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EVALUATION OF ORGANOPHOSPHATES RESIDUE IN STORED CEREALS FROM SOME SELECTED MARKETS IN JALINGO, NIGERIA

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Abstract

Cereal grains such rice, sorghum, maize and millet among others are the staple foods in large parts of the world, supplying most of the energy and bulk in diets. Pesticide residue analysis in cereals from the various sampling locations for this dissertation revealed the following organophosphate pesticide residue were present in cereals analyzed Dichlorvos, Diazinon, Phorate sulfon, Malathion, Phorate, Chloropyrifos, Methyl Parathion, Profenofos, Ethion, Dimethoate, Phorate Sulfoxide, Phosalone, Edifenfos, Fenitrothion and Chlorofenvinfos. The presence of pesticide residues is detected in the samples of cereals (Rice, Maize, Millet and sorghum) analyzed. This could be as a result of high utilization of various pesticides during plant, cultivation and storage thus leading to the bioaccumulation of this substance in the individual cereals. It indicates high levels of non-carcinogenic risk associated with the life time consumption of cereals produce and sold within this region. Based on findings from this study's, I hereby make the following recommendations. Regulatory agencies in Nigeria should step up efforts to ensure compliance with the ban on these chemicals. Farmers and other pesticide users also need to be educated on the dangers of using banned products and on the over application of these pesticides. Furthermore, farmers should be educated on the properly usage of these chemical product, during plant, harvest and storage. Also, manufacturers of these chemicals should produce less toxic pesticide using organic materials in other to prevent the health risk associated with chemical pesticide and their residues in food crops and the environment.

Keywords: Cereal; Jalingo; Organophosphates; GC-MS

INTRODUCTION

Maintaining high agricultural output requires the use of pesticides, since, in high-input agricultural production systems, pests, among other crop invaders, including weed and fungi inevitably need to be managed (Mnif *et al.*, 2011). However, reliance on pesticides is unsustainable due to their harmful effects on the environment and human health. The risk to human health comes from direct or indirect exposure to pesticide residues in primary or derived agricultural products (Aravinna *et al.*, 2018; Bando *et al.*, 2022). Pesticide residue refers to the pesticides that may remain on or in food after they are applied to food crops. It is defined as any substance or mixture of substance in food for man or animals resulting from the use of pesticide and includes any specified derivatives, such as degradation and conversion products, metabolites, reaction products, and impurities that are considered to be of toxicological significance. Exposure to pesticide residues through the diet is assumed to be up to five times the magnitude of exposure through other routes such as air and drinking water (Zhang *et al.*, 2017). Infants, children and adults are commonly exposed to pesticides by eating them on and in our food (Zhang *et al.*, 2013). Pesticides play a role in many human health problems, and can exert acute effects, such as dizziness, headaches, rashes, and nausea, and chronic effects, such as cancers, neurotoxicity, genotoxicity, birth defects, impaired fertility, and endocrine system disruption (Aravinna *et al.*, 2018). Consequently, governments of different countries have enacted legislation in order to reduce consumer exposure to harmful pesticides, and regulate the appropriate use of pesticides in terms of the authorization that is granted, the type of registration (application rates and pre-harvest intervals), and allowing for free deliberation as to which products are to be treated with pesticides as long as the treatment complies with the established maximum residue limits (MRLs) (Mnif *et al*., 2011; Ishan, 2018).

Pesticides applied to food crops in the field can leave potentially harmful residues (Gao *et al*., 2008). According to Mazlan *et al*. (2017), after pesticides are applied to the crops, they may interact with the plant surfaces, be exposed to the environmental factors such as wind and sun and may be washed of during rainfall. The pesticide may be absorbed by the plant surface (waxy cuticle and root surfaces) and enter the plant transport system (systemic) or stay on the surface of the plant (contact). The pesticides that get into the plant tissues may be transformed (metabolised) or sequestered in the tissues to form the pesticide residue. 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 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 (Arowora *et al*., 2020). This research aimed to estimate the level of Organophosphates residue in some selected cereals produced consumed within Jalingo town, Taraba state, Nigeria.

METHODS

Study Area

Jalingo LGA is roughly located between latitudes 8^o 47' to 9^o 01'N and longitudes 11^o 09' and 11^o 30'E. It is bounded to the north by Lau Local Government Area, to the east by Yorro Local Government Area, to the south and west by Ardo Kola Local Government Area. It has a total land area of about 195km^2 with an estimated human population of 139,845 people according to the 2006 national population census.

Sample preparation

Cereal (Maize, millet, sorghum and rice samples) were cleaned by picking out stones, weevils and other non-essential materials. The different samples were then milled separately, first, using a mortar and pestle and then finally milled to powder using a hand-grinding machine. The bean samples were purchased in dry form and no further drying was required. Precautionary measures were taken to avoid cross-contamination of the different samples during and after milling.

Extraction

Extraction was done using the method of Zhang *et al.* (2011), with slight modifications. An aliquot of 10g of each powdered sample was weighed, using an electronic weighing balance, into a 250 ml beaker. Initial weight of the beaker was recorded as Wb and the weight of beaker with sample was recorded as Wb+s. 30 ml of the extraction solvent was introduced into 10g of the powdered sample contained in the beaker. The mixture was properly sealed airtight using foil and tape. This was allowed for 48 h for extraction. The samples after extraction were filtered using filter paper and funnel and then concentrated by evaporation at room temperature for 24 to 72 h. The organic residue was then diluted with 1ml n-hexane and stored in reagent bottles ready for Gas chromatography–mass spectrometry (GC-MS) analysis.

Identification and quantification

Pesticide residues were identified by comparison of the retention times, peak area and peak heights of the sample with those of the standards. Pesticide concentrations were within 5% of the standards.

Data analysis

Statistical analysis was done using SPSS version 20. Results were presented as mean ± standard deviation.

RESULTS

Table 1: organophosphate present in cereal samples obtained from Mile six markt

Mile six market			Cereals		
Organophosphate (ppb)	Rice	Sorghum	Maize	Millet	MRL(WHO)
Dichlorvos	0.032±0.001a	0.009±0.004^{a}	0.014±0.001^{a}	0.070±0.005^{a}	0.010
Diazinon	0.058±0.002^{ab}	0.016±0.002^{ab}	0.025±0.002b^{c}	0.127±0.002^{ab}	0.050
Phorate sulfon	0.099±0.004^{b}	0.028±0.002^{b}	0.043±0.002^{d}	0.217±0.002^{b}	0.010
Malathion	0.091±0.001^{b}	0.026±0.000^{b}	0.040±0.001d	0.199±0.004^{b}	0.005
Phorate	0.095±0.002^{b}	0.027±0.001^{b}	0.042±0.002^{d}	0.210±0.001^{b}	0.050
Chloropyrifos	0.068±0.003^{b}	0.019±0.002^{ab}	0.030±0.005^{c}	0.150±0.005^{ab}	0.300
Methyl Parathion	0.083±0.003^{b}	0.023±0.001^{b}	0.036±0.002^{cd}	0.182±0.000^{c}	0.020
Profenofos	0.107±0.002^{c}	0.030±0.005^{b}	0.047±0.002^{d}	0.235±0.002^{b}	0.040
Ethion	0.099±0.004^{b}	0.028±0.003^{b}	0.044±0.000^{d}	0.218±0.003^{b}	0.300
Dimethoate	0.111±0.001^{c}	0.031±0.001^{b}	0.049±0.004^{d}	0.243±0.003^{b}	0.020
PhorateSulfoxide	0.105±0.002^{c}	0.030±0.005^{bc}	0.046±0.001^{d}	0.231±0.001^{b}	0.020
Phosalone	0.082±0.002^{b}	0.023±0.000^{b}	0.036±0.001^{cd}	0.180±0.003^{b}	0.025
Edifenfos	0.082±0.003^{b}	0.023±0.003^{b}	0.036±0.000^{cd}	0.179±0.005^{b}	0.017
Fenitrothion	0.083±0.003^{b}	0.023±0.002^{b}	0.037±0.002^{cd}	0.183±0.001^{b}	0.010
Chlorofenvinfos	0.118±0.001^{c}	0.033±0.001^{c}	0.052±0.000^{e}	0.260±0.000^{c}	0.015

Result presented in mean ± standard deviation. Result with the same superscript down the column indicates no significant difference, while result within the same column with different superscripts indicates significant difference ($p \leq 0.005$).

Table 2: organophosphate present in cereal samples obtained from Jalingo main market

Jalingo main market	Cereals				
Organophosphate (ppb)	Rice	Sorghum	Maize	Millet	MRL (EU/WHO)
Dichlorvos	0.004±0.001[a]	0.003±0.001[a]	0.132±0.002[a]	0.041±0.001[a]	0.010
Diazinon	0.003±0.001[a]	0.003±0.001[a]	0.116±0.001[a]	0.036±0.002[a]	0.050
Phorate sulfon	0.007±0.002[b]	0.006±0.001[b]	0.260±0.005[bc]	0.081±0.003[b]	0.010
Malathion	0.010±0.000[b]	0.008±0.003[c]	0.363±0.003[c]	0.113±0.004[c]	0.005
Phorate	0.010±0.000[b]	0.008±0.003[c]	0.343±0.003[c]	0.107±0.002[c]	0.050
Chloropyrifos	0.007±0.002[b]	0.006±0.001[b]	0.250±0.005[bc]	0.078±0.003[b]	0.300
Methyl Parathion	0.004±0.001[a]	0.003±0.001[a]	0.130±0.005[a]	0.040±0.005[b]	0.020
Profenofos	0.006±0.001[b]	0.005±0.001[b]	0.195±0.002[b]	0.061±0.002[b]	0.040
Ethion	0.006±0.001[b]	0.005±0.001[b]	0.225±0.012[b]	0.070±0.001[b]	0.300
Dimethoate	0.010±0.000[b]	0.009±0.004[c]	0.365±0.001[c]	0.113±0.004[c]	0.020
PhorateSulfoxide	0.006±0.001[b]	0.005±0.000[b]	0.208±0.002[b]	0.065±0.006[b]	0.020
Phosalone	0.008±0.003[b]	0.006±0.001[b]	0.277±0.002[bc]	0.086±0.001[b]	0.025
Edifenfos	0.004±0.001[a]	0.003±0.000[a]	0.124±0.002[a]	0.038±0.003[a]	0.017
Fenitrothion	0.006±0.001[b]	0.005±0.000[b]	0.193±0.003[b]	0.060±0.005[b]	0.010
Chlorofenvinfos	0.010±0.000[b]	0.008±0.001[c]	0.354±0.002[c]	0.110±0.002[c]	0.015

Result presented in mean ± standard deviation. Result with the same superscript down the column indicates no significant difference, while result within the same column with different superscripts indicates significant difference ($p \leq 0.005$).

Table 3: organophosphate present in cereal samples obtained from Mayo dassa market

Mayo dassa market	**Cereals**				
Organophosphate (ppb)	Rice	Sorghum	Maize	Millet	MRL (EU/WHO)
Dichlorvos	0.016±0.001[b]	0.013±0.001[a]	0.554±0.002[b]	0.172±0.002[b]	0.010
Diazinon	0.017±0.002[b]	0.014±0.002[a]	0.583±0.003[b]	0.181±0.001[b]	0.050
Phorate sulfon	0.012±0.000[a]	0.010±0.001[a]	0.418±0.003[a]	0.130±0.003[a]	0.010
Malathion	0.014±0.001[a]	0.012±0.000[a]	0.506±0.001[b]	0.157±0.003[c]	0.005
Phorate	0.019±0.004[b]	0.015±0.001[b]	0.653±0.003[c]	0.203±0.001[b]	0.050
Chloropyrifos	0.017±0.001[b]	0.014±0.001[a]	0.605±0.001[c]	0.188±0.003[b]	0.300
Methyl Parathion	0.019±0.002[b]	0.016±0.002[b]	0.675±0.002[cd]	0.210±0.005[b]	0.020
Profenofos	0.018±0.003[b]	0.015±0.001[b]	0.641±0.001[c]	0.199±0.004[b]	0.040
Ethion	0.014±0.001[a]	0.012±0.001[a]	0.499±0.003[ab]	0.155±0.001[b]	0.300
Dimethoate	0.014±0.001[a]	0.012±0.000[a]	0.498±0.004[ab]	0.155±0.002[b]	0.020
PhorateSulfoxide	0.014±0.002[a]	0.012±0.000[a]	0.507±0.001[b]	0.157±0.002[b]	0.020
Phosalone	0.021±0.001[b]	0.017±0.003[b]	0.723±0.003[d]	0.224±0.001[b]	0.025
Edifenfos	0.018±0.003[b]	0.015±0.001[b]	0.621±0.002[c]	0.193±0.021[b]	0.017
Fenitrothion	0.010±0.000[a]	0.008±0.003[a]	0.350±0.001[a]	0.109±0.004[a]	0.010
Chlorofenvinfos	0.014±0.001[a]	0.011±0.002[a]	0.475±0.003[ab]	0.147±0.002[a]	0.015

Table 4: organophosphate present in cereal samples obtained from Mayo gwoi market

Mayo gwoi market	Cereals				
Organophosphate (ppb)	Rice	Sorghum	Maize	Millet	MRL (EU/WHO)
Dichlorvos	0.008 ± 0.003^{a}	0.006 ± 0.001^{b}	0.277 ± 0.002^{bc}	0.086 ± 0.001^{bc}	0.010
Diazinon	0.009 ± 0.002^{b}	0.007 ± 0.002^{b}	0.302 ± 0.002^{c}	0.094 ± 0.002^{bc}	0.050
Phorate sulfon	0.007 ± 0.002^{b}	0.006 ± 0.001^{b}	0.246 ± 0.001^{b}	0.076 ± 0.001^{b}	0.010
Malathion	0.004 ± 0.001^{a}	0.003 ± 0.001^{a}	0.132 ± 0.002^{a}	0.041 ± 0.001^{a}	0.005
Phorate	0.003 ± 0.001^{a}	0.003 ± 0.001^{a}	0.116 ± 0.001^{a}	0.036 ± 0.003^{a}	0.050
Chloropyrifos	0.007 ± 0.002^{b}	0.006 ± 0.002^{b}	0.260 ± 0.005^{bc}	0.081 ± 0.002^{bc}	0.300
Methyl Parathion	0.010 ± 0.000^{b}	0.008 ± 0.003^{b}	0.363 ± 0.003^{c}	0.113 ± 0.001^{c}	0.020
Profenofos	0.010 ± 0.001^{b}	0.008 ± 0.003^{b}	0.343 ± 0.001^{c}	0.107 ± 0.002^{c}	0.040
Ethen	0.007 ± 0.002^{b}	0.006 ± 0.001^{b}	0.250 ± 0.005^{bc}	0.078 ± 0.002^{b}	0.300
Dimethoate	0.004 ± 0.001^{a}	0.003 ± 0.000^{a}	0.130 ± 0.002^{a}	0.040 ± 0.005^{a}	0.020
PhorateSulfoxide	0.006 ± 0.002^{b}	0.005 ± 0.001^{b}	0.195 ± 0.002^{ab}	0.061 ± 0.001^{b}	0.020
Phosalone	0.006 ± 0.003^{b}	0.005 ± 0.001^{b}	0.225 ± 0.005^{b}	0.070 ± 0.005^{b}	0.025
Edifenfos	0.010 ± 0.005^{b}	0.009 ± 0.004^{b}	0.365 ± 0.003^{c}	0.113 ± 0.001^{c}	0.017
Fenitrothion	0.006 ± 0.001^{b}	0.005 ± 0.001^{b}	0.208 ± 0.003^{b}	0.065 ± 0.002^{b}	0.010
Chlorofenvinfos	0.008 ± 0.003^{b}	0.006 ± 0.002^{b}	0.277 ± 0.002^{bc}	0.086 ± 0.001^{bc}	0.015

Result presented in mean ± standard deviation. Result with the same superscript down the column indicates no significant difference, while result within the same column with different superscripts indicates significant difference ($p \leq 0.005$).

DISCUSSION

Analysis of residual pesticide in cereals at the various sampling locations within Jalingo metropolis of Taraba state revealed the presence of organophosphate in the various cereals samples at different concentration. The following organophosphates were confirmed in the cereals samples; Dichlorvos, Diazinon, Phorate sulfon, Malathion, Phorate, Chloropyrifos, Methyl Parathion, Profenofos, Ethion, Dimethoate, PhorateSulfoxide, Phosalone, Edifenfos, Fenitrothion and Chlorofenvinfos.

Organophosphates are highly potent compounds used majorly as insecticides in the control of storage insects in food crops (Bando *et al*., 2022). They are very toxic and more often involved in acute poisoning than other classes of pesticides (Zhang *et al*., 2011; Das *et al*., 2020). 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 (Bernardes *et al.,* 2015). In the analysis for organophosphate pesticide residue level, 15 different forms of organophosphate detected in the different cereals samples at the various sampling locations. In Mile six market, the organophosphate detected in rice, sorghum, maize and millet were within the ranges of 0.032±0.001 to 0.111±0.001, 0.016±0.002 to 0.031±0.001, 0.014±0.001 to 0.049±0.004, and 0.070±0.005 to 0.260±0.000 respectively with the highest value of organophosphate found in millet. Majority of the analyzed pesticide residue found in rice at Mile six market sampling location were above WHO MRLs with the exception of Choloropyrifos and Ethion whose residual concentrations are below MRLs. Similarly, the pesticide residual concentration in sorghum was above MRLs with the exception of Dichlorvos, Profenofos, and Ethion. The residual concentrations in millet revealed majority of the pesticide residues were above MRLs with exception of Diazinon and Phorate whose values were below MRLs. For millet only Ethion had a residual concentration below WHO MRLs while the rest of the residual pesticide present had a concentration above the MRL. The residual concentration of organophosphates in rice, Sorghum, Maize, Millet obtained from Jalingo main market ranges between 0.003±0.001 to 0.010±0.000 ppm, 0.003±0.001 to 0.009±0.004ppm, 0.116±0.001 to 0.365±0.003ppm, 0.036±0.002 to 0.113±0.004 ppm respectively. However, the pesticide residual concentrations in rice were below WHO MRLs with exception of Malathion. While for sorghum samples obtained from Jalingo main market, the residual concentrations were below WHO MRLs for each of the individual residual pesticide present. For maize and millet, the residual concentrations of pesticide for the individual pesticide were all above WHO MRLs. The residual concentration of organophosphates in rice, sorghum, maize, and millet obtained from Mayo dassa market ranges between 0.010±0.000 to 0.021±0.001 ppm, 0.008±0.001 to 0.017±0.003ppm, 0.350±0.001 to 0.723±0.003ppm, and 0.109±0.004 to 0.224±0.001ppm respectively. For pesticide residual concentration in rice, the residual concentrations are either slightly below or slightly WHO MRLs residual concentration in cereals, thus may not necessary pose any health implications. For sorghum at this sampling location, similarly to that of rice, the individual residual concentrations are slightly above or below WHO MRLs for pesticide residual concentration in cereals, however for maize and millet, the residual concentration of pesticide at this particular sampling location were highly above WHO MRLs residual pesticide concentration in cereals. The residual concentration of organophosphate in rice, sorghum, maize, and millet samples obtained from Mayo gwoi market ranges between 0.003±0.001 to 0.010±0.005ppm, 0.003±0.001 to 0.008±0.003ppm, 0.116±0.001 to 0.365±0.003ppm, 0.036±0.003 to 0.113±0.001ppm respectively. However, the residual concentration of pesticide in rice and sorghum were all below WHO MRLs residual pesticide levels in cereals while on the other hand, the residual concentration of maize and millet were above WHO MRLs, except for Chloropyrifos and phorate. 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 (Karami-Mohajeri and Abdollahi, 2011). These pesticides are also regularly used in other settings such as hospitals and schools with the purpose of controlling pests (Gao *et al.,* 2008). Organophosphate pesticides are known to be highly toxic, but they have a short biologic half-life when compared to pesticides such as DDT (Reiler *et al.*, 2015). 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 (Waddell *et al.*, 2001). The sensitization of populace to wash thoroughly before other, forms of processing to reduce the pesticide residue content at the point of consumption residues (Li *et al.,*2015) would greatly reduce the health hazards associated with pesticide residue levels in such foodstuffs, although, these insecticides were never completely eliminated by washing (Bando *et al.*, 2022). Eradication of all streets hawking of locally adulterated, unregistered, unlabelled, repackaged, uncertified and expired chemical pesticides in the form such as "Otapiapia" among others 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 such rice, sorghum, maize and millet among others are the staple foods in large parts of the world, supplying most of the energy and bulk in diets. Pesticide residue analysis in cereals from the various sampling locations for this dissertation revealed the following organophosphate pesticide residue were present in cereals analyzed Dichlorvos, Diazinon, Phorate sulfon, Malathion, Phorate, Chloropyrifos, Methyl Parathion, Profenofos, Ethion, Dimethoate, PhorateSulfoxide, Phosalone, Edifenfos, Fenitrothion and Chlorofenvinfos. The presence of pesticide residues is detected in the samples of cereals (Rice, Maize, Millet and sorghum) analyzed. This could be as a result of high utilization of various pesticides during plant, cultivation and storage thus leading to the bioaccumulation of this substance in the individual cereals. It indicates high levels of non-carcinogenic risk associated with the life time consumption of cereals produce and sold within this region.

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