

PESTICIDE RESIDUE IN MAIZE STORED IN BASSA, BOKKOS, JOS – NORTH AND MANGU LOCAL GOVERNMENT AREA WAREHOUSES, PLATEAU STATE

Atsen S.N.1*, Mafuyai G.M.1 and Eneji I.S.2

¹Department of Chemistry Faculty of Natural Sciences, University of Jos, Nigeria.

²Department of Chemistry College of Sciences Federal University of Agriculture Makurdi.

ABSTRACT: Maize grains are highly susceptible to infestation by weevils and are consequently often subjected to post-harvest treatment with pesticides, to maintain good quality during storage and to avoid economic losses. Pesticide residues have become a major group of environmental contaminants as a result of the application of pesticides on harvested maize. In this study, it was revealed that Dichlorvos T. found in maize, was below detectable limit in the four local government areas, while aluminium phosphide in all the areas studied was above the EU/WHO permissible limit of 0.01ppm. Atrazine, a herbicide used to control weeds in farms, was found to be 0.14ppm in maize in MG, higher than the permissible limit of 0.05ppm. Therefore, these may cause health hazards.

KEYWORDS: Pesticide, Contamination, Maize.

INTRODUCTION

Pesticides are chemical agents capable of destroying pests or controlling their growth, and used in agriculture to boost food supply by protecting crops against destructive pests, both in the field and during storage. They have gained widespread use in agriculture and food preservation, but have consequently become a major group of environmental contaminants that impact on human health (Antoniou *et al.*, 2006).

The use of pesticides varies from dressing of seeds, treatment of soil, spraying of fields and post-harvest treatment of farm produce. Pesticides are also applied to grains and pulses during storage to prevent pest infestation (Ogah and Coker, 2012). This pesticide or insecticide remains active in our food commodities—even after evaporation, distillation, filtration or any similar process—for a period of time. Maize (*Zea mays*) is the third most important cereal crop after rice and wheat. It has the widest distribution and is primarily grown for its grains; consumed as human food and animal feed. The crop is high yielding, easy to process and easily digestible; it matures early, costs less than other cereals and can be grown across a range of agro-ecological zones (Osipitan *et al.*, 2012).

Pesticides have become a major group of environmental contaminants. When used, they contaminate the environment and accumulate in the food chain, thereby posing a hazard to human health (Leong *et al.*, 2007). Therefore, there is a need for the establishment of legal and technical bodies to control their level and continue the search for those that are less persistent and less toxic (Blaco *et al.*, 2003).



Ogah and Coker (2012) reported pesticides concentrations on maize to range from 15.8 to 3951.2μ g/kg. Pirimiphos-methyl was the most frequently encountered, occurring in 43% sample while residues of fenitrothion occurred in 7% sample.

Maize, like most grains, is highly susceptible to infestation by weevils and is consequently often subjected to post-harvest treatment with pesticides, to maintain good quality during storage and to avoid economic loses. Apart from post-harvest treatment previously treated, contaminated soil can be a source of these pesticide residues in food crops. If the pesticide residue is found to exceed the maximum residue level (MRL) in a given food stuff, the food commodity is said to be adulterated because it contains an illegal amount of the residue. The occurrence of pesticide above MRLs in the maize sample is therefore an indication of some forms of misuse/abuse of these chemicals. Non-compliance with MRLs can impact negatively on international trade in agricultural produce, as each commodity must meet international standard or the standard of the receiving country.

Pesticide residues, mostly found in food samples like cereals (grains), originate from pesticides that are intentionally applied to grain before and after harvest for storage, to preserve the grains for consumption and for commercial purposes. Pesticide residues are substances or mixtures of substances in food; these substance or mixtures are specified derivatives, such as degradation and conversion products, metabolite reaction product impurities, which are considered to be of toxicological significance (Obida *et al.*, 2012).

The rate at which pesticides are used—to combat pests in the storage of grains and to prevent infestation—is alarming. This is because their residues in food commodities constitute a potential hazard to man; therefore, there is a need for all regulatory agencies and researchers to rise up to save Nigeria and the world from the dangers of consuming foods containing unacceptable levels of chemicals. The main aim of this study is to determine the amount of pesticide residues in maize storage as one way of monitoring effectiveness, regulatory control measures and ensuring safety of our food, and also contribute to building a data base of pesticide residues on maize grain, preserved in the four Local Government Areas.

METHODOLOGY

Study Area

The study was carried out in four Local Government Areas of Plateau State namely: Bassa (BS), Bokkos (BK), Jos – North (JN) and Mangu (MG) as shown in (Figure 1). The targeted Local Government Areas lie within 9^0 27'49''N to $10^010'56''N$ and $8^049'45''E$ to $9^09'22''E$. The total population in the area is extrapolated to be eight hundred and fifty-four thousand and forty-two (854,042) as at NPC, 2006. The major occupation in these areas is farming as over seventy percent (70%) of the entire population engage in farming activities.

Sampling

Four (4) samples each of equal weight were collected at different points from the stores of BS, BK, JN and MG Local Government Areas and each composite sample analysed for proximate composition using the Associate of Official Analytical Chemist (AOAC, 2010).



Samples were harvested directly from the maize farms during the period under review. All the composite samples in the four (4) Local Government Areas were analysed for pesticide residue, as described by Association of Analytical Chemists (AOAC, 2007). In the laboratory, the samples were stored at low temperature of 4°C to arrest any pesticide degradation before analysis.





Sample Storage /Preparation

Before analysis, the maize samples were stored at low temperature of 4^{0} C in an amber bottle in the refrigerator, to arrest any pesticide degradation (Rashid *et al.*, 2010). The maize samples were sorted out by picking out the stones and other foreign materials. Thereafter, the samples were pounded in a mortar with pestle before grinding, to homogenize, using a blender.

Extraction

5g of maize sample was transferred into a 50mL sample vial; 10 mL of de-ionize water was added and allowed to stand for 10 minutes, after which 15mL of 1% acetic acid in acetonitrile mixture was added. Exactly 4g of anhydrous magnesium sulphate and 2g of sodium acetate was added into the resultant mixture inside the sample vial. The mixture was shaken vigorously for 5 minutes using a vortex mixer and centrifuged at 2500rpm for 10 minutes.

D-SPE (Dispersion solid phase extraction cleanup)

Exactly 5mL from 50mL sample vial was transferred into a 15mL sample vial containing 75mg of anhydrous magnesium sulphate. About 12.5mg primary amine and 12.5mg secondary amine (PSA) were added. The extract was shaken in a vortex mixer and centrifuged at 2000rpm for 5 minutes. About 4mL from the 15mL sample vial was transferred into a sample tube for GC-MS analysis.







Preparation of Calibration Curves (Dichlorvos and Atrazine)

Stock solution: 500mg/mL reference standard solution of all the pesticides were prepared in 100mL each; this was followed by serial dilution to produce various concentrations (0.05 to 8.0mg/mL 50mL of individual pesticides). The stock standard solution was stored in an amber bottle at 4°C in a refrigerator and working standard solution was prepared fresh each time for use.

Standard solutions of pesticide were then run on a GC-MS under the set chromatographic condition of Agilent technologies 7890A, a detector mass spectrophotometer (MS) 5795C, column thickness of 0.25 micrometer and carrier gas helium rate of 1mL/min. The pesticide residue concentration was determined by comparing the sample peak area with those of standard.

 $CF = \frac{Peak area of standard}{total amount of standard inject}$ Pesticide content = $\frac{AS}{Wts} \times \frac{VF}{CF}$ where; AS = peak area of sample
VF = final volume of clean extract
Wt = weight of sample extracted
CF = Calibration factor

Pesticides residues were identified when the retention times match the retention time of the standard, and the relative abundance was within 10% of those of the standard. Identification of pesticides was quantified using the external standard method of comparing sample peak areas with that of pesticide standard under the same condition. Each composite sample was analysed base on the standard method.

RESULTS AND DISCUSSION

LGA	Dichlorvos	Atrazine
BS	Below detection	Below detection limit
	limit	
BK	Below detection	0.02
	limit	
JN	Below detection	0.02
	limit	
MG	Below detection	0.14
	limit	
FS	0.46	1.38
Max. Std Limit by WHO and	0.01	0.05
EU		

Table 1. Concentration (ppm) of Pesticides Residues in Maize from the Study Area

BDL: Below Detection Limit, BS: Bassa, BK:Bokkos, JN:Jos-North, MG:Mangu, FS: Field Sample.



The pesticide residues, which are mostly found in our food sample like cereals (maize grain), originate mainly from pesticides that are intentionally applied to the grains before and after harvest. The pesticides are applied for storage, to preserve the grain for consumption and economic purpose. Hence, residues which remain on the grain as a result of persistence constitute a potential health hazard to man (Leong *et al.*, 2007). The GC-MS chromatogram of the standard pesticides is shown in figure 3.

Dichlorvos

The mean result of dichlorvos concentration in (ppm) of maize samples from BS, BK, JN, MN and field sample in table 1, shows that it was below the detection limit (BDL) in the maize samples obtained from all the stores in the Local Government Areas studied, while 0.46 ppm was found in field samples. Although, different half-lives of dichlorvos have been reported in rat kidney (13.5 minutes), on wheat (54 hours), in aqueous solution at pH 7 (5.2 days) and 20mg/kg as emulsified concentrate (fogging), the half-life is 7 days (FAO, 1989). Comparing the result with maximum standard limit by World Health Organisation (who's) and European Union (EU) (2012), it is clear that the concentration of dichlorvos in the field sample exceeds the standard maximum residue level (MRL) of 0.01ppm. However, the presence of 0.46ppm from the field sample could be as a result of the time of application of pesticide with respect to climate variables like moisture, temperature and sunlight (Manathan *et al.*, 2001). Microbial decomposition is noted to increase with sunlight intensity (Halllar *et al.*, 2012).

Atrazine

The mean values obtained for atrazine—BS (not detected), BK (0.02ppm), JN (0.02ppm) and MN (0.14ppm) are shown in table 1. The results from BK and JN were below the standard permissive level of 0.05ppm standard, while the results from MG (0.14ppm) and field sample (1.38ppm) were above the standard permissible level of 0.05ppm (WHO and EU, 2012). The degradation of atrazine and plant uptake depends on environmental factors (soil chemistry and microbial activity) and its bioavailability for plant uptake. Atrazine degradation in soil is often slower at high pH, meaning that at pH above 7.0, atrazine has a longer half-life and more is made available for plant uptake (Hellear *et al.*, 2002).

Aluminium phosphide (AlP)

Maize samples show various mean concentrations of Aluminium phosphide (ALP) also called Justoxin, as analysed using UV-visible spectrophotometer as shown in table 2. The result shows the following mean concentrations (ppm) for BS (0.108), BK (0.101) and JN (0.099), while MN and field sample (0.082). The results of aluminum phosphide obtained in this work from the calibration curve (Figure 4) were high compared to the recommended permissible level of 0.01 ppm (EU and WHO, 2012). Therefore, the result obtained in this study poses a threat to human health as it has no antidote. The phosphine gas is the active pesticide component of aluminium phosphide, which is rapidly absorbed by inhalation, ingestion and skin contacts (Sudakin, 2005).



Name of Site	Concentration in mg/L
BS	0.108 ± 0.054
ВК	0.101 ± 0.051
JN	0.103 ± 0.052
MG	0.099 ± 0.049
FS	0.082 ± 0.021

Table (2.	Mean	Concentration	(nnm) of Aluminum	Phos	nhide in	Maize
I abit	4 •	witan	Concenti ation	(phu) VI AIUIIIIUIII	1 1105	pmue m	Maile

$A1P + 3H_2O \rightarrow Al (OH)_3 + PH_3$

This could be as a result of abuse of pesticide by the farmers; also the degradation of aluminium phosphide may be affected by environmental factors such as absolute humidity moisture. Xianchang (1998), reported that the rate of evolution of phosphine from aluminium phosphide was directly influenced by absolute humidity but was not directly influenced by temperature, and that the decomposition times ranged from 36 to 204 hours. The toxic effects of the AIP are due to deadly phosphine gas liberated when it reacts with water or hydrochloric acid in the stomach. This phosphine inhibits cellular oxygen utilization and can induce lipid peroxidation (Moghadamnia, 2012). Ferrer *et al.* (2009) reported that exactly three (3) grams of AIP releases 1 gram of phosphine and the fatal dose for a 70kg adult is 15–500mg. The permissible exposure limit is 0.3ppm over a period of 8 hours (Sudakin, 2005).

CONCLUSION

The pesticides audit revealed that three pesticides (atrazine, dichlorvos and aluminium phosphide) were the most common. While dichlorvos and aluminum phosphide were used for the preservation of maize, atrazine which is a herbicide, may have occured in the maize through plant uptake from the soil. The order of pesticide residues in the maize grains of the study areas were as follows:

Atrazine:	MG > BK = JN > BS
Aluminium phosphide:	BS > JN > BK > MG
Dichlorvos:	BS = BK = JN = MG

Generally, the concentration of dichlorvos in maize grains from all the study areas were below the detection limit except the field sample that was about a factor of fifty (50) higher than the recommended value.





Figure 3: GC-MS Chromatogram Standard Pesticides





Figure 4. Calibration Curve for Aluminium Phosphide

REFERENCES

- Antoniou CV, Koukouraki EE, Diamadopoulos E (2006). Determination of chlorinated volatile organic compounds in water and municipal wastewater using headspace-solid phase mic roextraction-ga schromatography. *Journal of Chromatographic A*, 1132(1-2), 310-314.
- Association of Analytical Chemists (AOAC) (2007). Pesticide Residues in food by Acetonitride extraction and portioning with magnesium sulfate. Retrieved March-April 2007 from http://www.eber;hu/pdf/Quechers/ Abac 2007-01 pdf.
- Blasco C., Fernandez M., Pena A., Lino C., Silveira M., Font G. and Pico Y. (2003). Assessment of pesticide residues in honey samples from Portugal and Spain. *Journal of Agriculture and Food Chemistry*.51 (27): 8132 – 8138.
- Ferrer, M. I., Alvarez, L. F., and Cepero, R. A. (2009). Suicide by Ingestion of Aluminium Phosphide: A case Report, *Emergencia*, 21: 228 231.
- Food and Agricultural Organization (FAO) (1989). *International code of conduct on the distribution and Use of Pesticides*, Rome, Italy.
- Hellar, H. (2002). Pesticides Residues in Sugarcane Plantations and Environs After Long-Term Use; The Case of TPC Ltd, Kilimanjaro Region, Tanzania.
- Leong K. H., Tan, L. B. and Mustafa, A. M. (2007). Contamination levels of selected organochlorineandorganophosphate pesticides in the Selangor River, Malaysia between 2002 and 2003. *Chemosphere*. 66(6): 1153 – 1159.
- Manahan, S.E. (2001). *Fundamentals of environmental chemistry second Edition*, USA: Lewis Publisher.
- Moghadamnia, A. (2012). An update on toxicology of aluminum phosphide, *DARU Journal* of *Pharmaceutical Sciences*. Pp. 1–8.
- National Population Census (NPC) (2006). Population of Bassa Bokkos, Jos North and Mangu.



- Obida M. Gwary, Stephen S. Hati, Goni A. Dimari and Victor O. Ogugbuaja. (2012). Pesticide residue in Beans sample from North Eastern Nigeria. Vol 2. pp 79-84. ARPN *Journal of Science and Technology*. University of Maiduguiri, Nigeria.
- Ogah, C. O. and Coker, H. B. (2012). Quantification of Organophosphate and Carbamate Pesticide Residues in Maize. *Journal of Applied Pharmaceutical Science*. 2(9):093 – 097.
- Osipitan A. A., Olaifa, O. K. and Lawal O. A. (2012). Evaluation of proximate composition of maize grains infested by weevil (StophilusZeamais L) (ColeopteraCurculionidae). *Munis Entomology and Zoology*, 7(1): 439 445.
- Rashid, A., Nawaz, S., Barker, H., Ahmad, I. and Ashraf, M. (2010). Development of a Simple Extraction and Clean-Up Procedure for Determination of Organochlorine. *Pesticides Chromatography* A, 1217 (17): 2933 – 2939.
- Sudakin, D. L. (2005). Occupational exposure to aluminium phosphide and phosphine gas. A suspected case report and review of the literature. *Human Experimental of Toxicology.*, 24: 27 – 33.
- World Health Organization and European Union (2001). *Chemistry and specification of pesticides. Technical reports series* 899. Geneva.
- Xianchang, T. (1998). Evolution of phosphine from aluminum phosphide at various temperature and humidity. Proceeding of the 6th international conference on stored-product protection, I: 201 203.

Copyright © 2020 The Author(s). This is an Open Access article distributed under the terms of Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0), which permits anyone to share, use, reproduce and redistribute in any medium, provided the original author and source are credited.