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Concentration of Pesticide Residue in Beans and Maize Grains in Bodija Market, Ibadan, Nigeria

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Abstract
Excessive pesticide application for food preservation constitutes a public health hazard. Cases of food poisoning from pesticide residue have been reported but little effort has been made on good pesticide application practices and Pesticide residue analysis. This study assessed levels of Pesticide residue in beans and maize grains in Bodija market, Ibadan. Nine composites, each comprising 14 grab samples of beans were collected from 3 sources: A, B, C, from 126 beans sellers. Six composites, each comprising 24 grab samples of maize were collected from 2 sources: X_1 and X_2, from 144 maize sellers. Samples were collected in triplicate by Systematic Sampling Technique. Collected samples were prepared and analyzed with Gas Chromatography- Mass Spectrometry. Mean concentration of Pesticide residue in food samples were compared with codex standard (2ppm). Data were analyzed using descriptive statistics. Mean concentration of Pesticide residue in beans A,B and C were:253±34.9ppm, 4.8±3.2ppm,16.2±13.6ppm ($p<0.05$), while that of maize X1 and X2 were 0.62±0.04 ppm and 0.65+0.06 ppm respectively. The concentration of Pesticide residue in the beans was high, thus toxic to human while that of maize was within Codex acceptable limits. Therefore, education on pesticide use and promotion of good pesticide application should be adopted.

Concentration de résidus de pesticides dans les haricots et les grains de maïs au marché de Bodija, Ibadan. Nigéria

Résumé
Application excessive de pesticides pour la conservation des aliments pose un danger pour la santé publique. Des cas d'intoxication alimentaire par des résidus de pesticides ont été signalés, mais peu d'efforts ont été déployés pour appliquer de bonnes pratiques d'application de pesticides et analyser les résidus de pesticides. Cette étude a évalué les niveaux de résidus de pesticides dans les haricots et les grains de maïs au marché de Bodija, Ibadan. Neuf composites, comprenant chacun 14 échantillons choisis de haricots ont été collectés à partir de 3 sources : A, B, C, provenant de 126 vendeurs de haricots. Six composites comprenant chacun 24 échantillons de maïs ont été

collectés à partir de 2 sources : X1 et X2, auprès de 144 vendeurs de maïs. Les échantillons ont été recueillis en triple par technique d'échantillonnage systématique. Les échantillons recueillis ont été préparés et analysés par chromatographie en phase gazeuse-spectrométrie de masse. La concentration moyenne de résidus de pesticides dans les échantillons d'aliments a été comparée au codex standard (2 ppm). Les données ont été analysées à l'aide de statistiques descriptives. La concentration moyenne de résidus de pesticides dans les fèves A, B et C étaient les suivants : 253 + 34.9ppm, 4,8 + 3.2ppm, 16,2 + 13.6ppm (p <0,05), tandis que celle de maïs X1 et X2 0,62 + 0,04 et 0,65 ppm + 0,06 ppm respectivement. La concentration de résidus de pesticides dans les haricots était élevée, donc toxique pour l'homme, tandis que celle du maïs se situait dans les limites acceptables du Codex. Par conséquent, une éducation sur l'utilisation des pesticides et la promotion d'une bonne application des pesticides devrait être adoptée.

Introduction

Pests constitute all kinds of organisms which cause injury, disease or destruction to crops and livestock, goods and structures. It constitutes an overall hazard to man himself. Man is waging a continuous struggle against these pests in order to protect his food, shelter and his living condition.In the developing world, pests caused an estimated $12.8bn, $145.2bn and $21.72bn losses in Africa, Asia, and Latin America respectively from 1988-1990 (Rosendahl *et al*. 2008).

An estimated 34% of the population in developing countries suffer from malnutrition; In 1985, the ratios for malnourished and healthy people were 1:3 in Africa, 1:5 in East Asia and 1:7 in Latin America. Current estimates put global losses due to insect pests, diseases and weeds at $US300 billion annually. (FAO/IAEA, 2003).

Pesticides have a long history of use against insect and other pests. In the beginning, these were either inorganic chemicals or compound extracted from plant and animal sources. Since before 20 BCE, humans have made use of pesticides to protect their crops (Miller, 2002) The first legislation providing federal authority for regulating pesticides was enacted in 1910. (Goldman, 2007). However, decades later, during the 1940s, manufacturers began to produce large amounts of synthetic pesticides and their use became widespread (Daly *et al.,*1998). Some sources consider the 1940s and 1950s to have been the start of the "pesticide era"(Graeme,2005).According to the World Health Organization (WHO), 20% of pesticide use in the world, is in developing countries, and this use is increasing. (WHO, UNEP, 1990). Previous studies have indicated that the unsafe use of pesticides is common in developing countries. (Ecobichon, 2001). It has been estimated that about 125,000 - 130,000metric tons of pesticides are applied every year in Nigeria. (Asogwa and Dongo, 2009).

Pesticides are important management tool in agricultural enterprises: they protect produce against pests at post-harvest and storage. They have continued to be the bedrock of agriculture in modern times because of its unquantifiable benefits one of which include enhancement of shelf life of stored agricultural products. (Olabode *et al.,* 2011). It is maintained that for every dollar spent on pesticide for crop yield and storage, four dollars is saved. (Cooper and Dobson, 2007).

Grain storage plays an important role in the ability of any nation to feed its citizens. In predominantly agricultural countries, there is usually an abundance of food immediately after harvest. Where appropriate storage technology is available, the surplus is usually stored against the period of scarcity in countries where food storage has been perfected, such as in the United States of America and parts of Europe. In these countries, a period of scarcity has practically ceased to exist, as food is made regularly available irrespective of harvest time. (Nasiru, 2010).It is estimated that in the tropics between 25 and 40% of stored agricultural products is lost because of the inadequate farm- and village-level storage every year. (Jelle, 2003).

Grains are frequently stored for long term (3-36 months) at ambient temperature in bulk silos where insecticides may be applied post-harvest to reduce losses from storage pests. (Holland *et al* 1994). Grain- based foods, therefore, have the potential to be a major source of residue in the diet for these insecticides.

Cowpea *(Vignaunguiculata* (L.) Walp), one of the grains that suffer postharvest losses most, is a warm season, annual, herbaceous legume. It suffers heavily from insects, both in the field and when grains are stored after harvest. Yield reductions caused by insects can reach as high as 95%, depending on location, year, and cultivar. (Carlos,2000). Insect pests are major constraints to the production of cowpea. Cowpea is severely attacked at every stage of its growth by a myriad of insects, thus making the use of tolerant varieties and insecticide sprays, imperative. (Dugje *et al*., 2009).

In an attempt to reduce the incidence of insect pests of cowpea in the field and storage, the use of insecticides is usually relied upon. These insecticides are misused, overused or unnecessarily used by farmers and retailers who have very limited or no information about how to apply them or their health implications when present in foodstuffs.

Hence, harmful levels of pesticide residues or metabolites are left to be absorbed into the foodstuffs to which they are applied. For example, in Northern Nigeria, about 95 percent of stored cowpea is treated with insecticides and farmers use these insecticides even when they are not required.(Lowenberg-DeBoer and Ibro, 2008) while at the wholesale level, traders add pesticides after buying beans, before transporting them to market locations (Integrated Regional Information Networks, IRIN, 2008).

The indiscriminate use of insecticides in Nigeria has resulted in the occurrence of the residues in biotic and other abiotic compartments (Adeyemi *et al.,* 2008). Several cases of food poisoning after the consumption of meals prepared from cowpea grains and yam flour produced from dried yam chips which are suspected to contain an appreciable amount of organochlorine insecticide residues have been reported. (Adedoyin *et al*., 2008; Pesticide News,2008; Adeleke, 2009).

Pesticides may reach food and drinking water in a variety of ways, with the most obvious being through direct contamination of produce as the result of deliberate application to control pests on the growing crop. Residues in storage or transport facilities could also conceivably contaminate subsequently stored produce. (Jack and Sinclair, 2004.).

Exposure to pesticide residues through diet is assumed to be five orders of magnitude higher than other exposure routes, such as air and drinking water.(Juraske *et al.,* 2009). FAO/WHO (1990) stated that an approximately three million people are poisoned and 220,000 die each year around the world from insecticide poisoning, the majority of which occur in developing countries, although far greater quantities are used in developed countries (Bhanti *et al*., 2004).

Limited number of pesticide residues monitoring effort in the country have revealed the presence of pesticide residues in fish (Ogunfowokan *et al*., 2012); cereals (Osibanjo and Adeyeye, 1995), meat (Osibanjo and Adeyeye, 1997), fruits, vegetables and fresh yam tubers (Adeyeye and Osibanjo, 1999), blood of cocoa farmers and drinking water of farming communities (Sosan *et al*., 2008), smoked fish (Musa *et al.,* 2010), agricultural soils (Oyekunle *et. al*., 2011); maize samples (Ogar *et al*., 2011) and beans (*Phaseolus vulgaris* L.) (Ogah*et al*., 2012).Insecticide residues in food products are not properly monitored in Nigeria with virtually no data available on the levels of insecticide residues in cowpea grains and dried yam chips which constitute an important part of the meal of people of Nigeria. There is evidence that this group of chemicals is still being used in agriculture clandestinely under unknown trade names in developing countries such as Nigeria, (Fatoki and Awofolu, 2003; Sosan *et al*., 2008).

The objective of this study is to assess the concentration of pesticide residue in beans and maize grains in Bodija market, Oyo state, Nigeria.

Methodology

Study Area

The study was carried out in Bodija market in Ibadan North L.G.A of Oyo state, Nigeria in the year 2010. Bodija market is a central and popular market in Oyo state. It is known for storage and merchandise of agricultural produce such as maize grains, yam, yam chips, meat, cowpea and other cereals, etc.

Study design

The study was laboratory based. It involved analysis of pesticide residue in beans grains and maize grains collected from different beans and maize sellers in Bodija market.

Collection of beans sample

The beans samples were collected in triplicate from three different sources: A- beans that were just treated with pesticides by the raw food sellers, in preparation for storage, B- beans that were stored for 6 months after treatment, C- beans that were stored for two months after treatment. From each source, 14 grab samples of beans were collected from 14 different beans sellers using systematic sampling technique, and mixed together to form a composite sample. Three composites of beans were collected from each source to make a total of nine composite samples from 126 beans sellers in the market. A total of 126 samples were collected.

Collection of maize samples

Maize samples were collected in triplicate from 2 sources, X_1- maize in stores and X_{2-} maize on sale, respectively.

From each source, 24 grab samples of maize were collected from 24 different maize sellers using systematic sampling technique, and mixed together to form a composite of the sample. Three composites of maize were collected from each source, making six composites from a total of 144 maize sellers in the market. A total of 144 maize samples were collected.

The composite samples of beans and maize were collected with clean polythene bags, tied, properly labeled and transported to the laboratory immediately for analysis.

Laboratory analysis
Reagents and Chemicals

All reagents and chemicals used in this study were of analytical grade. All glass wares used were thoroughly washed and copiously rinsed with distilled water.

Sample preparation

The composite samples were ground properly with a blender until a homogeneous sample was obtained.

Sample extraction:

For each food sample, 5g of the homogeneous sample was weighed into a 50ml Teflon tube, 5ml of distilled water was added to it, 10ml acetonitrile was also added, and was shaken vigorously. A mixture of 6.0g extracts salt (4g MgSO4, 1g of Na Citrate dehydrate, 0.5g Na_2HCitratesesquihydrate) was then added and shaken properly. The mixture was then centrifuged for 1 minute and decanted.

Sample clean- up:

After the sample extraction, 6ml of the supernatant from the extract was transferred into a 10ml Teflon tube, 1.05g of the cleanup salts (a mixture of 900 mg of $MgSO_4$ and 150 ml of PSA) was added and was shaken properly for 20 seconds and then centrifuged.

Sample analysis:

1ml of the cleaned up extracts was taken and dried up in Nitrogen to remove acetonitrile and was then mixed up with 1 ml acetone. The mixture was shaken, and transferred into vials and was injected into the gas chromatography/mass spectrometry (GC/MS) machine for pesticide residue analysis, using quick, easy, cheap, effective, rugged and safe method designed by Michelangelo *et al*

2003. The sample blank and the solvent blank were prepared, the standard solution of the pesticides at 3 levels (0.50, 0.1, 0.2 mg/l) were analyzed to obtain a calibration curve.

Data analysis

The laboratory result was computed and analyzed using Statistical Package for Social Sciences (SPSS) version 17. Data on mean concentration of pesticide residue in the food samples were analyzed using descriptive statistics. Concentration of pesticide residue in the food samples was compared with 1993 Codex maximum residual limit (2 ppm). Comparison of the mean concentration of pesticide residue in the composite samples from different sources was done. The results were presented in frequency tables, and figures.

Result

The laboratory analysis of the beans and maize grains shows the presence of Dichlorvos (organophosphate) pesticide. There were nine composites of beans samples consisting of 126 grab samples. Their concentrations ranged from 1.27 ppm to 281.74ppm. Concentration (ppm) of pesticide residue in the beans samples from the different sources of collection are presented in Table 1 and this shows that the concentration of pesticide residue in all except one of the beans samples stored for six months after treatment, was high when compared to the 1993 codex standard (2ppm) of pesticide residue in grain food.

Table 1: Concentration of Pesticide Residue in the Composites of Beans Samples from different sources in Bodija market. (N=9 composites)

Analyte	A1	A2	A3	B1	B2	B3	C1	C2	C3
	Just treated with pesticide			stored for 6 months, on sale			stored for 2 months		
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Dichlorvos	214.58	281.74	264.54	5.38	7.66	1.27	9.82	31.82	6.97
Carbofuran	ND	ND	ND	ND	ND	ND	ND	ND	ND
Mevinfos	ND	ND	ND	ND	ND	ND	ND	ND	ND
Carbaryl	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dimethoate	ND	ND	ND	ND	ND	ND	ND	ND	ND
Diazinon	ND	ND	ND	ND	ND	ND	ND	ND	ND
Anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND	ND	ND	ND	ND	ND	ND
Clorfenvifos	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methidathior	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pf-38	ND	ND	ND	ND	ND	ND	ND	ND	ND

Data is mean of 3 replicates
ND ≥ Not Detected
Each composite A1,A2, A3 contains 14 grab samples of beans just treated with pesticides
Each composite B1, B2, B3 contains 14 grab samples of beans stored for 6 months after pesticide application before sale

Each composite C1, C2, C3 contains 14 grab samples of beans stored for 2 months after pesticide application

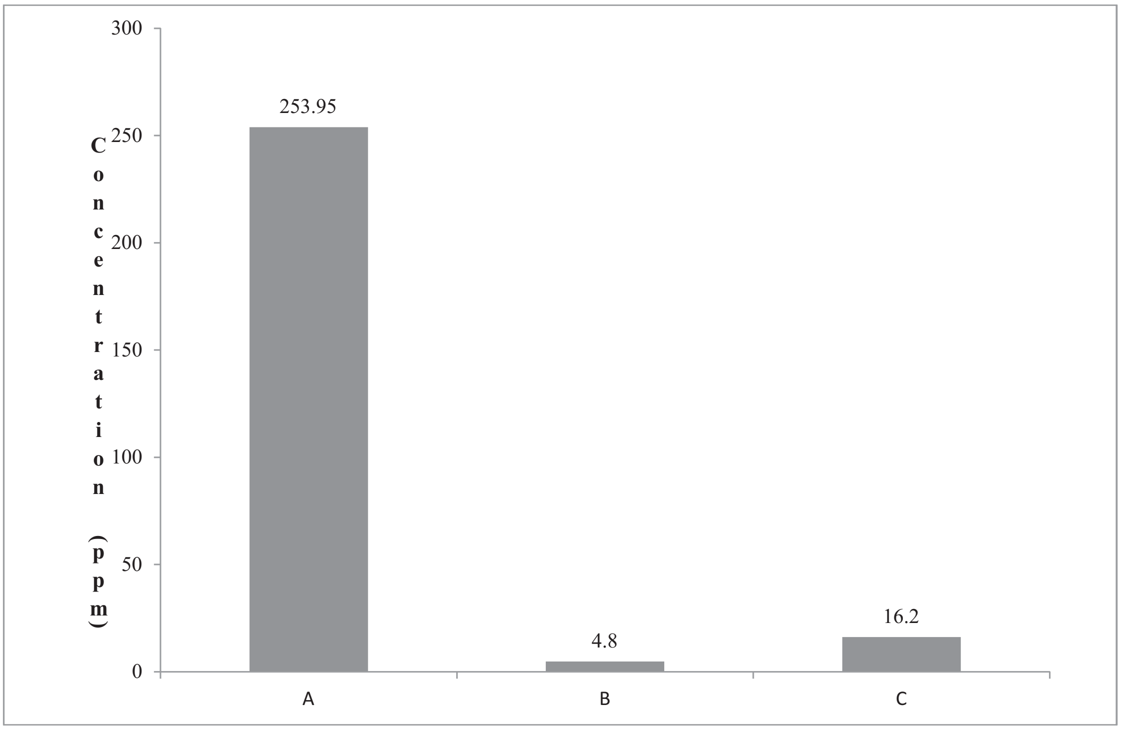

Figure 1: Comparison of the mean concentration of pesticide residue in the Composite of beans samples from different sources.

Note: A≥ Composite of beans samples just treated with pesticides
C≥ Composite of beans treated with pesticide and stored for about 2 months before sale
B≥ Composite of beans treated with pesticides and stored for 6 months before sale
Each composite contains 42 grab samples

Comparing the mean concentration of pesticide residue in the different composites of beans samples as shown in Figure1, the concentration of pesticide residue was highest in the beans that were just sprinkled with pesticides; (253.95ppm), followed by the beans stored for two months after pesticide application; (16.2ppm) and least in the beans stored for six months after pesticide application and ready for sale to consumers (4.8ppm).

Table 2: Mean concentration of pesticide residue in the composites of maize samples

Analyte	Composite of Maize in Stores X_1 (ppm)	Composite of Maize on Sale to Consumers X_2 (ppm)
Dichlorvos	0.62±0.04	0.58±0.03
Carbofuran	ND	ND
Mevinfos	ND	ND
Carbaryl	ND	ND
Dimethoate	ND	ND
Diazinon	ND	ND
Anthracene	ND	ND
Chlorpyrifos	ND	ND
Clorfenvifos	ND	ND
Methidathior	ND	ND
Pf-38	ND	ND

ND≥ Not Detected
X1≥ mean of 3 composites of maize in stores,
X2≥ mean of 3 composites of maize on sale
Each composite contains 24 grab samples

The mean concentration of pesticide residue in maize samples from different sources as presented in Table 2 shows that the concentration of pesticide residue in maize samples (X_1) from stores (0.62±0.04 ppm) was higher than maize sample X_2 (0.58±0.03ppm) on sale. The type of pesticide detected was Dichlorvos(Organophosphate).

Discussion

In order to ensure adequate food safety, it is important to know the concentration of pesticide residue in the food samples collected from the food sellers.

In this study, the type of pesticide present in the beans and maize grains was Dichlorvos (an organophosphate pesticide). Concentration (ppm) of pesticide residue in all the beans samples was high when compared to the 1993 codex standard (2ppm) of pesticide residue in grain food; this may be as a result of misuse of pesticide or failure of the food sellers to carry out good agricultural practice, which includes: practice in the control of pests during storage, transport, marketing, and processing foods. (Pym *et al.* 1984). This is in agreement with the findings of Adeyemi et al,2008 that the indiscriminate use of insecticides in Nigeria has resulted in the occurrence of the residues in biotic and other abiotic compartments.

The concentration of pesticide residue was highest in the beans that were just treated with pesticides, followed by the beans stored for about two months after treatment and it was least in the beans stored for six months after pesticide application and ready for sale to consumers. This is in agreement with the findings of Cengiz *et al.* 2006 which indicated that residue levels in samples, which were collected after 4 days following the pesticide application, were significantly lower than the samples collected after 4 hours subsequent to the pesticide application.

The high concentration in the beans on sale is also probably as a result of the food sellers not exercising patience till the pesticide expires in the food simply because they were in need of money or when it was profitable to sell cowpea. This is in agreement with the findings of Margam, (2008) which stated that treated cowpea sometimes makes its way into the market either when the farmers are in need of money or when it is profitable to sell.

Conclusion

The result obtained in this study revealed that the concentration of pesticide residue in the beans grains was high which makes it toxic to humans as bioaccumulation of these residues was likely to pose health risks to the consumers while that of maize was within acceptable limits.

Recommendation

Highly toxic pesticides should be substituted with harmless pesticide, there should be regular monitoring of pesticide residue in foods and humans in order to assess the food safety risk and the population exposure to pesticides. Consumers should be enlightened on the health implications of pesticide residue in food and the importance of proper washing and cooking of their food. There should be the enactment of law and regulations on the sale and purchase of pesticides with the use of prescription from a specialist. Farmers and grain merchants should be trained on the safer and cheaper methods of grain storage that do not require the use of harmful insecticides. More systematic studies should be done to document insecticide residues on cowpea in the markets and the number of cases of food poisoning due to insecticide residues in food grain.

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