

**INTERNATIONAL JOURNAL OF SCIENCE FOR GLOBAL SUSTAINABILITY****Investigation on Pesticide Residue Levels and Heavy Metal Concentrations in *Zea-Mays* and *Oryza Sativa* Grains in Biu Area****Chinda, B. and Yunus, M.M.**

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***Corresponding Author's Email:**ibnyunus2@gmail.com. **Tel:** +2348064683360, +2348027946665**Received on:** November 2018**Revised and Accepted on:** September 2019**ABSTRACT**

This work reports the result of the investigation of pesticide residues in maize and rice grains grown during the rainy season farming around Biu plateau area. The study aimed at assessing the amount of pesticides residue as well as determine the concentrations of some heavy metals like Cd, Cr, Pb and Mn present in the studied samples. The samples were treated under standard laboratory procedures and were analyzed for pesticide residues using GC-MS technique. The heavy metals presence was investigated using digital colorimeter (DR 3900, HACH). The study showed no presence of pesticide residues in the samples analyzed but revealed the presence of some heavy metals. Those of particular interest include Cd (0.079-0.087 mg/l), Pb (0.65-0.102mg/l) and Mn (0.699-0.770mg/l) as recorded for maize grains. While the results of the metals for rice grains reads as follows. Cd (0.106-0.111mg/l), Pb (0.060-0.065mg/l) and Mn (0.548-0.566mg/l). All the three heavy metals listed were found in maize and rice samples at levels slightly higher than the permissible limits stipulated by W.H.O./F.A.O. The element chromium was not detected among the samples studied.

Keywords: Assessment, Post-Harvest, Pesticides, Grain-Cereals, Organophosphorus**1. INTRODUCTION**

Pesticides are substances intended for controlling, preventing, repelling or destroying any biological organism deemed to be a pest. A plant or animal detrimental to humans or human concerns as in agriculture or livestock production is a pest or a pest is a competitor of humanity (Gressel, 2002, Ogah and Coker, 2012). Pesticides are widely used in producing food. Their residues may remain in small amounts in or on fruits, grains, vegetables and other foods. Research evidence have shown that pesticides or their residues have negative impact on the environment and human as well as animal health since they are exposed to them through their diets. The growing interest on consumption of organic products which provide a relatively high human nutritional value increases the production of organic crops. The use of pesticides have increased significantly in recent years, because of the growing demand for food production (Walorczyk,(2010), Kurtagic and Copra-Janicijevic, 2016 and Nadaf *et al.*,(2015).

Pesticides when used properly are of tremendous benefits to human beings but their indiscriminate use however may cause considerable hazards to health and environment. The controversy of use and abuse of pesticides has surfaced. Water pollution by pesticides result from massive application of these chemicals in agriculture and other branches of economy. The introduction of pesticide residues in the environment through agricultural processes is a serious environmental problem. Many organochlorine compounds, including pesticides such as DDT, DDE and HCB belong to the group of persistent organic pollutants and are among the most studied contaminants. Persistent organic compounds, are one of the greatest environmental pollutants which are environmentally harmful, because they have lipophilic properties, resistance to degradation, bio-accumulative capacity in the food chain, environmental mobility, carcinogenicity and metabolic disruptors, which pose threats toxic to humans and animals (Koskela, 2010;Tette *et.al.*, 2016 and Rosario *et*

al., 2016). Pesticides present the only group of chemicals that are purposely applied to the environment with aim to suppress plant and animal pests and to protect agricultural and industrial products. However, majority of pesticides are not specifically targeting the pest only as on application they also affect non-target plants and animals. Repeated application leads to loss of biodiversity. Many of them are not easily degradable. They persist in soil, leach to groundwater, surface water and contaminate wide environment. Depending on their chemical nature, pesticides enters an organism, bioaccumulate in food chain and consequently influence human health. Intensive pesticide application results in many negative effects in the environment that cannot be ignored (Winter and Kurtz, 2012). Presently, there is serious implication on environmental pollutants in relation to food security as several studies link pesticides presence of alterations in the health of people (Bergkvist *et al.*, 2012 and Lekei *et al.*, 2014).

Heavy metal contamination of food items is one of the most important aspects of food quality assurance (Khan *et al.*, 2012). Some of these heavy metals are necessary for humans in minute amounts (copper, chromium, manganese, nickel, lead, cadmium) while others are carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead, arsenic), the kidneys or liver (mercury, lead, cadmium, copper) or skin, bones, or teeth (nickel, cadmium, copper, chromium) (Zevenhoven and Kilpinen, 2011, Michalke, 2005; and Silva *et al.*, 2005). Through precipitation of their compounds or by ion exchange into soils and muds, heavy metal pollutants can localize and lay dormant. Unlike organic pollutants, heavy metals do not decay and thus pose a different kind of challenge for remediation. The production of grains using contaminated water raises concerns about the safety of such grains with respect to their heavy metal content. Heavy metals are kept under environmental pollutant category due to their toxic effect to plant, animals and human beings (Sharma *et al.*, 2006). Toxic metals can damage or reduce mental and central nervous function and damage blood composition, lungs, kidneys,

liver and other vital organs. It is not possible to completely avoid exposure to toxic metals, but their toxicity risk can be reduced through lifestyle choices that diminish the probability of harmful heavy metal uptake, such as dietary measures that may promote safe metabolism or excretion of ingested heavy metals (Singh, 2012). The contamination of grains with pesticides and heavy metals from soil or water poses a threat to human life. Large portion of maize crops are grown for purposes other than human consumption, rice is the most important grain with regard to human nutrition and caloric intake, providing more than one fifth of the calories consumed Worldwide by humans (Smith and Bruce; 1998).

So far, very few studies have been reported on the pesticides residue levels and heavy metals contamination in maize and rice from Biu area. This study aimed at assessing the amount of pesticides residue present in the grain cereals grown in the Biu plateau area of Borno and determine the concentrations of some heavy metals cadmium (Cd), chromium (Cr), lead (Pb) and manganese (Mn) in the would be studied grains.

2. MATERIALS AND METHODS

2.1 The Study Area

The study area is Biu in Borno State of Nigeria located on longitude 12.195°E and latitude 10.629°N. It lies on Biu plateau at an elevation of 626m altitude. The rainy season span between April – October (12.7mm to 15.25mm) with the month of August having the highest rainfall (228.60mm). The Area has two seasons, rainy and dry. The coldest months are November to February of another year while the hottest months are March to May. Only one harvest in a year is practiced in the area and is at the end of rainy season.

2.2 Sample Collection and Treatment

The samples of maize and rice grains were collected from different farmers' fields during harvest in an air tight polythene zip cover bags and transported to the laboratory within a day. The samples were stored in refrigerator till analysis is conducted. About 1-2 kg of each

sample was collected for extraction and purification during analysis.

2.2.1 Extraction and purification

Twenty grams (20.0g) each of powdered maize and rice samples were weighed and placed into two separate flasks. 80mL of Analar grade acetonitrile was added to each of the samples and extracted for 30 minutes using Ultrasonicator (model: AS 3120). The solutions were centrifuged at 6000rpm for 15mins. Supernatants were collected in different vessels for further treatments. 100mL of petroleum ether and dichloromethane (50:50 v/v) was added and allowed to stand for 10mins. The resultant solution was filtered through Buchner funnel containing (20g) anhydrous sodium sulphate to absorb the residual moisture. The extracts of samples were collected and transferred to 5mL glass vials for further analysis by GC-MS as reported with minor modification by Chang *et al.*, 2005.

2.2.2 Digestion of Samples

Two (2.0) grams of maize and rice (powdered) samples each were weighed and placed into a plastic microwave tube (Teflon vessel) and treated with 15ml mixture of HNO₃/HCl. This was allowed to stand for 15mins. The plastic tube was covered and placed in to a microwave digester (Master 40, Sino; China) and digested at 95°C for 45mins. the digest was cooled and filtered, then diluted to 25mL mark with distilled water. The heavy elements content of the samples were determined using digital Colorimeter (DR 3900 HACH, USA).

2.2.3 Samples Analysis

Analysis of samples for pesticide presence was performed using GC-MS machine (make: Agilent, model no.7890B, 5977A MSD; and HP-5MS) with fused silica capillary column of dimensions (30m x 0.25mm x 0.25 µm) for all the runs. Helium was used as carrier gas with a flow rate of 1.6mL/min. A 1µl aliquot of the extract was injected using the splitless mode. The oven temperature programmed at 60°C for 1min. and then raised to 210°C at 45°C/min. A mass hunter GC—MS solution software was used as the data analysis system.

3. RESULTS AND DISCUSSION

Although the application of synthetic chemical pesticides is not allowed in organic agriculture, there can be no assurance that crops are entirely free of pesticides (Walorczyk *et al.*, 2013).

The results of the study for pesticide residue analysis in maize sample grown in Biu area (Yamarkumi, Tum, Piku and Malang) are shown in Table 1.0. From the results, it suggests that the presence of pesticide residues were not detected. This could mean that the studied areas may be free from pesticide residue contamination. Table 2.0 shows the results for rice samples from the afore listed areas in Biu. The results indicate that the rice samples studied may also be free from pesticide residues contamination. Absence/presence of pesticide residues in crop samples depends on the frequency of use or otherwise of organic fertilizers. Farmers in rural areas have the option of using manure or organic fertilizers. In a situation the former uses manure in a farming season, presence of pesticide (organochlorine) residue in the farm produce is very slim.

Table 1: Concentration of Pesticide Residues (mg/L) in Maize Samples Collected at Different Places in Biu Area of Borno

Samples collection Area code		Ymk	Tm	Pk	Mln	Mean
Pesticides	El'tal Compositions					
Aldrin	C ₁₂ H ₉ Cl ₆	N.D.	N.D.	N.D.	N.D.	Nil
Lindane	C ₆ H ₆ Cl ₆	N.D.	N.D.	N.D.	N.D.	Nil
Chlorothalonil	C ₈ N ₂ Cl ₄	N.D.	N.D.	N.D.	N.D.	Nil
Diazinon	C ₁₂ H ₂₁ N ₂ O ₃ P ₅	N.D.	N.D.	N.D.	N.D.	Nil
Ethion	C ₉ H ₂₂ O ₄ P ₂ S ₄	N.D.	N.D.	N.D.	N.D.	Nil
Dichlorobenzophenone	C ₁₃ H ₈ Cl ₂ O	N.D.	N.D.	N.D.	N.D.	Nil
Dichlorodiphenyltrichloroethane	C ₁₄ H ₉ Cl ₅	N.D.	N.D.	N.D.	N.D.	Nil
α,Phenylphenol	C ₁₂ H ₉ OH	N.D.	N.D.	N.D.	N.D.	Nil
Malathion	C ₁₀ H ₁₉ O ₆ PS ₂	N.D.	N.D.	N.D.	N.D.	Nil
Chloropyrifos methyl	C ₇ H ₇ Cl ₃ NO ₃ PS	N.D.	N.D.	N.D.	N.D.	Nil

Ymk= Yamarkumi, Tm= Tum, Pk= Piku, Mln= Malang.

El'tal = Elemental, N.D. = Not Detected

On the other hand, absence of pesticide residues amongst the samples may be due to crops washed away by water runoff which may be

possible considering the undulating topography of the Biu plateau area.

Table 2: Concentration of Pesticide Residues (mg/L) in Rice Samples Collected at Different Places in Biu Area of Borno

Samples collection Area code		Ymk	Tm	Pk	Mln	Mean
Pesticides	El'tal Compositions	N.D.	N.D.	N.D.	N.D.	Nil
Aldrin	C ₁₃ H ₉ Cl ₆	N.D.	N.D.	N.D.	N.D.	Nil.
Lindane	C ₆ H ₆ Cl ₆	N.D.	N.D.	N.D.	N.D.	Nil.
Chlorothalonil	C ₈ N ₂ Cl ₄	N.D.	N.D.	N.D.	N.D.	Nil
Diazinon	C ₁₂ H ₂₁ N ₂ O ₃ P ₅	N.D.	N.D.	N.D.	N.D.	Nil
Ethion	C ₉ H ₂₂ O ₄ P ₂ S ₄	N.D.	N.D.	N.D.	N.D.	Nil
Dichlorobenzophenone	C ₁₃ H ₈ Cl ₂ O	N.D.	N.D.	N.D.	N.D.	Nil
Dichlorodiphenyltrichloroethane	C ₁₄ H ₉ Cl ₅	N.D.	N.D.	N.D.	N.D.	Nil
α,Phenylphenol	C ₁₂ H ₉ OH	N.D.	N.D.	N.D.	N.D.	Nil
Malathion	C ₁₀ H ₁₉ O ₆ PS ₂	N.D.	N.D.	N.D.	N.D.	Nil
Chloropyrifos methyl	C ₇ H ₇ Cl ₃ NO ₃ PS	N.D.	N.D.	N.D.	N.D.	Nil

Pesticide residues were not found in this study, thus; the results of this work suggests that, the areas studied are not polluted and are suitable for the development of grain crops such as maize and rice. Absence of insecticide residue in the maize and rice samples analyzed is highly significant in this study, because of its impact on public health and food safety. In many occasions, pollution of cereal crops is caused by pesticide application in the surrounding areas or by environmental contamination both of which didn't manifest here. Tamer and kaya (2013) investigated wheat and honey samples for the presence of organo phosphorus/organochlorine

insecticides in 30 different cities of Turkey using gas chromatography. No insecticide residue was detected in the samples analyzed.

From their study, they concluded that food grains may be cross contaminated in storage possibly by post-harvest application of pesticide. Therefore, measures need to be taken for continues monitoring and evaluation of pesticide residue even at consumer level.

The mean concentrations of cadmium (Cd), lead (Pb), chromium (Cr) and manganese (Mn) in maize and rice samples analyzed from the local communities around Biu are presented in Tables 3.0 and 4.0 respectively.

Table 3.0: Concentration of some heavy metals (mg/L) in Maize Samples Collected around Biu area

Samples collection Area code	Yamarkumi				Piku				Malang			
Elements	Ymk ₁	Ymk ₂	Ymk ₃	Mean	Pk ₁	Pk ₂	Pk ₃	Mean	Mln ₁	Mln ₂	Mln ₃	Mean
Cadmium (Cd)	0.085	0.080	0.089	0.085	0.077	0.074	0.085	0.079	0.085	0.091	0.084	0.087
Chromium (Cr)	N.D.	N.D.	N.D.	Nil	N.D.	N.D.	N.D.	Nil	N.D.	N.D.	N.D.	Nil
Lead (Pb)	0.074	0.059	0.049	0.065	0.079	0.069	0.085	0.078	0.101	0.099	0.105	0.102
Manganese (Mn)	0.766	0.756	0.748	0.757	0.688	0.706	0.702	0.699	0.768	0.769	0.772	0.770

Ymk= Yamarkumi, Pk= Piku, Mln= Malang. N.D. = Not Detected

Table 3.0 shows that, the mean concentrations of cadmium in maize samples analyzed ranged from 0.085 to 0.087 mg/l. The results indicated that Cd concentrations in maize samples studied is higher than the maximum allowed limit by the

world Health Organization (WHO) of 2012 and 2015. The mean concentrations of lead and manganese in maize samples analyzed are equally reported in the same table. The results showed that lead concentrations in maize

samples ranged from 0.065 to 0.102 mg/l, while that of manganese from same samples ranged from 0.699 to 0.770 mg/l, respectively. Values recorded for the two heavy metals in maize samples (lead and manganese) are on the high side compared to those of World Health Organization permissible levels. These values

can be attributed to leaching effect or water run off which originate from the hill top of the rocky surface, then flows to the lower level where the maize crops are grown. The heavy metals might have accumulated in the soil at the lower level due to leaching which manifested in the grain crops planted on the soil of that area.

Table 4.0 : Concentration of some heavy metals (mg/L) in Rice Samples Collected around Biu area

Samples collection Area code												
	<i>Yamarkumi</i>				<i>Piku</i>			<i>Malang</i>				
Elements	Ymk ₁	Ymk ₂	Ymk ₃	Mean	Pk ₁	Pk ₂	Pk ₃	Mean	Mln ₁	Mln ₂	Mln ₃	Mean
Cadmium (Cd)	0.117	0.097	0.104	0.106	0.112	0.102	0.110	0.108	0.105	0.113	0.115	0.111
Chromium (Cr)	N.D.	N.D.	N.D.	Nil	N.D.	N.D.	N.D.	Nil	N.D.	N.D.	N.D.	Nil
Lead (Pb)	0.068	0.059	0.065	0.065	0.066	0.061	0.068	0.060	0.068	0.058	0.071	0.064
Manganese (Mn)	0.548	0.564	0.559	0.556	0.545	0.560	0.554	0.548	0.554	0.549	0.540	0.553

Heavy metals may enter the human body via consumption of contaminated drinking water or ingestion of soil or crops grown on contaminated land as reported by Dudka and Miller (1999) and Cambra *et al.*, 1999. Metals such as lead, mercury, cadmium and copper are cumulative poisons, cause environmental hazards and are reported to be exceptionally toxic (Yargholi and Azimi, 2010). Bioaccumulation of these heavy metals in man, animals and plants result in metal poisoning (Audu and Lawal, 2005). The two results suggested that, concentrations of both heavy metals in the maize samples analyzed are slightly higher than the recommended levels by WHO and standard organization of Nigeria (SON).

Table 4.0 shows that, the mean concentrations of cadmium in Rice samples analyzed ranged from 0.105 to 0.111 mg/l. The results indicated that Cd concentrations in rice samples studied is higher than the maximum allowed limit by the world Health Organization (WHO) of 2012 and 2015. The mean concentrations of lead and manganese in rice samples analyzed are equally reported in Table 4.0. The results showed that lead concentrations in rice samples analyzed ranged from 0.060 to 0.065 mg/l, while that of manganese from same samples ranged from 0.548 to 0.556 mg/l, respectively. The study also indicated no presence of chromium element in all the samples analyzed. This suggests one of the two possibilities. It could possibly mean that,

the results suggested that, no trace of Cr in the samples were detected, or it could be the concentration of chromium in the studied samples (maize and rice) is far less than the amount the sensitivity of the machine used can detect; undetectable to our test.

Lead is the main cause for concern in terms of contamination of cereals and vegetables. Lead is toxic and can be harmful to plant, though the plants usually show ability to accumulate large amounts of lead without showing visible changes in their appearance or yield (Wierzbicka, 1995).

Lead is a trace element in soil and there has been concern about its toxicity to organisms. It has been used in leaded petrol, diesel oil, and there has been concern that it is the main pollutant from traffic activities (Monaci *et al.*, 2000, Oliva and Espinosa, 2007). Literature revealed that, pollution of Pb from the fertilizers was minor when compared to the atmospheric deposition (de Vries *et al.*, 2002). The three elements discussed above which include; Lead, Cadmium and Manganese were detected in the dried Maize and Rice samples and were found to be slightly in concentrations higher than the permissible limits as authorized by WHO. These values could be influenced by many factors which may include heavy use of chemical fertilizers, pesticides/herbicides or anthropogenic activity.

4.0 CONCLUSION

The results of the study showed that maize and rice samples analyzed do not contained pesticide residues. Hence the cereal grains are not contaminated by pesticides. However, the study reveals the presence of cadmium, lead and manganese in both the maize and rice samples.

The concentrations of these elements are in all cases slightly higher than the permissible limits of consumption by W.H.O. and F.A.O. The implication of this is that, continuous consumption of these grains will eventually result to health consequences. This result for now, would serve as a baseline data for assessing the distribution of these heavy metals in the grains grown around Biu area of Borno state.

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