0.1	34.23±4	11.54±0.2	ND	12.60±0.1
18	*Finish 68*	ND	41.64±1	14.17±0.6	ND	34.11±0.5
19	*Sunsate*	0.45±0.2	41.06±2	12.70±0.8	ND	0.59±0.1
20.	*Star combi*	0.56±0.2	46.44±5	12.21±1.1	ND	4.36±1.2

Results presented as Mean±SD, n=3 replicate

Heavy metals concentration in soils of crops

The mean concentration of heavy metals in the corresponding soils of all the studied crops grown in 2018 season ranged from 5.76-14.78, 1.11-3.22, 12.17-19.42, 3.08-10.98, 4.89-6.33 mg/kg for Cd, Pb, Cr, Cu, and Zn respectively (Table 3).The mean concentration of heavy metals in the corresponding soils of all the studied crops for Cd, Pb, Cr, Cu, and Zn were below the permissible set by (UNEP, 2013) and NESREA, (2011) for agricultural soil, except for Cd in the soils of some crops (*Capsicum cerasiforme, Capsicum annuum, Allium cepa, Zea mays*) which had exceeded the (UNEP, 2013) limits. The concentration of heavy metals among the studied shown that *Oryza sativa* soil had highest concentration for Cd*, Zea mays* for Pb, *Capsicum cerasiforme* for Cr, *Solanumlycopersium* for Cu, and *Zea mays* for Zn respectively (Table 3).

Bioaccumulation factor (BAF)

The result for heavy metals transfer factor in crops grown in 2018 seasons showed variability in BAF values among the different studied crops and among different metals (Table 4). The Bioaccumulation factor (BAF) in the studied crops grown in 2018 season ranged from0.03-0.54, 6.51-25.55, 0.04-1.27, 1.36-115.19, 0.11-0.80 for Cd, Pb, Cr, Cu, and Zn respectively (Table 4).Bioaccumulation factor was highest for Cu (115.19) in *Oryza sativa*, followed by Pb (25.55) in *Solanumlycopersium* for Cr (1.27), and Cd (0.54) in *Spinaciaoleracea* , and for Zn (0.80) in *Zea mays* (Table 4).Bioaccumulation factor shown a trend of decreasing order Cu>Pb>Cr>Zn>Cd and all the studied crops showed BAF>1 for Cu and Pb.

Pollution indices of heavy metals

The result of the computed pollution indices (PI) in the edible parts of crops grown in the study area 2018 seasons are given in (Table 5).The PI value in crops grown in 2018 season ranges from1.67-19.46, 5.83-115.28, 0.29-7.32, 0.27-10.92, and 0.01-0.03 for Cd, Pb, Cr, Cu, and Zn respectively (Table 5).Pollution indices were highest for Pb compared to other metals and all the studied crops showed PI>1 for Pb and Cd indicating high pollution load (Table 5).Among the studied crops, PI values was highest (115.28) in *Zea mays*, followed by (125) in *Capsicum annuum*, (94) in *Solanumlycopersicum,* (19.46) in *Spinaciaoleracea*, (10.92) in *Oryza sativa* (Table 5).The trend of pollution indices in the edible parts of the studied cropswas in decreasing order of health risk of Pb>Cd>Cu>Cr>Zn.

Table 2a. Concentration of Heavy Metals in Crops Grown in Kwadam Gombe State (2018)

Name of Sample	Botanical Name	Hausa Name	Heavy metals mg/kg				
			Cd	Pb	Cr	Cu	Zn
Tomato	*Solanumlycopersicum*	Tomatur					
Root			2.55a	21.12a	5.00a	21.03b	0.82a
Stem			4.68b	26.20b	8.50b	29.68bc	2.43b
Leaf			0.93a	25.80b	ND	14.22a	0.65a
Fruit			2.13a	28.32b	ND	26.14b	0.60a
Pepper	*Capsicum annuum*	Attarugu					
Root			1.31a	ND	0.83	13.78a	0.17a
Stem			3.72b	18.28ab	9.17	50.01a	20.80b
Leaf			0.53a	35.70b	ND	18.93a	1.18a
Fruit			0.43a	19.58ab	0.67	60.03a	1.55a
Sweet Pepper	*Capsicum annuum*	Tattase					
Root			1.54ab	38.08b	ND	39.83b	1.47b
Stem			1.26a	37.63b	ND	34.32b	0.95a
Leaf			1.38a	36.28b	ND	13.57a	1.20b
Fruit			2.01b	37.66b	ND	33.58b	1.31b
Onion	*Allium cepa*	Albasa					
Root			2.52a	11.69a	ND	9.83a	0.81a
Stem			ND	ND	ND	ND	ND
Leaf			4.05b	12.10a	ND	17.08b	0.85a
Bulb			2.28a	15.96b	ND	10.62a	1.00a
Spinach	*Spinaciaoleracea*	Alayyaho					
Root			3.60a	4.62a	15.67a	13.96a	1.40a
Stem			3.77a	8.09a	15.08a	12.27a	1.08a
Leaf			3.89a	6.72a	15.42a	24.89b	0.95a
Safe limits[a]			0.2	0.3	2.3	40	60

FAO/WHO(2019)

Mean followed with same letter across the column are not significantly different p>0.05, n=6 replicates

Table 2b. Concentration of Heavy Metals in Crops Grown in Kwadam Gombe State (2018)

Name of Sample	Botanical Name	Hausa Name	Heavy metals mg/kg				
			Cd	Pb	Cr	Cu	Zn
Lettuce	*Lactuca sativa*	Salad					
Root			2.19a	23.46b	ND	9.01a	1.23a
Stem			3.05a	9.15a	14.17a	13.08a	2.52b
Leaf			3.43a	10.79a	16.83a	13.00a	1.89a
Maize	*Zea mays*	Masara					
Root			1.90a	34.20a	8.33b	113.68a	2.15b
Stem			0.75b	32.84a	ND	85.56a	1.11a
Leaf			0.63b	34.58a	3.67b	67.56a	1.93ab
Fruit			0.33b	34.58a	4.17b	92.30a	1.73ab
Rice	*Oryza sativa*	Shinkafa					
Root			0.85a	ND	10.33b	43.14b	1.52a
Stem			ND	ND	3.92a	22.65a	1.62a
Leaf			ND	ND	ND	ND	ND
Fruit			0.87a	1.75	2.17a	436.75c	1.70a
Safe limits[a]			0.2a	0.3	2.3	40	60

FAO/WHO(2019), Mean followed with same letter across the column are not significantly different p>0.05, n=6 replicates

Table 3. Heavy Metals Concentration in the Soils of Crops Grown in Kwadam Gombe State (2018)

Soil from the land of	Botanical Name	Hausa Name	Heavy metals mg/kg				
			Cd	Pb	Cr	Cu	Zn
Tomato	*Solanumlycopersicum*	Tomatur	5.76a	1.11a	14.17ab	10.98d	5.32a
Pepper	*Capsicum annuum*	Attarugu	11.38cd	0.95a	18.67c	7.50c	5.63a
Cayanne Pepper	*Capsicum frutescens*	Borkono	13.42d	ND	19.42c	3.88ab	5.28a
Onion	*Allium cepa*	Albasa	11.08bcd	2.45b	15.08b	6.69b	5.50a
Spinach	*Spinaciaoleracea*	Alayyaho	7.14abc	ND	12.17a	3.08a	4.89a
Lettuce	*Lactuca sativa*	Salad	7.94ab	ND	14.50ab	5.05abc	5.18a
Maize	*Zea mays*	Masara	10.82bcd	3.22b	18.25c	6.96bc	6.33a
Rice	*Oryza sativa*	Shinkafa	14.78d	ND	18.83c	3.79ab	5.06a
Control	Control soil	Control	0.02	0.06	0.08	3.00	2.87
limits[a]UNEP, (2013)			10	200	200	50	250
NESREA, (2011)			3	NIL	100	100	NIL

Permissible Limits: UNEP, 2013

Mean followed with same letter across the column are not significantly different p>0.05, n=6 replicate

Table 4. Bioaccumulation Factor (BAF) Of Heavy Metals in the Edible Parts of Crops Grown in Kwadam Gombe State(2018)

Name of Sample	Botanical Name	Hausa Name	BAF				
			Cd	Pb	Cr	Cu	Zn
Tomato	*Solanumlycopersicum*	Tomatur	0.37	25.55	ND	2.38	0.11
Pepper	*Capsicum annuum*	Attarugu	0.32	20.61	0.04	1.36	0.28
Cayanne Pepper	*Capsiciumfrutescens*	Borkono	0.15	ND	ND	8.67	0.25
Onion	*Allium cepa*	Albasa	0.21	6.51	ND	1.59	0.18
Spinach	*Spinaciaoleracea*	Alayyaho	0.54	ND	1.27	8.07	0.19
Lettuce	*Lactuca sativa*	Salad	0.43	ND	1.16	2.57	0.36
Maize	*Zea mays*	Masara	0.03	10.75	0.23	13.26	0.80
Rice	*Oryza sativa*	Shinkafa	0.06	ND	0.06	115.19	0.34

BAF value greater than >1 is indicating high uptake of metal

Estimated daily intake (EDI)

The result of the estimated daily intake of metals for adults (average age 60 years) in crops grown in 2018 season are presented in (Table 6). The result of the estimated daily intake from the consumption of all the studied cropsranged from 0.0006-0.0056, 0.0025-0.0540, 0.0010-0.0241, 0.0186-0.6260, 0.0009-0.0027 mg/kg/bw/day for Cd, Pb, Cr, Cu, and Zn respectively (Table 6).The EDI result showed that the consumption of all crops for Cd, Pb and Cu in *Capsicum annuum*, *Capsicum cerasiforme ,Zea mays, Oryza sativa* grown in 2018 season had exceeded the oral reference dose RfD US-EPA, (2013) and could pose human health risk

Estimated Hazard Quotient (HQ) and Hazard Index (HI)

The result of the estimated hazard quotient through the consumption of the studied crops grown in 2018 season are presented in (Table 7). The result of this study indicated that the consumption of all the studied crops grown in 2018 seasons are unlikely to pose health risk to human as the HQ values are less than < 1 for all heavy metals (Table 7.) except for Pb (1.15) in *Capsicum annuum*.. Therefore HQ>1 showed through the consumption of *Capsicum annuum* (1.15) for Pb can cause health risk in human. The result of the estimated hazard index for all metals through the consumption of all the studied crops grown in 2018 ranged from (0.79) in *Lactuca sativa* to (1.49) in *Oryza sativa* (Table 7).However HI> 1 through the consumption of *Oryza sativa*, *Zea mays*, and *Solanumlycopersicum* grown in 2018 for all heavy metals could cause severe heath risk to human.

Table 5. Pollution Indices of Heavy Metals in the Edible Parts of Crops Grown in Kwadam Gombe State (2018)

Name of Sample	Botanical Name	Hausa Name	Pollution index				
			Cd	Pb	Cr	Cu	Zn
Tomato	*Solanumlycopersicum*	Tomatur	10.63	94.39	ND	0.65	0.01
Pepper	*Capsicum annuum*	Attarugu	2.13	65.28	0.29	1.50	0.03
Cayanne Pepper	*Capsicum frutescens*	Borkono	10.04	125.53	ND	0.84	0.02
Onion	*Allium cepa*	Albasa	11.38	53.19	ND	0.27	0.02
Spinach	*Spinaciaoleracea*	Alayyaho	19.46	22.39	7.32	0.62	0.02
Lettuce	*Lactuca sativa*	Salad	17.13	35.97	1.81	0.33	0.03
Maize	*Zea mays*	Masara	1.67	115.28	0.94	2.31	0.03
Rice	*Oryza sativa*	Shinkafa	4.33	5.83	6.70	10.92	0.03

N.B PI value greater than >1 is indicating high pollution load

Table 6. Estimated Daily Intake of Metals (EDI) (Mg/Kg/Bw/Day) Through Consumption of Crops Grown in GombeState (2018)

Name of Sample	Botanical Name	Hausa Name	Estimated daily intake				
			Cd	Pb	Cr	Cu	Zn
Tomato	*Solanumlycopersicum*	Tomatur	0.0030	0.0406	ND	0.0375	0.0009
Pepper	*Capsicum annuum*	Attarugu	0.0006	0.0281	0.0010	0.0860	0.0022
Cayanne Pepper	*Capsicum frutescens*	Borkono	0.0029	0.0540	ND	0.0481	0.0019
Onion	*Allium cepa*	Albasa	0.0033	0.0229	ND	0.0152	0.0014
Spinach	*Spinaciaoleracea*	Alayyaho	0.0056	0.0096	0.0241	0.0357	0.0014
Lettuce	*Lactuca sativa*	Salad	0.0049	0.0155	0.0060	0.0186	0.0027
Maize	*Zea mays*	Masara	0.0005	0.0496	0.0031	0.1323	0.0025
Rice	*Oryza sativa*	Shinkafa	0.0012	0.0025	0.0221	0.6260	0.0024
	RfD[a]		0.001	0.004	1.5	0.04	0.30

Oralreference dose (RfD):US-EPA, (2013)

Table 7. Hazard Quotient and Hazard Index for Adult Population through the Consumption of Crops Grown in Gombe(2018)

Name of Sample	Botanical Name	Hausa Name	Hazard Quotient(HQ)					Hazard Index(HI
			Cd	Pb	Cr	Cu	Zn	
Tomato	*Solanumlycopersicum*	Tomatur	0.26	0.86	ND	0.08	0.0002	1.20
Pepper	*Capsicum annuum*	Attarugu	0.05	0.60	0.00	0.18	0.0006	0.83
Cayanne Pepper	*Capsicum frutescens*	Borkono	0.24	1.15	ND	0.10	0.0005	1.49
Onion	*Allium cepa*	Albasa	0.28	0.49	ND	0.03	0.00040	0.80
Spinach	*Spinaciaoleracea*	Alayyaho	0.47	0.20	0.00136	0.08	0.00076	0.75
Lettuce	*Lactuca sativa*	Salad	0.42	0.33	0.00033	0.04	0.00070	0.79
Maize	*Zea mays*	Masara	0.04	1.05	0.00017	0.28	0.00069	1.38
Rice	*Oryza sativa*	Shinkafa	0.11	0.05	0.00125	0.08	0.00038	1.49

DISCUSSION

In this study, heavy metals concentrations Cd,Pb, Cr, Cu and Zn were detected in twenty commonly used pesticides (Insecticides, fungicides, herbicides). The concentration of cadmium, lead, and chromium in all the studied pesticides had exceeded the WHO, (2019) permissible limits. This indicates that the application of these pesticides by farmers in the study areas may lead to build up of heavy metals in the soil and uptake by plants. Plants fumigated with these pesticides may absorb these metals through soil-plant transfer to the edible parts and pose potential health risk to humans through consumption. Thus heavy metals from agrochemicals especially metal-based pesticides accumulate in soil and contaminate food crops through soil -plant heavy metals transfer (Wang a*et al.,* 2013). Defarge *et al.* (2018) in France have revealed for the presence of As (600ppb), Co (300ppb), Cr (200ppb), Ni,(1200ppb)Pb, (100ppb) as contaminants in 22 pesticide formulations at levels well above admissible ones in water at their recommended dilutions rate in Europe. Similarly, Gimeno-Gracia*et al.,* (1996) have previously revealed the presence of heavy metals in pesticides Cd (1.94 mg/kg) in Antracol, Cu (13.00 mg/kg) in Saturn-G, Pb(10.00 mg/kg) in Saturn-G, Zn (55.00 mg/kg) in Saturn G.

The presence of heavy metals in all these pesticides in northern Nigeria have been shown for the first time at levels well above the manufacturers recommended dilution rate. This maybe due to lack of effective monitoring and screening of these agrochemicals for heavy metals and other chemicals by regulatory agencies.

The concentrations of Cd, Pb and Cr in all the crops fumigated with pesticides were above the permissible limits by FAO/WHO (FAO/WHO, 2019),thus indicating contamination of these crops by Cd, Pb and Cr and might be as a result of high concentration of these metals in pesticides used. The presence of these metals have been detected in all the twenty pesticides used by farmers on these crops at recommended dilution rate. Heavy metals contents in pesticides have been previously established by Yuguda *et al.,* (2015); Defarge *et al.,* (2018). This study indicated that crops fumigated with metal based pesticides have resulted in higher accumulation of Cd, Pb, and Cr in all the crops at levels above the WHO, (2019) permissible limits and could therefore pose health risk to consumers. The maximum cadmium concentration of 4.68 mg/kg in *Solanumlycopersicum* stem was substantially higher than 0.67, 1.20, 0.41 mg/kg reported in Pakistan, Saudi Arabia,and Ethiopia Khannum *et al*. (2017); Balkhair and Ashraf, (2016); Eliku and Leta, (2017). Lead concentration of 38.08 mg/kg in *Capsicum cerasiforme* root was higher compared to 2.18, 0.47, 2.76 mg/kg reported in India, China, and Pakistan by Kumar *et al*., (2017); Hongwen, *et al*., (2017;Khannum, *et al*., (2017). The maximum chromium concentration of 16.83 mg/kg in *Lactucasativa* leaf was several fold higher than 0.84, 0.32, 0.077 mg/kg reported in Nigeria, India, and China Peters *et al*., (2018); Kulkarni *et al*., (2017);Liang *et al*., (2019). Cadmium has been shown to accumulate in human bones, lungs, liver, kidneys, nerve tissues, leading to their damage and malfunction (Tsutsumi *et a*l., 2014; Chakraborty *et al*., 2013).Lead has been linked to incidence of neurological disorders, hypertension, cognitive impairment, renal dysfunction, arthritis, hallucination, and vertigo (Patrick, 2006).).Chromium has been shown to cause ulcer, perforation of nasal septum, respiratory cancer and alterations in replication and transcription of DNA, and chromosomal aberrations in humans (Spector *et al*., 2011; O'Brien *et al*., 2001).

Zinc and copper concentrations in all crops were below the permissible limits WHO, (2019) except in some crops *Capsicum annuum* (stem, fruit), *Zea mays* (root, stem, leaf, fruit), *Oryza sativa* (root, fruit) for copper.This might be due difference in uptake capabilities, soil physicochemical properties, plant type, soil organic matter, pH, among others (Wang *et al*., 2013a, Sharma *et al*, 2008).

The mean concentration of heavy metals in the corresponding soils of all the studied crops for Cd, Pb, Cr, Cu, and Zn were below the permissible set by UNEP, (2013) and NESREA, (2011) for agricultural soil, except for Cd in the soils of some crops (*Capsicum cerasiforme, Capsicum annuum, Allium cepa, Zea mays*) which had exceeded the UNEP, (2013) limits. High heavy metals soil-plant transfer could be responsible for low heavy metals concentration in the corresponding soil of the crops. Osu and Ogoko (2014) and Jolly *et al*. (2013) have indicated that low metals concentration in soil than crops tissues reflects relatively poor retention in soil and greater efficiency of crops to absorb metals.

The ratio of soil –plant heavy metals transfer bioaccumulation factor showed that all the studied crops had BAF>1 for Cu and Pb and a decreasing order trend of Cu>Pb>Cr>Zn>Cd . This could be attributed to indiscriminate use of metal based pesticides with high traces of Cu and Pb. Bioaccumulation (BAF) is a key pathway of human exposure to heavy metals through food chain (Khan *et al*., 2008; Cui *et al*., 2004). Bioaccumulation factor values greater than one for Cu and Pb obtained in all the crops fumigated with metal based pesticides could be one of the possible reasons for health risks in humans through food consumption. Bioaccumulation factor values values varied among the studied crops and metals and this could be attributed to the differences in concentration of pesticides use, metal uptake, and plant types among others. The highest BAF values of 115.19 in *Oryza sativa* for Cu observed in this study was substantially higher than 0.16, 0.20, 0.15 reported in Ethiopia, Pakistan and Nigeria by (Eliku and Leta, 2017; Mahmood and Malik, 2014; Oti, 2015).

The pollution index (PI) values indicated all the studied crops had values greater than one for Pb and Cd indicating that these crops are considered unsafe for human consumption. This could be due to the presence of high traces of lead and cadmium in the pesticides. The maximum PI value of 115.28 observed in *Zea mays* was similar to 124.0 found in Beni seed by Oti, (2015) in Nigeria.

The estimated daily intake of metals revealed that the consumption of all crops for Cd, Pb and Cu in *Capsicum annuum*, *Capsicum cerasiforme, Zea mays, Oryza sativa* grown in 2018 season had exceeded the oral reference dose RfD US-

EPA, (2013) and could pose human health risk. The estimated daily intake was in a decreasing order of health risk Cd>Pb>Cu>Cr>Zn and the highest EDI value was 0.6260 *in Oryza sativa* for Cu, while the least was 0.0009 mg/kg/bw/day in *Solanumlycopersicum* for Zn. This result suggest that Cd and Pb were the major metals contributing significantly to the potential health risk through consumption of the studied food crops in the study area.

Hazard quotient revealed that the consumption of all the studied crops grown in 2018 seasons are unlikely to pose health risk to human as the HQ values are < 1 for all heavy metals. However, Hazard quotient through the consumption of *Capsicum annuum* (1.15) was >1 for Pband can cause slight health risk in human in the study area and even beyond.

The estimate of the potential health risk posed through the consumption of crops fumigated with heavy metals for more than one heavy metals Hazard index (HI), indicated that the inhabitants may experience adverse health risk through the consumption of *Oryza sativa*, *Zea mays*, *Solanumlycopersicum, and Capsicum frutescens* grown. The maximum hazard index value in this study (1.49) was substantially lower than HI value (7.315) in rice from industrial area in Bangladesh by Proshad *et al*., (2019).The estimated potential health risk could be attributed to the traces of heavy metals in pesticides used in the study area.

CONCLUSION

Despite the ban use of heavy metals in agrochemicals in (particular pesticides), this study revealed the presence of trace metals (Cd, Pb, Cr, Cu, and Zn) in twenty commonly selected pesticides use in agricultural farms in northern Nigeria. The concentrations of heavy metals (Cd, Pb, and Cr,) in all the pesticides (Insecticides, fungicides, and herbicides) had exceeded the WHO, (2019) permissible limits. Heavy metals (Cd, Pb, and Cr) concentrations in crops from agricultural farms fumigated with pesticides as the only source of contamination had exceeded the permissible limits by WHO, (2019). The heavy metals concentrations in the corresponding soils of the crops were below the permissible limit by (UNEP, 2013) and NESREA, (2011) for agricultural soil. Bioaccumulation factor (BAF) varied among studied crops and metals and BAF> 1 were observed in all the crops for Pb and Cu. Hazard quotient revealed potential health risk from the consumption of *Capsicum annuum* for Pb. However, the estimate of potential cumulative health risk from the consumption of crops for more than one metal (HI) indicated that the inhabitants may experience adverse health risk through the consumption of *Oryza sativa, Zea mays, Solanumlycopersicum, and Capsicum frutescens*. Regular screening and monitoring of heavy metals in pesticides should be enforced to minimize health risk of metals from the consumption of food crops fumigated with the pesticides.

Conflict of interest

The authors declare that they do not have conflict of interest.

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