Residues of Organochlorine Pesticide in Dried Beans 
(Vigna unguiculata) Originating from Nigeria

V. Isegbe¹, M. Habib¹, J. Obaje¹, S. Ekoro¹, S. Solomon¹

¹Nigeria Agricultural Quarantine Service, Abuja. Nigeria
Solomonpq@yahoo.com

ABSTRACT
Organochlorine pesticide residues constitute major threat to human health and environment. A nationwide sampling of dried beans for organochlorine pesticide residues was carried out in some markets in Kano, Lagos and Abuja in December 2015. Each dried beans sample was subjected to organochlorine pesticide residue analysis using EPA method 8081B. The study revealed the presence of Endrin-aldehyde, α-chlordane, endrine keto, Heptachlor epoxide, Endosulfan I and d-BHC in the sampled dried beans. These results therefore, provided baseline information on contamination level of organochlorine pesticides residues in dried beans originating from Nigeria with a view to controlling them.

Keywords: pesticide residues, dried beans, Organochlorine, Nigeria

INTRODUCTION
Cowpea (Vigna unguiculata) is a leguminous crop of the tribe phaseolae, family leguminosae widely grown in tropics and subtropics for human as well as for animal food (Bliss, 1972). More than 5.4 million tons of dried cowpeas are produced worldwide, with Africa producing nearly 5.2 million. Nigeria, the largest producer and consumer, accounts for 61% of production in Africa and 58% worldwide (FAOSTAT, 2012). Cowpeas cultivars in Nigeria vary in seed size, seed coat texture and colour. Brown cowpeas (beans) and white cowpeas (beans) are common. Majority of people have preference for brown beans as a pulse.

The crop is grown primarily for its seeds locally called beans which are eaten fresh when semi-ripe and as a pulse when dry and mature, or ground into flour. Cowpeas provide a rich source of proteins and calories, as well as minerals and vitamins. A cowpea seed can consist of 25% protein and is low in anti-nutritional factors (Rangel et al., 2003). This diet complements the mainly cereal diet in countries that grow cowpeas as a major food crop.

Despite the importance of the cowpea crop for human welfare and needs, it is faced with the problems of pest infestation right from the field to storage. Jackal and Daoust (1986) reported that insects are a major factor in the low yields of African cowpea crops, and they affect each tissue component and developmental stage of the plant. In heavy infestations, insect pressure is responsible for over 90% loss in yield. The legume pod borer Maruca (testulalis) vitrata is the main pre-harvest pest of the cowpea (Sharma, 1998). It causes damage to the flower buds, flowers and pods of the plant. Other important pests include pod sucking bugs, thrips and the post-harvest weevil Callosobruchus maculatus (Jackal Iand Daoust, 1986). Kemabonta and Odebhiyi (2005) reported that the pest spectrum of cowpea is wide and practically every part of the plant has an adopted pest species.

Additionally, the extent of field infestation has led to pre-harvest prophylaxis in the crop to reduce storage losses. In food for human consumption, prevention is clearly preferable to postharvest control measures. Thus an effective pre-harvest control must make the grain inhospitable to insects (Keri, 2009). This is usually achieved to some extent by either the use of organic pesticides which are not as effective as synthetic pesticide or planting insect resistance varieties. However, in the absence of these adaptive varieties, chemical control of pests is the best alternative to reducing crop losses, hence
the expanded usage of pesticides on crops on the farm and in storage (Agyen-Sampong 1978). Similarly, as the demand for food has grown worldwide, agricultural production has intensified with a concomitant expansion in pesticide application.

Pesticides are poisons; they are produced because they are toxic to one pests or the other (Banjo et al., 2010). Pesticides are an important management tool in agricultural enterprise; they increase yields and increase protection against insects at post-harvest and storage, and it has 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). Cooper and Dobson (2007) maintained that for every dollar spent on pesticide for crop yield and storage four dollars in crops is saved; since 10 billion dollars worth of agro-chemicals is used for crops globally annually then 40 billion worth of crops is saved annually.

The use of synthetic insecticides has adverse effects on human health (Otitodun et al., 2012). The undesirable consequences of pesticides use on human health have become more evident from the 1950s onward (Morner et al., 2002). According to Ogunjimi and Farinde (2012) pesticides use in Nigeria has been on the increase after it was introduced in the early 1950s and particularly in 1957 when Lindane was introduced and recommended for use in Nigeria. In the face of a growing human population, and increased urbanization in Nigeria, the demand for pesticide increased in the early 1960s after her Independence and the risk of pesticide whether real or perceived forced changes in the ways these chemicals are used.

Organochlorine pesticides are chlorinated hydrocarbons used extensively from the 1940s through the 1960s in agriculture. Representative compounds in this group include DDT, Methoxychlor, dieldrin, chlordane, toxaphene, mirex, kepone, lindane and benzene hexachloride. Booth and Dowell, (1975) reported that long term exposure to organochlorine pesticides may damage the liver, kidney, central nervous system, thyroid and bladder. There is evidence indicating that organochlorine pesticides may also cause cancer in human (Parbhu et al., 2009).

Significant contamination of cowpea has been reported in Nigeria. For examples, in 2010 it was reported that 20 fast food outlets were closed in Nigeria because of fatalities traced to pesticide residue in their products (Chikwe, 2010). In the Nation newspaper on Sunday, April 5 2015, it was reported that 42 food items produced in the country were rejected by United Kindom (UK) for quality defects. Again, in the Editorial newspaper Thursday, July 30 2015, European Union (EU) suspended the exportation of cowpea seeds (dried beans) originating from Nigeria as a result of pesticide residues in them.

In a bid for Nigeria Agricultural Quarantine Service (NAQS) to carry out one of her functional objectives which is to facilitate international trade in agricultural products by enforcing compliance with World Trade Organization (WTO) and Sanitary and Phytosanitary (SPS) standards, there is need to determine level of pesticide residues in cowpea from the country. Similarly, concern about the health effects of pesticides have increased over the past years considering the rates at which scholars have put into the study of the phenomenon. However, there is no quantitative information on the levels of pesticide residues in cowpea from the country. The aim of this study therefore, was to provide baseline information on contamination level of organochlorine pesticides residues in dried beans originating from Nigeria with a view to controlling them.

MATERIAL AND METHODS

Survey site

Nationwide sampling of dried beans for organochlorine pesticide residues was carried out in some markets in Kano, Lagos and Abuja in December, 2015. Kano (Longitude 12 °N, Latitude 8.5167 °E) is a city located in Northwestern geopolitical zone of Nigeria and the commercial nerve center of northern Nigeria. Lagos (Longitude 6.583°N, Latitude 3.750 °E) is a city located in Southwestern geopolitical zone of Nigeria and the economic nerve center of Nigeria. Abuja (Longitude 9.067 °N, Latitude 7.483 °E) is a capital city of Nigeria located in Northcentral geopolitical zone. These towns were purposefully selected owing to the fact that cowpea grains from different rural areas are assembled and transported to these places for sale and are also the locations of International airports where exporters could easily purchase the grains for export.
Dried beans sampling
Dried beans stores and markets were randomly selected in Kano, Lagos and Abuja for sample collection. In each of the store and market selected, five hundred grams of each white and brown cowpea grain was measured. Each sample was sealed in polythene bag, properly labeled and taken to Jawura Environmental Services Limited laboratory for organochlorine Pesticide residues analysis.

Procedure for Analysis of Organochlorine Pesticide Residues in Beans Sample (EPA Method 8081B)
Prior to analysis all glass wares were soaked in chromic acid overnight, washed with plenty amount of water, rinsed with distilled water and acetone before oven drying. The beans samples were transferred into the Blender which was used to blend the beans to fine powdery form. About 5g of blended beans sample was weighed and transferred into the beaker for extraction.
Ultra sonic bath extraction was used for the extraction of the samples using Dichloromethane (DCM) and Acetone as the extracting solvent in ratio 1:1, 50ml of the extracting solvent was used. The extraction was done twice on each sample and ultrasonic bath was set for 30mins for each extraction.
After each extraction, organic solution was collected into a clean beaker using filter paper with sodium sulphate. The solution was concentrated to 5ml using rotary evaporator and 10ml of hexane was added to it and finally concentrated to 2ml.
Extract was then cleaned up by packing the column using silica gel, glass fibre and sodium sulphate. The packed column was pre-cleaned using 10ml of DCM and 10ml of hexane. 1ml of extract sample was then added to packed column and 20ml each of DCM and Hexane was added to the sample. Eluting solvent was collected in a clean beaker and concentrated to 2ml using rotary evaporator. The extract was transferred to 2ml vial for GC analysis.

GC Condition
Model: Agilent GC7890B
Standard used for Calibration: AccuStandard
Chromatographic Column: 30 m x 0.32 mm I.D., 0.25 μm
Oven Temperature Program Initial oven temperature 110°C holds time 0.5min; to 320 °C @ 15°C/min, hold time 2min
Sample/autosampler Injection 1μl
Mode: Split
Split ratio: 10:1
Injection Port Temperature: 250°C
Inlet Pressure: 13.5psi.
Column flow: 2.54 ml/min
Column pressure: 13.5psi
Average Velocity: 45cm/sec
Detector Temperature: 320°C (ECD)

Calculation
OCP (μg/g) = Instrument Reading (μg/ml) x Volume of Extract sample (ml)
Sample weight (g)

RESULTS
Results of Analysis of Organochlorine Pesticide Residues in Beans Sample (EPA Method 8081B)
Endrin-aldehyde, a-chlordane and endrine keto were found in dried bean samples from Tarumi market Kano, Dawano store Kano, Ikotun market Lagos, Dawano market Kano, Tarumi store Kano, Yankaba market Kano, Lugbe market Abuja, Agege and Ketu market Lagos.
Heptachlor epoxide was found in dried bean samples from Ketu market Lagos, Tarumi and Dawano market Kano. Endosulfan I was detected in samples from Ketu market Lagos and Tarumi store Kano while d-BHC was only found in the bean sample from Tarumi store Kano.

DISCUSSION
The organochlorines are a chemically diverse group of substances and are used in grocery stores and food storage facilities to manage rodents and insects that infest food such as grain. However, organochlorine pesticides have been banned in most countries worldwide because of their persistence.
in the environment and human toxicity (Parbhu et al., 2009). In these results, the organochloine pesticide residues level found on the dry beans taken from the stores is higher than that of the samples from the open markets. This is may be due to application of the organochlorine pesticides in stores against storage insects as well as the weather condition of the stores which is cool-dry place favourable to pesticide toxicity. This is in agreement with the findings of Oktay et al., (2003) who reported that most organochlorines have a “negative temperature coefficient,” meaning they are more toxic at lower temperatures. This property renders organochlorine agents more toxic to cold-blooded creatures such as insects than to mammals and other more complex life-forms. The general mechanism of pesticidal actions of these agents is neurotoxicity that renders insects and other pests unable to move or breathe (Stephen et al., 1993).

This study revealed the presence of Endrin-aldehyde, a-chlordane, endrine keto, Heptachlor epoxide, Endosulfan I and d-BHC in the sampled dried beans. This is in agreement with the findings of Roberts et al., (2004) who reported the presence of these active agents among others in grains and further stated that most of these organochlorines active agents are harmful to health and enviroment. They further added that the organochlorines undergo hepatic metabolism which some agents can become metabolized to epoxides or other active compounds as a result of this metabolism (for example, aldrin is converted in the liver to dieldrin, another active organochlorine agent) (Echobichon, 1996).

Different active agents of organochlorines have been found on the nationwide samples of dried beans in Nigeria. This sampling on dried beans in Nigeria is the first definitive work carried out by NAQS to ascertain the levels organochlorine pesticide residues on dried beans in Nigeria has provided information on the various active agents of organochlorines found on the dried beans in Nigeria. These were: Endrin-aldehyde, a-chlordane, endrine keto, Heptachlor epoxide, Endosulfan I and d-BHC.

Based on the outcome of the analysis, it is desirable and hereby recommended that awareness should be provided among the stakeholders such as exporters, warehouse owners and farmers on the dangers associated with the indiscriminate use of pesticides.

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## ORGANOCHLORINE PESTICIDE RESIDUES IN BEANS

| Components       | GKYRS | GKYW | GALW | GKYR | GALR | NLAW | NLR | NLMW | NLMR | NLKW | NLKR | NLIR | PKTW | PKTR | PKDWS | NLIW | PKDR | PKDWM | PKTRS | PKDRS |
|------------------|-------|------|------|------|------|------|-----|------|------|------|------|------|------|------|------|-------|------|------|-------|-------|-------|
| a-BHC            | 0     | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 0     |
| b-BHC            | 0     | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 0     |
| g-BHC            | 0     | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 0     |
| d-BHC            | 0     | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 2.18  |
| Heptachlor       | 0     | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 0     |
| Aldrin           | 0     | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 0     |
| Heptachlor epoxide | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 0     |
| g-Chlordane      | 0     | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 0     |
| Endosulfan I     | 0     | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 0.33  |
| a-Chlordane      | 0.92  | 0.92 | 0    | 0    | 0.92 | 0    | 0   | 0    | 0.95 | 0    | 0    | 0.93 | 0.92 | 0.92 | 0.92 | 0.92  | 0.92  | 0.92 | 0.92  | 0.92  | 0.99  |
| Dieldrin         | 0     | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 0     |
| p,p-DDD          | 0     | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 0     |
| Endrin           | 0     | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 0     |
| Endosulfan II    | 0     | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 0     |
| p,p-DDD          | 0     | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 0     |
| Endrin aldehyde  | 0.25  | 0.25 | 0    | 0    | 0.25 | 0    | 0   | 2.74 | 0    | 0    | 0    | 2.54 | 2.56 | 2.65 | 0    | 2.7   | 2.72 | 0    | 2.7   | 2.72 | 0     |
| Endosulfan sulfate | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| p,p-DDT          | 0     | 0    | 0    | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0    | 0    | 0     | 0     | 0     |
| Endrin ketone    | 0.37  | 0.36 | 0    | 0    | 0.35 | 0    | 0   | 0    | 0    | 0    | 0    | 3.6  | 3.44 | 3.54 | 0    | 3.49  | 3.33 | 0    | 3.49  | 3.33 | 0     |
| Methoxychlor     | 0     | 0    | 0    | 0    | 0    | 0    | 7   | 0    | 0    | 0    | 12.82| 0    | 0.56 | 10.1 | 10.3  | 7.11 | 0    | 7.11  | 9.55 | 0     |

GKYRS=Kano Yankaba store brown, GKYW=Kano Yankaba market white, GALW= Abuja Lugbe white, GKYWS= Kano Yankaba store white, GALR= Abuja Lugbe brown, NLAW= Lagos Agege market white, NLR= Lagos Agege market brown, NLMW= Lagos Mowe market white, NLMR= Lagos Mowe market brown, NLKW= Lagos Ketu market white, NLKR= Lagos Ketumarket brown, NLIR= Lagos Ikoropo market brown, NLIW= Lagos Ikoropo market white, PKTW=Kano Tarum market white, PKTR=Kano Tarum market brown, PKTRS=Kano Tarum store brown, PKDWS= Kano Dawano store white, PKDRS= Kano Dawano store brown, PKDRM= Kano Dawano market brown, PKDWM= Kano Dawano market white