EVALUATION OF PESTICIDE RESIDUES IN SOME FRUITS AND VEGETABLES IN OSOGBO, SOUTH WESTERN NIGERIA

Adebisi Segun Akanmu[1*], Olatunji Abigail Oluwafisayo[1]and Awojide Shola Hezekiah[1]

[1]Department of Pure and Applied Chemistry , Osun State University, Osogbo, Osun State, Nigeria.

***Correspondence Author email: adebisioluwasegun@yahoo.com**

ABSTRACT

This study evaluated the quantities of 26 pesticide residues present in some vegetables and fruits samples in comparison with the maximum quantity in which they should be present in the samples. Vegetables and fruits samples (onion, okra, tomatoes, carrot, cashew) were bought at Igbonna Local Market, Osogbo, Osun state. The pesticide residue extraction and analysis were carried out by following the modified standard methods of: Determination of Organochlorine in water by Capillary Column Gas Chromatography, ASTMD 5812-96, Manual of Analytical Methods for the Analysis of Pesticide Residues in Human and Environmental Samples. EPA-600/8-80-038. The test methods covered the capillary gas chromatographic determination of various pesticides, including some of their degradation products and related compounds. The maximum residue limits were obtained from the EPA database. Results obtained showed that the 26 pesticide residues are present in the samples. Comparison of the results obtained with the maximum residue revealed from that there was no significant by-pass of the maximum residue limits of the residues determined. Since these pesticide residues are present but are still below the maximum residue limits, it is imperative not to increase the quantity of the pesticides used. Otherwise, other alternative to pesticide use should be employed.

Keywords: Pesticide Residues, Vegetables, Fruit, Maximum Residue Limits.

INTRODUCTION

Overtime, technological advancement in agricultural sector has led to the development of fertilizers and agrochemicals to boost crop production, reduce pest infestation hence save farmers' money by preventing losses to insects and other pests. Thus, pesticides and insecticides have become widely used farm inputs for crop production. Over the years, the number of pesticides analyzed has increased and was 249 in 2011. The number of substances including isomers and metabolites was approximately 275. The results have been published each year in the period 2004-2011 (Pesticidrester i fødevarer, 2004; Christensen et al., 2005; Christensen et al., 2006; Christensen et al., 2007; Petersen et al., 2008; Jensen et al., 2009; Jensen et al., 2010; Jensen et al., 2011).

The historical background of pesticides use in agriculture is dated back to the beginning of Agriculture itself and it became more pronounced with time due to increased pest population paralleled with decreasing soil fertility (Muir, 2002). However, the use of modern pesticides in agriculture and public health is dated back to the 19th century. The first generation of pesticides involved the use of highly toxic compounds, arsenic (calcium arsenate and lead arsenate) and a fumigant hydrogen cyanide in 1860's for the control of such pests like fungi, insects and bacteria. Other compounds included Bordeaux mixture (copper sulphate, lime and water) and sulphur. Their use was abandoned because of their toxicity and ineffectiveness. The second generation involved the use of synthetic organic compounds. The first important synthetic organic pesticide was dichlorodiphenyltrichloroethane (DDT) first synthesized by a German scientist Ziedler in 1873 (Othmer, 1996) and its insecticidal effect discovered by a Swiss chemist Paul Muller in 1939. In its early days DDT was hailed as a miracle because of its broad-spectrum activity, persistence, insolubility, inexpensive and ease to apply (Keneth, 1992).

According to The Stockholm Convention on Persistent Organic Pollutants, 9 of 12 most dangerous and persistent chemicals are pesticides (Gilden et al., 2010). The United States Environmental protection Agency finished a 10-year review of organophosphate pesticides following the 1996 Food Quality Protection Act, but did little to account for developmental neurotoxic effects, drawing strong criticism from within the agency and from outside researchers (Phillips, 2006). A chromatographic methodology was developed to identify and quantify some

types of organochlorine and organophosphorous insecticide residue in fruit samples produced in Ceara State (Brazil).

There are concerns that pesticides used to control pests on food crops are dangerous to people who consume those foods. These concerns are one reason for the organic food movement. Many food crops, including fruits and vegetables, contain pesticide residues after being washed or peeled. Chemicals that are no longer used but that are resistant to breakdown for long periods may remain in soil and water and thus in food (Cornell, 1999).

The United Nations Codex Alimentarius Commission has recommended international standards for maximum residue limits (MRLs), for individual pesticides in food(CAC/RCP 20-1979)

Strawberries and tomatoes are the two crops with the most intensive use of soil fumigants. They are particularly vulnerable to several types of diseases, insects, mites, and parasitic worms. In 2003, in California alone, 3.7 million pounds (1,700 metric tons) of metham sodium were used on tomatoes. In recent years other farmers have demonstrated that it is possible to produce strawberries and tomatoes without the use of harmful chemicals and in a cost-effective way.

The most frequently used detectors for pesticide residues analysis include ECD, NPD, FPD and MSD. However, it is well known that ECD has been the most used detector in pesticide residue analysis due to its high sensitivity, in particular to halogenated pesticides although all kinds of electron-attracting functional groups such as nitro groups and aromatic structures also give a response to the detector.

A multiresidue method based on matrix solid-phase dispersion (MSPD) is studied to determine chlorfenvinfos, chlorpyrifos, fenarimol, iprodione, procimydone, propiconazole, tetradifon, triadimefon and vinclozolin in artichokes, green beans, lettuce and tomatoes. Alumina, silica and Florisil were assessed as extracting phases, and the extracts from Florisil were the cleanest. To facilitate manual extraction, sand was added to the sample together with the dispersing phase. Three eluting systems were then studied, and dichloromethane proved to be the best. Futher purification can be performed using phase cleanup after diluting extracts with aqueous solutions. Octyl- and octadecyl-silica, modifications of the aqueous diluted extracts and

several eluting solvents were studied. Determination was done by capillary gas chromatography (GC) with electron-capture detection. (JCA, 1996).

This current work attempts to evaluate pesticide residues in some fruits and vegetables like Cashew, Carrot, Tomatoes, Onion and Okra in Osogbo, South Western Nigeria.

MATERIALS AND METHODS

MATERIALS:

Different samples of vegetables and fruits (tomatoes, onions, okra, carrot, cashew) were bought from Igbonna market in Osogbo, Osun state. Samples were put in sterile polythene bags and transported to the laboratory.

Material Preparation:. The samples were stored at 4°C until analysis. The samples were chopped and placed in a stainless steel jar 1L

METHODS:

Extraction: The samples were extracted with 200 mL of acetonitrile and 10 g celite, the blender was vigorously homogenized into high speed for 2 min, and the mixture was filtrated by using Buchner funnel fitted with shark-skin filter paper into 500 mL suction flask (Buchi, Switzerland). An aliquot of organic was transferred to 1L separator funnel and added 100 mL of petroleum ether (PE) and the mixture was vigorously shaken for 1-2 min and then was added 100 ml saturated solution of NaCl and 600 water. The mixture was vigorously mixed and the separator funnel was allowed to be held at horizontal position for few minutes. The aqueous layer was discarded and the solvent layer was washed with twice time 100 mL portions of distilled water and the washed layer was transferred into 100 mL beaker and washed with 15 g of anhydrous sodium sulphate. Finally, the extract was concentrated to 5 mL volume and transferred directly to florisil column.

Pesticide residue analysis: The pesticide residue analysis were carried out by following the modified standard methods of

1. Determination of Organochlorine in water by Capillary Column Gas Chromatography, ASTMD 5812-96
2. Manual of Analytical Methods for the Analysis of Pesticide Residues in Human and Environmental Samples. EPA-600/8-80-038

The test methods covered the capillary gas chromatographic determination of various pesticides, including some of their degradation products and related compounds.

The sub-sampled material was pulverized using laboratory milling machine of maker Janke & Kunkel (IKA Labortechnik) in the laboratory.

Clean Up: The cleanup of the concentrated extract was followed by packing the column with the florisil. The concentrated extract was eluted with the Hexane and later concentrated to the required final volume of 5ml.

The gas chromatography with Pulsed Flame Photometric Detector (PFPD) conditions for the analysis was attached.

GC Conditions For The Analysis Of Pesticide Residue

GC : HP 5890/6890 Powered with HP ChemStation Rev.A 09.01[1206] Software

Injection Temperature: Split Injection

Split Ratio: 20:1

Carrier Gas: Hydrogen

Flow Rate: 1.0ml/min

Inlet Temperature: 250^0C

Column Dimensions: 30m x 0.25mm x 0.25µm

Oven Program: Initial @60^0C for 2 minutes, First Ramp @ 10^0C/min to 200^0C, Second Ramp @ 8^0C/min to 300^0C constant at 5mins

Detector: PFPD

Detector temperature: 300^0C

Hydrogen Pressure: 22psi

Compressed Air: 28psi

RESULT AND DISCUSSION

Table 1 shows the result of the Capillary Column Gas Chromatography analysis carried out on the samples of cashew, carrot, tomatoes, onion, and okra.

Evaluation shows that there are pesticides residues present in each samples in small quantities.

The values for the maximum residue limits of each residue are recorded in Table 2.

Comparison between the results and the standard shows that the maximum residue limits were not exceeded. This may be due to the fact that just small quantities of pesticides were applied during cultivation.

Table 1: Pesticide Residues Composition

	AMOUNT[mg/kg]						
	PESTICIDE RESIDUE	CASHEW	CARROT	ONION	TOMATO	OKRA	AVERAGE
1.	GLYPHOSATE	1.76746e-1	2.71935e-2	1.41879e-1	3.74448e-2	1.64216e-1	1.09448e-1
2.	DICHLORVOS	1.39438e-3	3.19600e-4	1.44853e-3	3.29495e-4	1.70261e-3	1.03892e-3
3.	PIRIMICARB	9.77617e-4	4.42690e-4	9.63393e-4	4.82191e-4	1.14666e-3	8.02510e-4
4.	FLUDIOXONIL	1.94828e-3	1.33024e-3	2.40959e-3	1.33024e-3	2.52595e-3	1.90886e-3
5.	IMIDACHLOPRID	1.72700e-3	2.72627e-3	1.99973e-3	2.72627e-3	2.22243e-3	2.28034e-3
6.	FENITROTHION	1.50231e-3	4.22172e-4	1.80985e-3	4.22172e-4	1.93582e-3	6.09235e-3
7.	METALAXYL	2.28356e-3	1.78796e-3	2.83495e-3	1.78796e-3	2.93486e-3	2.32586e-3
8.	TTRIADIMEFON	1.40728e-3	8.88962e-4	1.52487e-3	8.99172e-4	1.75714e-3	1.29548e-3
9.	CYPROCONAZOLE	4.17470e-3	3.64428e-3	5.17193e-3	3.64428e-3	4.46621e-3	4.22028e-3
10.	TRIADIMENOL	1.42007e-3	1.25761e-3	1.63518e-3	1.25761e-3	1.81106e-3	1.47631e-3
11.	PIRIMIPHOS-METHYL	1.04176e-1	2.28688e-2	1.30520e-1	2.28824e-2	1.32544e-1	8.25982e-2
12.	METHOPRENE	2.45356e-4	4.48684e-3	2.98409e-3	4.48684e-3	3.19871e-3	3.08037e-3

13.	TRIAZOPHOS	7.95506e-4	4.50364e-4	9.65444e-4	4.51326e-4	9.75796e-4	7.27687e-4
14.	FLUSILAZOLE	6.19607e-3	1.36840e-3	7.94657e-3	1.37829e-3	8.20834e-3	5.01953e-3
15.	PYRETHRIN I	2.87054e-4	3.21458e-4	3.23884e-4	3.25755e-4	3.35136e-4	3.18657e-4
16.	PIPERONYL BUTOXIDE	3.92484e-4	4.41065e-4	4.65884e-4	4.44008e-4	4.80375e-4	4.44763e-4
17.	BOSCALID	3.44482e-3	1.43415e-3	4.26286e-3	1.44432e-3	6.41727e-3	3.40068e-3
18.	DDT	1.89472e-3	9.41915e-4	2.10568e-3	9.31720e-4	2.39729e-3	1.65426e-3
19.	GUAZATINE	1.88327e-3	6.17760e-4	2.19654e-3	6.17760e-4	2.31213e-3	1.52549e-3
20.	ALDRIN	1.22373e-4	1.18131e-4	1.23214e-4	1.18505e-4	1.23517e-4	1.21148e-4
21.	HEPTACHLOR	7.45960e-4	1.34792e-3	9.00264e-4	1.35818e-3	1.05995e-3	1.08245e-3
22.	PYRETHRIN II	3.24941e-4	1.12155e-3	4.14847e-4	1.13005e-3	4.40298e-4	6.86337e-4
23.	PROCHLORAZ	2.25941e-3	6.03788e-4	2.67651e-3	6.39696e-4	2.95023e-3	1.82593e-3
24.	DIELDRIN	1.26487e-3	8.46611e-4	1.44550e-3	8.46611e-4	1.54673e-3	1.19006e-3
25.	PERMETHRIN	4.22928e-4	1.65074e-4	4.65124e-4	1.63284e-4	5.23355e-4	3.47953e-4
26.	CHLORDANE	1.18385e-4	8.42770e-5	9.27992e-5	9.36500e-5	1.08270e-4	9.94762e-5
		3.20364e-1	7.72314e-2	3.19566e-1	8.76365e-2	3.48341e-1	

Table 2: Maximum Residue Limits profile

PESTICIDE RESIDUE	MRL (mg/kg)
GLYPHOSATE	0.1
DICHLORVOS	0.01
PIRIMICARB	0.5 – 1
FLUDIOXONIL	0.01 -1
IMIDACHLOPRID	0.1 -0.5
FENITROTHION	0.01 – 0.02
METALAXYL	0.05 -0.5
TRIADIMEFON	0.1 – 1
CYPROCONAZOLE	0.05

TRIADIMENOL	0.1 – 1
PIRIMIPHOS-METHYL	0.05 – 1
METHOPRENE	0.02 – 0.05
TRIAZOPHOS	0.01
FLUSILAZOLE	0.01
PYRETHRIN I	1
PIPERONYL BUTOXIDE	1
BOSCALID	2 – 5
DDT	0.05
GUAZATINE	0.1
ALDRIN	0.01
HEPTACHLOR	0.01
PYRETHRIN II	1
PROCHLORAZ	0.05
DIELDRIN	0.01
PERMETHRIN	0.05
CHLORDANE	0.01

CONCLUSION

In conclusion, results obtained have shown that there was significant presence of 26 pesticide residues in cashew, carrot, tomatoes, onion and okra but not beyond the permissive level. This shows that pesticides were moderately used for cultivation of the vegetables and fruits samples.

REFERENCE

- Achria, James Tano (2011). *Identity, Physical and Chemical Properties of Pesticides, Pesticides in the Modern World - Trends in Pesticides Analysis* 7217 Pesticide Residues in Bean Samples from Northeastern Nigeria VOL. 2, NO. 2, March 2012 ISSN 2225-1

- Arnold P. Appleby, Franz Müller, Serge Carpy (2002), "*Weed Control" in Ullmann's Encyclopedia of Industrial Chemistry Wiley-VCH, Weinheim.*
- Carolyn Randall (ed.) et al. (2013) *National Pesticide Applicator Certification Core Manual National Association of State Departments of Agriculture* Research Foundation, Washington, DC, Ch.1
- Codex Alimentarius Commission(1985) *Code of Ethics for International Trade in Food*. CAC/RCP 20-1979 (Rev. 1-1985).
- Cook SM, Khan ZR, Pickett JA (2007). "The use of push-pull strategies in integrated pest management". *Annu. Rev. Entomol.* **52**: 375–400.
- Cornell University, College of Veterinary Medicine (March 1999), *Consumer concerns about pesticides in food*.
- Cornell University. Toxicity of pesticides. Pesticide fact sheets and tutorial, module 4. Pesticide Safety Education Program.
- [e] Kamrin MA. (1997). *Pesticide Profiles: toxicity, environmental impact, and fate.* CRC Press.
- EurekAlert. (2009). New 'green' pesticides are first to exploit plant defenses in battle of the fungi.
- Food and Agriculture Organization of the United Nations (2002), International Code of Conduct on the Distribution and Use of Pesticides. Retrieved on 2007-10-25.
- Gilden RC, Huffling K, Sattler B (January 2010). "*Pesticides and health risks*". *J Obstet Gynecol Neonatal Nurs* **39** (1): 103–10

- Ingber SZ, Buser MC, Pohl HR, Abadin HG, Murray HE, Scinicariello F (December 2013). "*DDT/DDE and breast cancer: a meta-analysis*". *Regul. Toxicol. Pharmacol.* **67** (3): 421–33. d
- Jensen B.H., Petersen A., Andersen J.H., Hilbert G., Grossmann A., Holm M., Pesticidrester i Fødevarer, (in Danish) 2011. "*Danish Veterinary and Food Administration."*
- Kellogg RL, Nehring R, Grube A, Goss DW, and Plotkin S (February 2000), *Environmental indicators of pesticide leaching and runoff from farm fields*. United States Department of Agriculture Natural Resources Conservation Service.
- Knutson, R. (1999). *Economic Impact of Reduced Pesticide Use in the United States.Agricultural and Food Policy Center.* Texas A&M University
- Kuniuki S (2001). *Effects of organic fertilization and pesticide application on growth and yield of field-grown rice for 10 years. Japanese Journal of Crop Science* Volume 70, Issue 4, Pages 530-540
- Lamberth C, Jeanmart S, Luksch T, Plant A (2013). "*Current Challenges and Trends in the Discovery of Agrochemicals". Science* **341** (6147): 742–6.
- Linde, C. D. (1994). *Physico-Chemical Properties and Environmental Fate of Pesticides, Environmental Hazards Assessment Program, California, USA*
- Mallhot, H. and Peters, R. (1988). *Empirical Relationships between 1-Octanol/Water Partition Coefficient and Nine Physiochemical Properties, Environmental Science and Technology*, 22, 1479-1487
- Miller GT (2004), *Sustaining the Earth*, 6th edition. Thompson Learning, Inc. Pacific Grove, California. Chapter 9, Pages 211-216.

- N. Abu Bakar ; *Sample preparation method for pesticide analysisin food matrices and environmental samples by chromatography-based techniques*
- Pedersen, A.N., Fagt, S., Groth, M.V., Christensen, T., Biltoft-Jensen, A.P., Matthiessen, J., Andersen, N.L., Kørup, K., Hartkopp, H.B., Ygil, K.H., Hinsch, H-J., Saxholt, E., Trolle, .E, 2010, Danskernes kostvaner 2003 – 2008, Hovedresultater (Dietary habits in Denmark 2003-2008, Main results), National Food Institute, Technical University of Denmark
- Purdue.edu. *The benefits of pesticides: A story worth telling*. Retrieved on September 15, 2007
- U.S. Environmental Protection Agency (1999), *Spray drift of pesticides*
- U.S. Environmental Protection Agency (July 24, 2007), *Setting tolerances for pesticide residues in foods*
- World Health Organization (2006), *WHO gives indoor use of DDT a clean bill of health for controlling malaria*