NUTRITIONAL COMPOSITION AND PESTICIDE RESIDUE LEVELS OF SOME CEREAL GRAINS SOLD IN WUKARI, TARABA STATE

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Abstract: This study investigated the nutritional composition and pesticide residue levels in cereal grains sold in Wukari market, Taraba State, Nigeria. Standard methods of AOAC were used for the nutrient analysis of the samples (wheat, sorghum, millet and maize). The organophosphate pesticide residue analysis was based on QuEchERs (Quick, easy, cheap, effective, rugged and safe) method. The analysis was carried out using HP 5890 Gas Chromatograph equipped with electron capture detector (ECD) using helium as the carrier gas. Organochlorine residues were analysed using Shimadzu Gas Chromatograph 2010 equipped with Nitrogen Phosphorus Detector (NPD), using nitrogen as carrier gas. The results showed that wheat had the highest moisture and ash contents of 9.19 and 2.92%, respectively; while the lowest ash value was obtained for maize. The following ranges were observed for the nutrient analysis carried out: crude fibre 2.38 (millet) to 5.18% (wheat), ether extract 2.19 (wheat) to 5.45% (millet); crude protein 9.87(maize) to 12.80% (wheat) and nitrogen free extract NFE 7.69(wheat) to 80.86% (maize). The results for the Organophosphate pesticide residues were below the Maximum Residue Limits (MRLs) of European Council, for organochlorine it was observed that the following Organochlorine Residues; aldrin, heptachlor, lindane and Methoxychlor detected were slightly above Maximum Residue Limits. Therefore, control of organochlorine pesticide in cereal grain is necessary for food safety.

Keywords: Cereal grains, organochlorine, organophosphate, nutritional composition, crude protein

Introduction

Cereal grains are the seeds that come from grasses such as wheat, millet, rice, barley, oats, rye, triticale, sorghum, and maize (corn). About 80 percent of the protein and over 50 percent of the calories consumed by humans and livestock come from cereal grains (Sarwar, 2008). The United States is a major supplier of cereal grains to the rest of the world and some impoverished countries depend on gifts of both unmilled and processed grains from America to keep their people from starving. The global importance of cereal crops to the human diet and on the written history of man and agriculture cannot be over emphasised. Cereal grains are also referred to as the fruit of plants belonging to the grass family (*Gramineae*). Pesticides are chemical substances widely used against plant pests and diseases.

The use of pesticides in commercial agriculture has led to an increase in farm productivity (Krol *et al.*, 2000). The use of pesticides in agriculture is necessary to combat a variety of pests that could destroy crops and to improve the quality of the food produced (Goto *et al.*, 2003). However, the use of pesticides requires great care and control as they can pollute the environment and harm human health. Pesticides are essential in modern agricultural practices but due to their biocide activity and potential risk to consumers, the control of the presence of pesticide residues in foods is a growing source of concern for the general population (Torres *et al.*, 1996). A substantial body of laboratory and epidemiological evidence suggests that certain pesticides are associated with carcinogenesis, immunotoxicity, neurotoxicity, behavioural impairment, reproductive dysfunction, endocrine disruption, developmental disabilities, skin conditions and respiratory diseases, such as asthma (Solomon *et al.*, 2000).

The presence of pesticide residues in fruits and vegetables can be a significant route to human exposure and most of organochlorine pesticides have been banned because they are highly persistent insecticides, and their residues still appear as pollutants in food as well as in the environment (EC, 1990). Organochlorine pesticides are characterized by high lipid solubility and high persistence and hence they tend to accumulate in fatty tissue. To ensure the safety of food for consumers, numerous legislations such as the EC directives (European Council Directives) have established maximum residue limits (MRLs) for pesticides in food. However, limited information is available regarding the contamination of pesticide residues in Turkey (Yildirim and Ozcan, 2007). Wheat is a staple for a larger section of the Kenyan population in Turkey. Although dissipation of organophosphorus pesticides in wheat during pasta processing have been determined in Turkey (Uygun *et al.*, 2008). Pesticides protect crops from pests and are economically beneficial. However, these substances can transfer to the food and affect consumers health, especially in the food consumed by infants and children, who are a vulnerable risk group (Gentili *et al*., 2004; Hercegova *et al.*, 2007). Dairy foods like milk and yoghurt are important nutritive foods for infant and the children because these include vitamin A, vitamin B12, riboflavin, calcium, carbohydrate, magnesium, phosphorus, protein, potassium, and zinc (Nutrition Australia, 2009; Abou-Dounia *et al.*, 2010). Moreover, processed foods such as cereals are particularly used as healthy food supplements for infants and young children. Infants and children are more vulnerable to the effects of pesticides as compared to adults because of high food consumption rate per kilogram of their body weight and low immunity (Repetto *et al.*, 1997). The European Commission Directive 2006/125/EC of 5 December 2006 set a limit for pesticides in cereal based foods and baby foods for infants and young children. According to this regulation, pesticides in cereal-based foods and baby foods must not contain residues of individual pesticides at levels exceeding 10 µg/kg (MRL).

The food crops treated with pesticides invariably contain unpredictable amount of these chemicals, therefore, it becomes imperative to find out some alternatives for decontamination of foods. The washing with water or soaking in solutions of salt and some chemicals e.g. chlorine, chlorine dioxide, hydrogen peroxide, ozone, acetic acid, hydroxy peracetic acid, iprodione and detergents are reported to be highly effective in reducing the level of pesticides.

The aim of this study was to evaluate the nutrient composition and pesticide residue levels of some cereal grains sold in Wukari, Taraba State.

Materials and Methods

Materials

Maize, millet, sorghum and wheat samples were purchased from Wukari market, Taraba State, Nigeria. The cereal grains were properly cleaned and sorted to remove stones, dirts, chaffs, weevil and other extraneous matter before they were milled into a fine powdered form. The samples were then packaged in polythene bags and stored at room temperature pending analysis.

Methods for analysis

Proximate composition was determined by the Standard Methods of AOAC (2000). Gross energy was theoretically calculated using the method of AOAC (1990). The Organophosphate Pesticide Residue analysis method was based on QuEchERs. The analysis was carried out using HP 5890 Gas Chromatograph equipped with electron capture detector and helium was used as the carrier gas, while for organochlorine, homogenized sample was extracted using dichloromethane solvent and then cleaned up using activated silica conditioned with dichloromethane. The analysis was carried out using Shimadzu Gas Chromatograph 2010 equipped with fused silica column, Nitrogen Phosphorus Detector (NPD) and Nitrogen as carrier gas.

Pesticide residues of organophosphates using QuEchERs

Stage 1: Sample Extraction

The procedure was as follows:

i. Cereal samples were homogenized; 10 g of homogenized sample was put into 50 ml polypropylene centrifuge tube.
ii. 10 ml of distilled water was added to the homogenised sample, and then add 10 ml of acetonitrile, vigorously shaken for good extraction, centrifuged at 5000 rpm and allow separation into phases. Exraction salts (4 g of $MgSO_4$ and 1 g of NaCl) were added, shaken and then centrifuged at 8000 rpm for 10 min.

Stage 2: Sample Clean-up

A subsample of the organic solvent extract from stage 1 was cleaned up through the use of dSPE (dispersive solid phase extraction) and primary secondary amine added as adsorbent. 1 ml of supernatant was transferred to autosampler vial. The analysis was carried out using HP 5890 Gas Chromatograph equipped with electron capture detector and helium was used as the carrier gas, 1 ul of the extract was analysed.

Results and Discussion

Moisture

The moisture content of the samples analysed ranged from 8.12±0.04 to 9.19±0.03% (Table 1) with the highest value observed in wheat and the lowest value observed in maize. The vulnerability of grain to biodeterioration could be by its own metabolic activity or by the action of insects, mites or moulds which is strongly related to moisture content (Yadav *et al.,* 2012). Low moisture content of maize could be attributed to the variety of maize used, environmental factors, agronomic practices and period of drying. Previous research reported moisture content of maize as 9 – 19% (Samir *et al.,* 1998). The cereal grains used in this work can be stored for a longer shelf life because they fall below the safe moisture level which is 12 to 13%. In addition, physical properties such as hardness, coefficient of friction, specific weight and electrical characteristics are also influenced by moisture. The lower the moisture content of the cereal grain, the longer the allowable storage time (Bern *et al.,* 2013). Pasta is made from wheat because of its high level of moisture content.

Ash

The ash content analysis ranged from 1.41±0.01% to 2.92±0.04% (Table 1). The highest value was observed in wheat while the lowest value was found in maize. The percentage ash content falls within the range reported in the literature; Enyisi *et al.* (2014) reported ash content of maize within the range of 1.4 to 3.3%. When food samples are ashed, micronutrients such as calcium, potassium, phosphorus and magnesium are left in the food samples and ash contents indicate the level present in the sample (Ndukwe, 2015). Micronutrient malnutrition greatly increases mortality and morbidity rates, diminishes cognitive abilities of children and lowers their educational attainment, reduces labour productivity, stagnates national development efforts, contributes to continued high population growth rates and reduces the livelihood and quality of life for all those affected (Arthur, 1999).

Crude fibre

The values obtained from the determination of crude fibre content of the cereal grains in this study ranged from 2.89±0.06 to 5.18±0.12% (Table 1). Studies have shown that percentage crude fibre range from 0.80 to 2.32% (Ikram and Haleem, 2010); this range is lower than the values obtained in this research. But the result of maize sample in this research is similar to that of other researches which had the range 2.07 to 2.77% (Ujabadeniyi & Adebolu, 2005). Among the benefits of dietary fibre consumption are protection against heart disease, cancer, normalization of blood lipids, regulation of glucose absorption and insulin secretion, prevention of constipation and diverticular disease are largely pronounced (Lopez *et al.,* 2001; Adnan *et al*., 2010). The American Diabetes Association recommends that people with diabetes should consume 25 – 50 g of fibre per day (Trinidad *et al*., 2006). Dietary fibre is highest in the bran layer (and the hull) and lowest in milled cereal grains. The Proteins Advisory Group (PAG) of the United Nations suggested an upper limit of 5.0% crude fibre in supplementary food (PAG Compendium). However, the values obtained for this research (2.89 to 5.18%) fell within the recommended ranges for infants which is 2.0 to 2.5% (USDA, 2004).

Table 1: The proximate composition of cereal grains on dry matter basis (%)

Samples	Moisture Content	Ash	Crude Fibre	Ether Extract	Crude protein	NFE
Wheat	9.19±0.03	2.92±0.44	5.18 ±0.12	2.19 ±0.05	12.80±0.19	76.91±0.35
Sorghum	8.76 ±0.18	1.96 ±0.04	2.67 ±0.02	3.55 ±0.04	11.88±0.13	79.95±0.35
Millet	9.09 ±0.05	2.18 ±0.04	2.38 ±0.06	5.45±0.13	12.04±0.31	77.95 ±0.31
Maize	8.12±0.04	1.41 ±0.01	2.89±0.10	4.97±0.07	9.87±0.06	80.86 ±0.24

Mean value ± standard deviation, where n=3. Values are mean ± standard deviation of triplicate determination

Ether extract

The results of the analysis in this study show that the fat content of the cereal grains ranges from 2.19±0.05 to 5.45±0.13% (Table 1) with the highest value observed in millet and the lowest value in wheat. Depending on cereal species, average lipid contents of 1.7 to 7% in the grains are present according to research (Lorenz and Hwang, 1986). Fatty acids found in cereal grains were mainly linoleic acid, oleic acid and palmitic acid; although they are relatively in minor constituents in cereal grains (Fliedel *et al.,* 2003). Triglycerides are the dominating lipid class in the germ and the aleurone layer, phosphor and glycolipids are present in the endosperm (Hoseney, 1994). Glycolipids have been shown to contribute to the high baking performance of wheat flour (Selmair and Koehler, 2008). The use of fats and oils in baked goods determines the oxidative stability of the product altering the shelf life as well as the nutritive content (Gunstone, 2002).Fat is essential to a healthy diet. Fat in the diet has a vital role in metabolic and membrane functions and physiological processes such as storing energy, protecting and insulating the body, aiding intestinal absorption of fat-soluble vitamins, as eicosanoids, and as essential fatty acids (Kritchevsky, 2002). These essential fatty acids are linoleic acid (18:2n-6) and -linolenic acid (18:3n-3) (Chapkin, 2000). High fat intakes have been associated with several chronic diseases, e.g. type-2 diabetes, arteriosclerosis, cancer, cardiovascular heart disease and increased risk of obesity (Health, 2002). Low fat diets, in some studies, have also been associated with adverse effects such as decreased high-density lipoprotein (HDL) cholesterol, increased fibrinogen (Elmer , 1996), and ischaemic stroke (McGee *et al.,* 1985). However, a recent review suggests a more broad and moderate range, 25 to 35%, of calories from fat in the diet 5 (Kris-Etherton *et al.,* 2002).

Crude protein

The values obtained for the analysis of crude protein range from 9.87±0.06 to 12.80±0.19% (Table 1) with the highest value observed in wheat and the lowest in maize. For other research, the range of crude protein is between 11.2 to 23.7% (Maleki *et al.,* 2010). The average protein content of cereal grains range from 6 to 15% of which the protein level in this research work is within the range (Goldberg, 2003). This range depends on the genotype (cereal, species, variety) and the growing conditions (soil, climate, fertilization); amount and time of nitrogen fertilization are of particular importance. High protein is as a result of germ and aleurone layer of cereal, the starchy endosperm and the bran (Belitz *et al.,* 2009). A large number of these biofunctional peptides have been isolated from food proteins including anti-cancer, anti-inflammatory, immunomodulatory, muscle-stimulating and angiotensin converting enzyme (ACE) inhibitory peptides. Their only biological function is to supply the seedling with nitrogen and amino acids during germination. Protein is a nutrient needed by the human body for growth and maintenance (Genton *et al.,* 2010). Aside from water, proteins are the most abundant kind of molecules in the body. Protein can be found in all cells of the body and is the major structural component of all cells in the body, especially muscle (FNB, 2005; Genton *et al.,* 2010).

Nitrogen free extract (NFE)

The values of the Nitrogen free extract (NFE) for this analysis is in the range 69.83±0.35 to 74.28±0.24% (Table 1) with the highest value observed in maize and the lowest value observed in wheat. Carbohydrate values of other research work is 66 to 76% (Olowalana, 2014), but the value gotten from this study is slightly high. The carbohydrate values in the cereal grains are high, making them rich-energy foods for both humans and livestock (Ape *et al*., 2016).

Cereal grains contain 66 to 76% carbohydrates and the cereals used in this analysis are within this range. Nitrogen free extract (NFE) also known as digestible carbohydrate is the most abundant group of constituent. The major carbohydrate is starch, followed by minor constituents such as arabinoxylans, β-glucans, sugars, cellulose, and glucofructans (Zeeman *et al.,* 2010). Because of its unique properties starch is important for the textural properties of many foods, in particular bread and other baked goods. It is an important feedstock for bio-ethanol or biogas production (Goesaert *et al.,* 2005).

Gross energy (Kcal/100g)

Calculated energy values of the cereal grains are between 374.51±0.16 to 343.74±0.23 with maize having the highest value while wheat has the least value (Table 2). The energy value of maize grains in a previous study was found to be 387.7 kcal/100g, this value was slightly higher than what was determine in this work (Kouakou *et al*., 2008) In another study, the energy value of 447 kcal/100g was recorded for yellow maize which is higher than the values determined in this study (Ejigue *et al.,* 2005). The difference in the energy level is due to differences in the proximate composition of the varieties. The results of this study show that these maize varieties are rich source of energy.

Table 2: Gross energy composition of cereal grains

Samples	A(Kcal/ 100g)	B(Kcal/ 100g)	Mean Value (Kcal/100g)	KJ/100g
Wheat	343.55	343.93	343.74 ± 0.23	1443.71
Sorghum	363.90	364.71	364.30 ± 0.47	1530.06
Millet	372.15	371.46	371.81 ± 0.42	1561.60
Maize	374.41	374.61	374.51 ± 0.16	1572.94

Mean value ± standard deviation, where n=3 Values are mean ± standard deviation of triplicate determination

Table 3: Organochlorine levels in cereal grains (mg/kg)

Organochlorine	Wheat	Sorghum	Maize	Millet
Aldrin	0.12±0.02	0.07±0.00	0.06±0.02	0.14±0.01
Dichloran	0.03±0.01	0.03±0.01	0.03±0.02	0.04±0.01
Dieldrin	0.03±0.01	0.03±0.01	0.04±0.02	0.04±0.03
Endrin	0.05±0.01	0.05±0.01	0.001±0.0001	0.05±0.01
Endosulfan	0.05±0.01	0.04±0.01	0.01±0.002	0.04±0.01
Mirex	0.05±0.01	0.06±0.01	0.01±0.01	0.05±0.01
Lindane	1.11±0.10	1.15±0.10	1.19±0.08	1.31±0.03
Methoxychlor	0.04±0.01	0.07±0.03	1.31±0.03	0.07±0.01
Heptachlor Epoxide	0.06±0.01	0.05±0.02	0.04±0.00	0.04±0.01
1,1,1-Trichloroethane	0.06±0.01	0.06±0.01	0.06±0.00	0.05±0.01
Hexachlorocyclohexane	0.06±0.01	0.04±0.01	0.05±0.01	0.06±0.01
2,2-bis(p-chlorophenyl)	0.07±0.01	0.04±0.01	0.06±0.01	0.06±0.01

Mean value ± standard deviation, where n=3 Values are mean ± standard deviation of triplicate determination

Organochlorine pesticide residue level

There were 12 different forms of organochlorine pesticide residues observed in the course of this analysis and they ranged from 0.025±0.007 to 1.19±0.084 mg/kg (Table 3) with the lowest value in wheat and the organochlorine pesticide was aldrin, while the highest value was obtained for maize in which the organochlorine pesticide residue was lindane. According to literature, the Maximum Residue Limit (MRLs) range of organochlorine is from 0.01 – 1.00 mg/kg (EC, 1990); and of which the cereal grains used in this analysis are found to be in this range with exception of lindane. The organochlorine pesticides and their metabolites are mainly classified into three categories; namely diphenylaliphatics, cyclodienes and hexachlorocyclohexanes (Nur-Banu and Semra, 2004). These pesticides are typically very persistent in the environment, and are known to accumulate in sediments, plants and animals (Agbeve *et al.,* 2014). Most of them break down slowly and can remain in the environment long after application and in organisms long after exposure, this contamination which is closely correlated to human activities, agricultural applications and deforestation which leads to soil erosion (Nur-Banu and Semra, 2004; Bhattacharya *et al.,* 2006). This explains the high concentration of the pesticide at a depth of 21-30 cm. Organochlorine pesticides are broad spectrum insecticides, active against a great variety of pests in field and during storage and they vary in their chemical structures. The presence of pesticide residues in cereal grains is one important concern for consumers due to their possible long adverse health effects; especially for children, as they consume a higher proportion of cereal grains and its products in relation to their body weight and are more susceptible to chemicals since they are in early developmental stages (Zawiyah *et al*., 2007).lindane formulation are registered for use in public health practices to control vector borne diseases and for pest control in selected crops (Gupta 2005; Zhang and LiuCAPE 2016). Organochlorine pesticides and their metabolites are highly toxic and have been implicated in a wide range of adverse health effects such as cancer, neurological damage, reproductive system deformities, birth defect, and damage to the immune system (Ahlborg *et al.*, 1995; Sosan *et al*., 2008; Leena *et al.*, 2012).

Organophosphate pesticide residue level

In the analysis for organophosphate pesticide residue level, 15 different forms of organophosphate were detected with the values ranging from 0.001±0.00 to 0.017±0.018 mg/kg with the lowest value observed in wheat and sorghum that had phorate sulfone as the organophosphate, the highest value of organophosphate was found in maize which was phorate sulphoxide (Table 4). A number of factors such as non availability to farmers and or non application of these insecticides during the period of study, and also from low concentration levels below the limits of quantitation (CLSI, 2004) may be responsible of the non detection of other forms of pesticides. Residues at harvest from these circumstances are usually low and often below the limit of determination, but the majority of significant residues at harvest result from applications when the edible part of the plant is already present (Bates, 1990; Tadeo *et al.*, 2008).

Table 4: Organophosphate levels in cereal grains (mg/kg)

Organophosphate	Wheat	Sorghum	Maize	Millet
Dichlorvos	0.001±0.001	0.003±0.001	0.004±0.001	0.005±0.001
Diazinon	0.005±0.002	0.004±0.002	0.004±0.002	0.005±0.001
Phorate sulfon	0.001±0.001	0.001±0.001	0.002±0.001	0.003±0.001
Malathion	0.003±0.003	0.003±0.002	0.003±0.002	0.002±0.001
Phorate	0.003±0.001	0.003±0.001	0.003±0.001	0.003±0.001
Chloropyrifos	0.004±0.002	0.003±0.002	0.003±0.002	0.004±0.002
MethylParathion	0.007±0.004	0.006±0.003	0.005±0.003	0.007±0.004
Profenofos	0.008±0.003	0.007±0.004	0.007±0.004	0.007±0.005
Ethion	0.008±0.003	0.006±0.001	0.005±0.001	0.006±0.003
Dimethoate	0.01±0.003	0.007±0.002	0.008±0.004	0.008±0.002
PhorateSulfoxide	0.005±0.001	0.004±0.001	0.017±0.018	0.004±0.001
Phosalone	0.004±0.001	0.003±0.001	0.003±0.00	0.003±0.001
Edifenfos	0.003±0.001	0.003±0.001	0.003±0.001	0.003±0.001
Fenitrothion	0.013±0.001	0.010±0.001	0.01±0.001	0.01±0.001
Chlorofenvinfos	0.005±0.001	0.003±0.001	0.004±0.001	0.003±0.001

Mean value ± standard deviation, where n=2 Values are mean ± standard deviation of triplicate determination

The Maximum Residue Limit (MRLs) for organophosphate is in the range of 0.05 – 1.00 mg/kg (EC, 1990). For the organophosphates (Diazinon and Dichlorvos) the U.S. EPA has established maximum permissible levels of dichlorvos in various food products ranging from 0.02 to 2 parts per million (ppm) (ATSDR, 1995). Previous research reported organophosphate pesticide residue level of food crops to be between 0.0194 to 0.455 mg/kg (Ogah and Coker *et al.*, 2011). Organophosphate (OP) pesticides are one group of insecticides commonly used for agricultural purposes. They are also used in the homes and in yards in smaller quantities to control pests and are currently the most commonly used household insecticides (Kamrin, 1997). These pesticides are also regularly used in other settings such as hospitals and schools with the purpose of controlling pests (Gao *et al.*, 1999). Organophosphate pesticides are known to be highly toxic, but they have a short biologic half-life when compared to pesticides such as DDT (Wigle *et al*., 2003). Health effects in adults are cancer, respiratory illnesses, and liver and renal injuries (EPA, 1998). However, pesticides can be more harmful to children than to adults because children breathe more air and consume more food and beverage per pound of body weight than do adults (Jurewicz and Hanke, 2008).

The sensitization of populace to wash thoroughly before other forms of processing to reduce the pesticide residue content at the point of consumption residues (Ogah and Coker *et al.*, 2011) would greatly reduce the health hazards associated with pesticide residue levels in such foodstuffs, although, these insecticides were never completely eliminated by washing (Bhuiyan, 2008; Ogah and Coker, 2011). Eradication of all streets hawking of locally adulterated, unregistered, unlabelled, repackaged, uncertified and expired chemical pesticides in the form such as "Otapiapia" among others (Musa *et al.*, 2010) as well as the need for more stringent monitoring of importation and use of these pesticides in agriculture and food storage in Nigeria are required.

Conclusion

Cereal grains are the staple foods in large parts of the world, supplying most of the energy and bulk in diets. The relative amounts of dietary constituents in cereals and cereal products depend largely on the degree of refinement and other forms of processing. The results of this study have revealed information on the variability in the nutritional composition of the cereal food samples consumed in Wukari. It has also revealed that maize had the highest energy and carbohydrate composition while the highest protein composition was found in wheat. Considering the variability in nutritional composition of these cereal grains, there would still be need to consume some of the cereal grains if not all so that one can derive the health benefits associated with bioactive compounds in the whole grains which are essentially fibre and phytochemicals which is responsible for lowering blood. Also, the findings in this study showed that cleaned/wholesome samples procured from Wukari market had levels of organochlorines and organophosphates which are below Maximum Residue Limits (MRLs), for organophosphate, hence they are safe for human and animal consumption and other processing utilization.

Conflict of Interest

Authors declare that there is no conflict of interest related to this study.

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