IODINE CONTENT AND PESTICIDE RESIDUES OF SOME NIGERIAN FOOD GRAINS

Etonihu A. C[1]., Aminu B. A[1]., Ambo A. I[1]., Etonihu K. I[2]
[1]Chemistry Department, Nasarawa State University, PMB 1022, Keffi, Nigeria, [2]Department of Agric.
Economics & Extension, Nasarawa State University, Lafia Campus

ABSTRACT
Samples of some Nigerian food grains (white maize, white beans and sorghum) were purchased randomly from open markets in Nasarawa and Plateau States. Using gas chromatography and titrimetry, the samples were analyzed for pesticide residues and nutritional iodine contents. The results showed a slightly higher residue level in the bean samples from Keffi market (54.68 x 10^{-3} mg/kg) than bean samples from Akwanga (54.14 x 10^{-3} mg/kg). While aldicarb residue was lowest concentration (0.28 x 10^{-3} mg/kg), DBCP had the highest residual concentration (3.64 x 10^{-3} mg/kg). When compared to the WHO, FAO, and the reports in literature, the pesticide residues in these samples appeared to be lower. Consequently these food grains, at the moment, do not pose health risk to the consumer. The iodine contents of the sample ranged from 68.8 mg/kg (for Keffi bean samples) to 89.9 mg/kg (for Mararaba maize samples). High nutritional iodine in food samples is important for good health.

KEYWORDS: food grains, iodine, Nigeria, pesticide residue

INTRODUCTION
Pesticides are chemical substances defined as poisons and used in certain circumstances to kill specifically targeted pests (Ahren, 1994). These highly stable compounds can last for years and decades before breaking down. They circulate globally, and persistent pesticides released in one part of the world can be transported through a repeated process of evaporation and deposit through the atmosphere to regions far away from the original source (Curran, 2001).

Although the benefits of pesticides cannot be overstated, their use raises a number of environmental concerns such as potential toxicity to humans and other animals (Kamrin, 1997). Over 98% of sprayed insecticides and 95% herbicides reach a destination other than their target species, including non- target species, air, water and soil. Pesticides are one of the causes of water pollution; some are persistent organic pollutant and contribute to soil contamination (Bradman, 1999).

Pesticides are toxic in nature and do not differentiate between targeted and non-targeted species, and hence should essentially be subject to safe and judicious use. Due to injudicious and indiscriminate use of pesticides, many accidents have occurred in different parts of the world and presence of pesticides in foods, fruits, vegetables and even in mother's milk is a matter of grave concern (WHO, 2002). Of all the pesticides released into the environment every year by human activity, persistent pesticides are among the most dangerous. They are highly toxic, causing an array of diverse effects, notably death, diseases and birth defects among human and animals. Specific effect can include cancer, allergies and hypersensitivity, damage to the central and peripheral nervous systems, reproductive disorders, and disruption of the immune system (Strong *et al.*, 2004).

The World Health Organization and the UN environment programmes estimate showed that each year, 3 million workers in agriculture in the developing countries experience severe poisoning from pesticides, resulting to about 18,000 deaths; while about 25 million workers suffer mild pesticide poisoning (Jaga, 2003; FAO, 2002). Many studies indicated that pesticide exposure is associated with long term health problems such as respiratory problems, depression, miscarriage, acute toxicity and birth defect (Lee, 2006).

Seventy-five percent of all pesticides in the world are used in developed countries, but use in developing countries is increasing (Lee, 2006). Many food crops including fruits and vegetables contain pesticides residue after being washed or peeled. The EPA sets the tolerance based on the toxicity of the pesticides and its breakdown products, the amount and frequency of pesticide residue in food by the time it is marketed (FAO,

2002). Exposure routes other than consuming food containing residues, in particular pesticide drift, are potentially significant to the general public (Kamel, 2003).

There is a dearth of information of pesticide residues in foodstuffs marketed in Nigeria. In recent times, there have been reported cases of food poisoning and deaths related to pesticide remnants in food materials. This work seeks to determine the content of nutritional iodine and pesticide residues in the samples of some marketed Nigerian food grains in order to assess their potential health risks and create public health awareness to consumers.

MATERIALS AND METHODS
Samples Collection
Samples of white maize, white beans and sorghum were purchased randomly from markets in Mararaba, Keffi, Akwanga and Lafia in Nasarawa State and Jos in Plateau State. Three different samples of maize, beans and sorghum were purchased from each of these five different markets to give a total of fifteen samples.

Sample Treatment
The samples were cleaned of unwanted solid particles. Each sample was ground into a fine powder using a mortar and pestle, properly labeled and stored for further analysis.

Determination of Percent Moisture Content
The powder sample (10g) was oven dried at 100ºC for 30 minutes, cooled in a desiccator and reweighed. The procedure was repeated until a constant weight and the difference in weight loss was calculated as percent moisture content.

Determination of Iodine Content
Each powder sample (10g) was dissolved in $30cm^3$ distilled water in 250 cm^3 volumetric flask with a stopper. The sample solution was made up to $50cm^3$ with distilled water to which 1mL of 1M H_2SO_4 and $5cm^3$ of 10% potassium iodide were added. Colour change to yellow indicated the presence of iodine. Using titrimetry method, a clean burette with 0.005M $Na_2S_2O_3$ was titrated against the grain sample solution in the flask until the solution turned pale yellow. To this solution was added $2cm^3$ of starch indicator and colour changed to dark purple. The titration was continued until the solution turned colourless that indicated the end point and final burrette reading (Jacobs, 1983). Using the conversion table the titre value (in cm^3) was converted to the equivalent iodine content in mg/kg (NIS/ SON, 2004).

Extraction of Pesticide Residue
The powder sample (100g) was extracted using benzene at 80ºC for 6 h in a Soxhlet extractor in order to isolate pesticide from fats (Jacobs, 1983). The extract from the Soxhlet extraction was concentrated to 50g and transferred into a clean $500cm^3$ beaker, to which was added 1L of carbon tetrachloride and 1L of 95% ethyl alcohol, and shaken vigorously for 1h in order to remove water content. 100g of anhydrous Na_2SO_4 was added. The liquid phase was transferred to a $500cm^3$ separatory funnel to which $200cm^3$ of water was added, and shaken vigorously for 2 to 3 minutes to allow the phases to separate. The aqueous phase was drained off and the process was repeated. In the first rinse, the aqueous phase contained about 30% alcohol in which CCl_4 was soluble only to about 1%. The various insecticides distributed themselves in favour of CCl_4, which contained only about 3% alcohol. This small amount of alcohol was removed by the second rinse, since virtually all the pesticides were concentrated in CCl_4. This extract was subjected to pesticide analysis by gas chromatography.

Determination of Pesticide Residues by Gas Chromatography
The extracts of the beans samples from Keffi market (KFBS) and Akwanga market (AKBS) were subjected to gas chromatography using HP 6890 Gas Chromatograph powered with HP ChemStation Rev. A09.01 [1206] software. The conditions of the gas chromatography analysis were as follow: hydrogen carrier gas with inlet temperature of 250ºC and flow rate of 1.0 ml/min, a PFPD detector of temperature 300ºC, and column dimension of 30 m x 0.25 mm x 0.25 μm.

RESULTS AND DISCUSSION
Table 1 showed that percent moisture varied among the food grains from 1.01% (for Mararaba maize samples) to 11.0 % (for bean samples from Jos). Moisture content varied as follows: 2 % (in AKBS) to 11 % (in JOBS) for bean samples; 1 % (KFMS) to 10 % (LAMS) for maize samples; 2 % (in JOSS) to 10 % (in AKSS).

Moisture content determination in food is important because moisture provides a number of biochemical and physiological changes in food (FAO, 2002).

Table 1: Moisture and iodine contents of selected Nigerian food grains

S/N	Grain Identification	Moisture (%)	Iodine (mg/kg)
1	AKBS	2.0	76.2
2	AKMS	5.0	85.7
3	AKSS	10.0	81.5
4	JOBS	11.0	74.1
5	JOMS	3.0	85.7
6	JOSS	2.0	83.6
7	KFBS	8.0	68.8
8	KFMS	3.0	84.6
9	KFSS	5.0	79.4
10	LABS	10.0	71.9
11	LAMS	10.0	86.8
12	LASS	5.0	85.7
13	MABS	5.0	73.0
14	MAMS	1.0	89.9
15	MASS	5.0	84.6

AK = Akwanga; JO = Jos; KF = Keffi samples; MA = Mararaba; LA = Lafia.
BS = Bean Sample; MS= Maize Sample; SS = Sorghum Sample.

Nutritional iodine was highest for maize samples from Mararaba (89.9 mg/kg) but lowest for the Keffi bean samples (68.8 mg/kg). The nutritional iodine ranged as follows: 68.8 (in KFBS) to 76.2 mg/kg (in AKBS) for bean samples; 84.6 (in KFMS) to 89.9 mg/kg (in MAMS) for maize samples; 79.4 (in KFSS) to 85.7 mg/kg (in LASS) for sorghum samples. The nutritional iodine contents of these samples were comparable to the iodine contents of edible salt deposits of parts of Nasarawa State of Nigeria that ranged from 37.1 to 246.7 mg/kg (Etonihu *et al.,* 2009).

Table 2 showed that the concentration of pesticide residues in AKBS ranged from 0.27×10^{-3} mg/kg (for aldicarb) to 3.64×10^{-3} mg/kg (for DBCP) and a total sum of 54.14×10^{-3} mg/kg of the pesticides in the bean samples from Akwanga.

Table 2: Concentrations of pesticide residues in AKBS (in mg/kg)

S/N	Pesticide	Amount per Area (x 10^{-5})	Amount (x 10^{-3} mg/kg)
1	Mollinate	5.63	1.76
2	Aldicarb	0.02	0.27
3	2,4,6-trichlorophenol	0.12	1.35
4	MCPA	1.62	2.91
5	Simazine	4.59	2.61
6	Isoproturon	3.27	2.00
7	Chlorotoluron	1.24	0.85
8	Mecoprop	4.36	2.64
9	Atrazine	2.79	2.44
10	2,4 – D	0.89	1.32
11	Carbofuran	0.39	1.20
12	Terbuthylazine	0.38	1.48
13	Dimethoate	0.65	2.91
14	Dichloroprop	0.55	2.89
15	DBCP	0.52	3.64
16	Cyanazine	0.55	3.23
17	Pentachlorophenol	0.37	2.18
18	Fenoprop	0.51	0.90
19	Alachlor	1.27	2.80
20	2,4 – DB	1.17	2.46
21	Pendimethalin	0.33	1.14
22	Metolachlor	0.30	1.11
23	Lindane	0.38	0.85
24	Trifluralyrixyfen	1.51	2.19
25	Methoxychlor	1.14	2.23
26	Chlorpyrifos	3.76	1.44
27	DDT	6.46	2.51
28	Aldrin	16.47	0.83
			$\sum = 54.14$

Long-term exposure to most pesticides could precipitate serious health problems, which may manifest months or years later. The effect of pesticides such as organochlorine (OC), organophosphorus (OP), carbamates may cause cancer, tumors, birth defects, blood disorders (Strong *et al*., 2004).

Table 3 showed the concentration of various pesticides in the food grains from Keffi market. The pesticide residues ranged from 0.28 x 10^{-3} mg/kg (for aldicarb) to 3.64 x 10^{-3} mg/kg (for DBCP). The total sum of the residues in the sample from Keffi market when compared with the threshold of 0.005 mg/kg by the WHO (2002) guideline, aldicarb residue in bean samples from Akwanga and Keffi were lower, so may not be harmful to the health of consumers. The 2,4,6-trichlorophenol residue (1.35 x 10^{-3} mg/kg) in these samples could favourably be compared with the values of 0.03 mg/kg reported by Jaga (2003) for 2,4,6-trichlorophenol.

Similarly, the lower concentrations of 2.93 x 10^{-3} mg/kg (for MCPA) and 2.18 x 10^{-3} mg/kg (for pentachlorophenol) could be comparable with the value of 0.10 mg/kg by Olshan and Daniels (1997). This indicated that these food grains were still safe for consumption. The concentrations of 2.62 x 10^{-3} mg/kg (for simazine) and 0.92 x 10^{-3} mg/kg (for fenoprop) were lower than 0.04 mg/kg recommended by FAO (2002).

The concentrations for isoproturon (2.02 x 10^{-3} mg/kg) and alachlor (2.81 x 10^{-3} mg/kg) were lower than the WHO (2002) recommendation of 0.1 mg/kg. The residues of 0.87 x 10^{-3} mg/kg (for chlorotoluron) and 2.50 x 10^{-3} mg/kg (for 2,4 - DB) were lower than the 0.5 mg/kg reported by Beselar *et al*. (2008).

The residues of 2.66 x 10^{-3} mg/kg (for mecoprop) and 1.17 x 10^{-3} mg/kg (for pendimethalin) in the bean samples were lower compared with the 1.00 mg/kg reported by Gorell *et al*. (1998). The concentrations of 2.46 x 10^{-3} mg/kg (for atrazine) and 1.13 x 10^{-3} mg/kg (for metolachlor) were lower compared with the 0.01 mg/kg reported by Reuber and Ritter (1981).

Table 3: Concentration of Pesticide Residues in KFBS (in mg/kg)

S/N	Pesticide	Amount per Area (x 10^{-5})		Amount (x 10^{-3} mg/kg)	
1	Mollinate		2.98		1.78
2	Aldicarb	0.02		0.28	
3	2,4,6-trichlorophenol	0.08		1.37	
4	MCPA	0.62		2.93	
5	Simazine		1.75		2.63
6	Isoproturon		10.12		2.02
7	Chlorotoluron	1.61		0.87	
8	Mecoprop		13.59		2.66
9	Atrazine	14.52		2.46	
10	2,4 – D	10.01		1.34	
11	Carbofuran		1.37		1.21
12	Terbuthylazine	2.12		1.50	
13	Dimethoate		1.62		2.93
14	Dichloroprop	1.32		2.91	
15	DBCP	1.03		3.64	
16	Cyanazine		0.97		3.25
17	Pentachlorophenol		0.62		2.18
18	Fenoprop		0.36		0.92
19	Alachlor	0.73		2.81	
20	2,4 – DB		0.70		2.50
21	Pendimethalin	0.40		1.17	
22	Metolachlor		0.37		1.13
23	Lindane	0.40		0.87	
24	Trifluralyrixyfen	1.86		2.21	
25	Methoxychlor	1.09		2.25	
26	Chlorpyrifos		3.90		1.47
27	DDT		18.99		2.55
28	Aldrin	21.99		0.85	
				$\sum = 54.68$	

The concentrations of 1.21 x 10^{-3} mg/kg (for carbofuran) and 2.21 x 10^{-3} mg/kg (for trifluralyriproxyfen) were lower compared with the 0.40 mg/kg reported by Rohlman *et al.* (2006), and the 0.10 mg/kg reported by Jiwan (2008) for maximum residues limits (mrls) in the food commodities in Nepal. The concentrations of 1.50 x 10^{-3} mg/kg (for terbuthylazine) and 2.25 x 10^{-3} mg/kg (for methoxychlor) were lower compared with the 0.001 mg/kg reported by Hoppin *et al.* (2008).

The concentrations of 2.93 x 10^{-3} mg/kg (for dimethoate) and 1.47 x 10^{-3} mg/kg (for chlorpyrifos) were lower compared with the 0.002 mg/kg WHO (2006) recommended. The concentrations of 2.91 x 10^{-3} mg/kg (for dichloroprop) and 2.55 x 10^{-3} mg/kg (for DDT) were lower compared with the 0.5 mg/kg standard by FAO (2002). Jiwan (2008) had reported higher residue levels of 0.05 mg/kg for chlorpyrifos and 1.00 mg/kg for dichloroprop for food grains in Nepal. The concentrations of 1.78 x 10^{-3} mg/kg (for mollinate) and 0.85 x 10^{-3} mg/kg (for aldrin) were lower compared with the 0.1mg/kg reported by Vanderlee *et al.* (2008).

CONCLUSION
The bean samples from Keffi market showed a slightly higher pesticide residue (54.68 x 10^{-3} mg/kg) than the Akwanga bean samples (54.14 x 10^{-3} mg/kg). In both cases, aldicarb had the lowest concentration (0.28 x 10^{-3} mg/kg) while DBCP had the highest concentration (3.64 x 10^{-3} mg/kg). When compared to the WHO, FAO, and the reports in literature, the pesticide residues in these samples appeared to be lower. Consequently these food grains, at the moment, do not pose health risk to the consumer. The iodine contents of the samples ranged from 68.8 mg/kg (for Keffi bean samples) to 89.9 mg/kg (for Mararaba maize samples). High nutritional iodine in food samples is important for good health.

RECOMMENDATIONS
i. Governments at all levels should encourage the use of safer insecticide or herbicide application on farmlands and food grain storages.

ii. Government should set up a task force that would regularly test and monitor the various food grains in Nigerian markets in order to ascertain their levels of pesticide residue.

iii. There should be a health enlightenment programme to enlighten citizens on the effects of pesticide residues in order to curb the potential health risk to consumers.

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Corresponding Author
Etonihu A. C
Chemistry Department, Nasarawa State University, PMB 1022, Keffi, Nigeria
Email: criseto@yahoo.com