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Health Risk Assessment of Organochlorine and Synthetic Pyrethroid Pesticide Residues via Dietary Intake of Field grown Fruits and Vegetables

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ABSTRACT

Background: The presence of pesticide residues in agricultural products raises serious health concerns for consumers, and consumption of pesticide contaminated vegetables and fruits pose a major threat to public health. The aim of this study was to assess the health risk of organochlorine and synthetic pyrethroid pesticide residues via dietary intake of field grown fruits and vegetables along River Galma in Zaria Kaduna state.

Methods: Samples were analysed for multi- pesticide residues using Gas Chromatography-Mass Spectrometry (GC – MS). The health risk indices (HRI) of the pesticide residues via dietary intake of vegetables and fruits were assessed according to the guidelines recommended by the USEPA, where the estimated daily intake (EDI) were compared with the acceptable daily intake (ADI).

Results:The human health risk assessment in all the samples analysed revealed that detected organochlorines pesticides such as heptachlor epoxide B, endosulfan II and delta- BHC can pose a threat to human health as they all have HRI values greater than one. Also, a – Cypemethrin, a synthetic pyrethroid with values of 1.01 and 1.86 in spinach and onion respectively greater than index of one. The highest health index values of 26.58, 23.22, and 6.93 were found for heptachlor epoxide B in onion, spinach and carrots respectively. However, some of the detected pesticides pose no health risk in the fruits and vegetables samples analysed.

Conclusion: Therefore, the results of this study suggest continuous monitoring and strict regulation of pesticide residues in vegetable and fruits to protect consumer health in the study area.

***Key words*— Fruits, gas chromatography, health risk, pesticide residues, and vegetables**

1. INTRODUCTION

Pesticides are used to control and prevent various kinds of pests and disease that affects crops and animals and also help in boosting agricultural production in order to cope with the demands of the populace. However, when pesticides are used indiscriminately, they pose danger and risk to human health [1]. Pesticides are also used worldwide to protect crops before and after harvest in agriculture, gardening, homes and soil treatment. Varieties of pesticides are used in current agricultural practices to manage pests and infections that spoil crops [2]. It was observed globally that pesticide usage has increased tremendously during the last three decades consequent with changes in farming practices and the increased intensive agriculture. Therefore, the extensive use of pesticides for agricultural and non-agricultural purposes has resulted in the presence of residues in various environmental matrices, especially food stuff providing the high risk of these chemicals to human health and environment [3]. Pesticide residue are substances or mixture of substances in food for man or animals resulting from the use of pesticide including any specified derivatives, such as degradation and conversion products, metabolites, reaction products and impurities considered to be of toxicological significance [4]. According to [5] report, about 849,000 people death globally from acute toxicity of the pesticide in 2001. Pesticide poisoning and deaths occurred in the developing countries [6]. Food safety is a major public concern worldwide. During the last decades, the increasing demand of food safety has stimulated research regarding the risk associated with consumption of foodstuffs, contaminated by pesticide [7]. Also, the increasing demand of food safety has stimulated research regarding the risk associated with consumption of fruit and vegetables as they constitute major part of human diet contributing nutrients, vitamins, minerals and fibres. However, these plants contain pesticide residues over a wide range of concentration. Therefore, residues of pesticides could affect the ultimate consumers especially when these

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commodities are known as carcinogens/or toxins and therefore, it is desirable to reduce these residues [8]. In the monitoring of pesticide residue intakes, numerous indices can be used. The maximum residue limit (MRL) is one such index which represents the maximum concentration of a pesticide residue (mg/kg) that the Codex Alimentarius Commission recommends be legally permitted in food commodities and animal feeds [9]. Also, the acceptable daily intake (ADI) which is the estimated amount of a substance in food (expressed on a body weight basis) that can be ingested daily over a lifetime without appreciable health risk to the consumer is very important. The estimated daily intake (EDI) of a pesticide residue in a given food is obtained by multiplying the residue level in the food by the amount of that food consumed. The EDI of pesticide residues should be less than its ADI. The hazard risk index (HRI) is applied to assess the potential health risk from consumption of pesticide residues containing foodstuff. Indeed, the aim of this paper was to determine the concentration of the selected pesticide residues in fruits and vegetables grown along River Galma in Zaria, Kaduna state and also to assess public health risk of pesticide residues in them via daily intake of pesticide contaminate fruits and vegetables commodities are freshly consumed. The total dietary intake of pesticide residues that remains on agricultural.

2. 0. MATERIALS AND METHODS

2.1 Materials

2.1.1 Equipment

SHIMADZU GC/MS ,High speed homogenizer, Centrifuge machine, Blender, Microcentrifuge, Centrifuge tubes, Volumetric flash, Measuring cylinders, Beakers, Micro pipette or Automatic pipettes, Injection vials, 1, 5 ml suitable for GC and LC auto-sampler, Powered funnel to fill to the openings of the centrifuge tubes, PTFE Screw cap (polytetrafluroethylene, PTFE), Vortex mixer.

2.1.2 *Chemicals/Reagents*

Certified reference standards of all the test pesticides of 98% purity were purchased ,Ethyl acetate, Acetonitrile, Methanol, Distilled water, Primary secondary amine (PSA, 40 cm) (Bondesil) sorbent , Anhydrous sodium sulphate, Magnesium sulphate, Methanol, Hexane, Sodium chloride, Acetic acid, Sodium acetate, Triphenyl phosphate.

2.1.3 Sampling

Samples were taken at five (5) random points (quadrant approach) at a farm land along River Galma, Zaria, Kaduna state and mixed to constitute a composite of 1 kg in plastic bags and immediately transported to the laboratory and kept refrigerated before analysis.

2.1.4 Sampling Preparation of Standard Solution

Stock solutions were prepared containing 1000 mg/dm^{-3} of each compound to be investigated by accurately weighing 10 mg ($\pm 0.01\ mg$) of each analyte in volumetric flasks and dissolving in 10 cm^{3} of methanol or acetonitrile contained in a beaker. These would be stored in dark vials in a refrigerator at 4^{0}C. Working standards were also prepared by serial dilutions. Final concentration (in acetonitrile) of 0.05, 0.1, 0.25, 0.5, and 1.0 mg dm^{-3} for each analyte was prepared. The calibration parameter is presented in Table 1.

2.2 Methods

2.2.1 *Experimental Procedure: Sample Preparation and Clean up*

Homogenized samples (15 g) were weighted into a 50 cm^{3} polytetrafluro ethylene (PTFE) tube and 15 cm^{3} of acetonitrile containing 1% acetic acid (v/v) was added. Then 6g $MgSO_4$ and 2.5 sodium acetate trihydrate (equivalent to 1.5 g of anhydrous form) w$\pm$as added and the sample shaken forcefully for 4 min and kept in ice bath. The samples were then centrifuged at 4000 rpm for 5 min and 6 cm^{3} of the supernatant transferred to a 15 cm^{3} PTFE tube to which 900 mg $MgSO_4$ and 300 mg PSA was added. The extract would be shaken using a vortex mixer for 20 s and centrifuged at 4000 rpm again 5 min, approximately 2 cm^{3} of the supernatant was taken in a vial. This extract was evaporated to dryness under a stream of nitrogen and reconstituted in n-hexane in auto sampler tube for the GC – MS/Analysis [10].

2.3 Statistical Analysis

The obtained results were statistically analysed. Mean concentrations of the pesticide residue levels in various samples were expressed as mean $\pm$ standards deviations were calculated with use of statistical package 20.0.

3. RESULTS

The Concentration (mg/kg), ADI, EDI and Health Risk estimation of Organochlorine and synthetic pyrethroids pesticide residues in the Fruits and Vegetables were presented in Table 2 and 3. Health risk indices of the pesticide residues via dietary intake of vegetables and fruits was assessed according to the guidelines recommended by the

USEPA, where the estimated daily intake (EDI) were compared with the acceptable daily intake (ADI) [11]. Estimated daily intake (EDI) was found by multiplying the residual pesticide concentration (mg kg-1) by the food consumption rate (kg day^{-1}) and dividing by a body weight of 60 kg for adult population. The average daily vegetable and fruits intake for adults was considered to be 0.345 kg/person/day. Health Risk Index (HRI) was calculated using the equation.

$$HRI = \frac{EDI}{ADI}$$ [12]

Where EDI is estimated daily intake and ADI is acceptable daily intake. An index more than 1 is considered as not safe for human health [13].

Table 1: Calibration parameters of the detected pesticides

Pesticides	Linear range (ppm)	Equation	Correlation Coefficient (R^2)
Lindane	0.05 – 1.00	y = 8.736x – 0.039	0.998
delta – BHC	0.05 – 1.00	y = 4.102x – 0.119	0.999
Hepta. Epoxide B	0.05 – 1.00	y =3.084x + 0.027	0.999
Endosulfan I	0.05 – 1.00	y = 1.638x – 0.030	0.998
Endosulfan II	0.05 – 1.00	y = 3.343x – 0.010	0.998
Dieldrin	0.05 – 1.00	y = 5.998x + 0.040	0.999
a- Cypermethrin	0.05 - 1.00	y = 2.532x – 0.042	0.999
b- Cypermethrin	0.05 - 1.00	y = 1.306x – 0.022	0.998
z- Cypermethrin	0.05 – 1.00	y = 2.416x – 0.080	0.993

Table 2: Concentration (mg/kg), ADI, EDI and Health Risk estimation of Organochlorine Pesticide Residues in the Fruits and Vegetables

Commodity	Pesticides	Conc.(mg/kg)	MRL (mg/kg)	*ADI (mg/kg/day)	**EDI (mg/kg.bw/day)	HRI	Health risk
Spinach	delta-BHC	0.059 a ± 0.050	0.02	0.345	0.24	0.70	NO
	hept.epoxide B	2.011a ± 0.001	0.02	0.345	8.01	23.22	YES
	endosulfan I	0.038a ± 0,017	0.02	0.345	0.15	0.43	NO
	endosulfan II	0.090a ± 0.051	0.02	0.345	0.36	1.04	YES
Sorrel	lindane	ND	0.01	0.345	-	-	-
	delta -BHC	0.048 ± 0.001	0.02	0.345	0.20	0.58	NO
	hept.epoxide B	0.317a ± 0.001	0.02	0.345	1.26	3.65	YES
	endosulfan I	0.033a ± 0.001	0.02	0.345	0.13	0.38	NO
	endosulfan II	0.078a ± 0.001	0.02	0.345	0.31	0.90	NO
Onions	lindane	0.010 ± 0.001	0.01	0.345	0.04	0.12	NO
	delta-BHC	0.122a ± 0.013	0.02	0.345	0.45	1.30	YES
	hept.epoxide B	2.303a ± 0.001	0.02	0.345	9.17	26.58	YES
	endosulfan I	0.042a ± 0.001	0.02	0.345	0.17	0.49	NO
	endosulfan II	0.153a ± 0.129	0.02	0.345	0.61	1.77	YES
Carrots	lindane	0.007 ± 0.001	0.01	0.345	0.03	0.09	NO
	delta-BHC	0.030a ± 0.001	0.02	0.345	0.12	0.35	NO
	hept.epoxide B	0.600a ± 0.001	0.02	0.345	2. 39	6.93	YES
	endosulfan I	0.080a ± 0.021	0.02	0.345	0.32	0.93	NO
	dieldrin	0.008 ± 0.001	0.05	0.345	0.03	0.09	NO
	endosulfan II	0.271a ± 0.001	0.02	0.345	1.08	3.13	YES

a > MRL

ND = Not Detected; * = Acceptable Daily Intake (ADI) = 0.345/person/day; **= Estimated Daily Intake (EDI) = Exposure (mg/kg.bw/day) = Consumption (mg/kg.bw/day)× Residue Conc. (mg/kg). Food consumption = 239g/day; Average body weight= 60kg; HRI= Health Risk Index = 1

Table 3: Concentration (mg/kg), ADI, EDI and Health Risk estimation of Synthetic pyrethroids Pesticide Residues in the Fruits and Vegetables

Commodity	Pesticides	Conc. (mg/kg)	MRL(mg/kg)	*ADI(mg/kg/day)	**EDI(mg/kg.bw/day)	HRI	Health risk
Spinach	a-cypermethrin	0.088 ± 0.073	0.20	0.345	0.35	1.01	YES
	b-cypermethrin	0.029 ± 0.001	0.20	0.345	0.16	0.46	NO
	z-cypemethrin	0.011 ± 0.001	0.20	0.345	0.04	0.12	NO
Sorrel	a-cypemethrin	ND	0.20	0.345	-	-	-
	b-cypemethrin	ND	0.20	0.345	-	-	-
	z-cypemethrin	ND	0.20	0.345	-	-	-
Onions	a-cypemethrin	0.160 ± 0.001	0.20	0.345	0.64	1.86	YES
	b-cypemethrin	ND	0.20	0.345	-	-	-
	z-cypemethrin	0.004 ± 0.001	0.20	0.345	0.02	0.06	NO
Carrots	a-cypemethrin	0.020 ± 0.004	0.20	0.345	0.09	0.26	NO
	b-cypemethrin	ND	0.20	0.345	-	-	-
	z-cypemethrin	0.004 ± 0.001	0.20	0.345	0.16	0.46	NO

ND = Not Detected; *= Acceptable Daily Intake (ADI) = 0.345/person/day; **= Estimated Daily Intake (EDI) = Exposure (mg/kg.bw/day)= Consumption (mg/kg.bw/day)× Residue Conc. (mg/kg). Food consumption = 239g/day; Average body weight= 60kg; HRI= Health Risk Index = 1

4. DISCUSSION

The ADI, EDI and HRI of organochlorines pesticide residues are given in Table 2 and 3. From the Tables, all the detected organochlorines and synthetic pyrethroid in spinach sample analysed showed no health risk except for endosulfan II, a- Cypermethrin and heptachlor epoxide (B) with HRI values of 1.04, 1.01 and 23.22 respectively. It implies that consuming spinach from this study area with this high level of heptachlor epoxide (B) residue did portend a great health risk. Hence, the farmers in this area should properly be cautioned against excessive use of pesticide containing heptachlor epoxide (B) active ingredient. The present results were found to be very much higher when compared with the resuts of [14], who reported 0.21 which indicated no health risk. Also, from the Table 2 and 3, the organochlorines and synthetic pyrethroids health risk assessment of the detected pesticides in onions signified health risk to the consumers. The HRI values for delta-BHC, heptachlor-epoxide (B), endosulfan II and a- Cypermethrin pesticides were greatly higher than one which shows a great health risk when consuming onions from the study area. For the heptachlor epoxide (B) with HRI value of 26.58, the risk was very high implying that farmers in this area did not comply with the Good Agricultural Practice (GAP) for using these pesticides. Also, in sorrel, the health risk assessments of all the detected pesticides portend no health risk except for the heptachlor epoxide (B) with HRI value of 3.65. It is persistence organochlorines which is very dangerous to human health. It is very cheap and commonly found in the agrochemical shops in Nigeria.In the analysed carrot sample, those that posed health risk were all organochlorines: heptachlor epoxide (B) (6.93) and endosulfan II (3.13). The HRI values of these two pesticides were higher when compared to the one reported by [15]. Hence, farmers in this area must ensure a good agricultural practice (GAP) in the application of these pesticides. Well, the remaining pesticide residues (lindane, endosulfan I and dieldrin) present no risk if consumed. Likewise, in Table 3, the b- cypermethrin and z- cypemethrin detected in the samples all have HRI values less than 1, which portend no health risk when consumed.

5. CONCLUSION

The analysis revealed that spinach and onions contains organochlorines pesticide residues with doses above the reference of one especially for heptachlor epoxide B, delta- BHC and endosulfan II. Other organochlorine, b-cypemethrin and z- cypemrthrin hazard index for various residues revealed an HRI values below 1, suggesting that the pesticide residues, present in those samples incur no threat to human health, but there should be routine monitoring programs of heptachlor and endosulfan II levels especially in children, the most vulnerable population subgroup, which recorded HRI values close greatly above 1 in order to control, reduce, and minimize health risks.
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Conflict of Interest
The authors declare no conflict of interest.

Contribution of the Authors
All the authors participated in all parts of the work.

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