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Research Article

High Performance Liquid Chromatographic Determination of Residue pesticides in Samples of Apple, Cucumber, Guava, and Garden Egg

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Abstract: It has been established that certain foods, such as fruits and vegetables, contain high levels of pesticide residue; contaminated with pesticides during pre- and post-harvest. In order to avoid health risks to consumers, residue pesticides must be kept within the WHO/FAO-recommended limits. The aim of this study was to determine residues of Sniper (DDVP), Chlorpyrifos and Dimethoate in samples of apple, cucumber, garden egg and guava. A selection of apple, cucumber, garden egg, and guava were purchased from the localmarkets of Bayelsa State, Nigeria. Extraction of the pesticides was carried out in each fruit sample using a mixture of ethyl acetate, hexane, and sodium chloride in the ratio of 3:1: 1. The extract was cleaned up on a glass column (containing activated charcoal and anhydrous sodium sulphate) and pre-concentrated in a water bath maintained at 45^{o}C. Residue pesticides were detected in all the fruits except guava samples. Also, DDVP was not detected in apple samples. The concentrations of residue pesticides ranged from 0.05 – 0.2 mg per kg of fruit sample while the % contamination in respect of 50 g fruit sample ranged from 0.0001 – 0.0004. It was found that only contamination levels in cucumber were found to exceed the Maximum Residue Limits (MRL) of Codex Alimentarius Commission standard of 0.1 mg kg $^{-1}$ in fruits and vegetable.
Keywords: Determination, residue, pesticides, fruits

INTRODUCTION

Pesticides are used to improve the quantities and qualities of crops and foods either during pre- or post-harvest period [1]. However, it has been established in the literature that certain foods such as fruits, juices, and vegetables contain high levels of pesticide residue [2]). Because of the widespread use of pesticides in agricultural practices for field and post–harvest protection, it is necessary to have reliable data concerning their residence in food [3]. Pesticides wide use could lead to extensive pollution of the environment and constitutes a potential or deliberate risk to human health; some of these pesticides are classified as a portable human carcinogen[4]. Wildlife brought about the realization that these chemicals are not exclusively doing the job they were intended to do but also have adverse effects on ecological systems with which human welfare is inseparably bound [5].

The risk of short-and long-term exposure to pesticides has been reviewed [6]. Mass mortality of aquatic organisms has often been caused by pesticides exposure, especially caused by accidental or direct spraying of water bodies [7]. In order to protect consumers of different fruits, vegetables, etc., many researchers have determined residue pesticides in many matrices [8-11].

Pesticide is persistent and non-biodegradable and they can be bioaccumulated in food chains [12], therefore the presence of high amount of pesticide in the environment may pose a serious potential danger for human health and for the environment due to their extreme toxicity.

The serious economic importance of residue pesticides to man has informed the aim of this work which was to determine some residue pesticides in selected fruits sold in the markets of Bayelsa State, Nigeria. Pesticides such as 2, 2- dimethyl dichlorovinyl phosphate (DDVP), O, O –Diethyl O -3, 5, 6, -trichloropyridine-2-yl Phosphirothiate (Chlorpyrifos) and O, O- dimethyl- s-[2-(methylamino) -2-exoethyl] dithiophosphate (Dimethoate) were determined in four different samples of fruit which include: *psidum myrtecea* (Guava), *Solamum aethiopicum* (garden egg), *malus domestica* (apple) and *cucumis sativus* (cucumber).

MATERIALS AND METHODS

Acetonitrile (HPLC grade), anhydrous sodium sulphate, activated charcoal, ethyl acetate, sodium chloride and standards (‘Chlorpyrifos”, “Dichlorvos” and methoate”) were bought from Merck, Germany.

Agilent Chemstation software for controlling LC and data analysis. Agilent 1200 series HPLC (Agilent Technologies, Santa Clara, CA, USA).

Collection and preservation of samples

3-replicate samples (fresh, blemish-free and rot-free) of *psidum myrtecea* (Guava), *Solamum aethiopicum* (garden egg), *malus domestica* (apple) and *cucumis sativus* (cucumber) were bought from Opolo and Swali local markets in Bayelsa State. Following collection, the samples were refrigerated at 4 ± 1^{o}C overnight and analyzed the next day.

Sample Extraction

300 g of each fruit was chopped and a-50 g portion was macerated with ceramic mortar and pestle with a total volume of 50 mL of ethylacetate, hexane, and sodium chloride in the ratio of3 : 1 : 1. 20 g of anhydrous sodiumsulphate was added to dry the sample. The mixture was further macerated for 5 min. The samples were then centrifuged for 5 min at 3000 rpm,and the supernatant collected. The organic extract was concentrated to 5 mL using a vacuum rotary evaporator with water bath at 45^{o}C. The sample was then cleaned up with a glass column having 5 mL layer of anhydrous sodium sulphate and 10 g activated charcoal in order to remove any residual components that may interfere with the high performance liquid chromatographic analysis. The clean sample was further re-dissolved in 5 mL of acetonitrile for the HPLC analysis.

Analysis with HPLC

Following the cleaning of extract, the HPLC analyses were carried out on a Nucleosil 100, C_8 analytical column. A combination of 70% ACN and 30% water was used as the mobile phase, running at a flow rate of 1.0 mL/min and on isocratic mode. The column oven was maintained at 25 ^{o}C. All detections were done at 208 nm.

RESULTS AND DISCUSSION

The HPLC analyses of the fruit samples showed that samples were contaminated in the range of 0.05 – 0.2 mg per kg of sample. The extent of contamination was expressed in weight per weight basis and as percentages as presented in Tables 1 and 2 respectively. No pesticide under investigation was detected in the guava fruit and DDVP was not detected in apple.

Table 1: Contamination of pesticides in fruits (weight per weight)

Pesticide	Fruit	Concentration (mg/kg)
Sniper	Apple	*Nd
	Cucumber	0.2 ± 0.015
	Garden egg	0.1 ± 0.003
	Guava	*Nd
Chlorpyrifos	Apple	0.05 ± 0.001
	Cucumber	0.15 ± 0.002
	Garden egg	0.1 ± 0.021
	Guava	*Nd
Dimethoate	Apple	0.1 ± 0.001
	Cucumber	0.2 ± 0.022
	Garden egg	0.15 ± 0.015
	Guava	*Nd

*Nd = not detected

Table 2: Contamination of pesticides in fruits expressed in percentages

Sample	Pesticides	% contamination with respect to the weight (50 g) of fruit
Apple	Sniper	-
	Chlorpyrifos	0.0001
	Dimethoate	0.0002
Cucumber	Sniper	0.0004
	Chlorpyrifos	0.0003
	Dimethoate	0.0004
Garden egg	Sniper	0.0002
	Chlorpyrifos	0.0002
	Dimethoate	0.0003
Guava	Sniper	-
	Chlorpyrifos	-
	Dimethoate	-

The contamination levels in apple for all the studied pesticides were found to fall within the acceptable limits. Among these fruits tested, contamination of Chlorpyrifos (0.15mg/kg) and Dimethoate (0.2mg/kg) in cucumber and Dimethoate (0.15mg/kg) in garden egg were found to slightly exceed the Maximum Residue Limits (MRL) of Codex Alimentarius Commission. The Codex Alimentarius Commission of the Food and Agricultural Organization (FAO) of the United Nation and World Health Organization (WHO) have recommended an acceptable MRL in fruits and vegetables to be 0.1 mg kg^{-1}

CONCLUSION

The contamination levels in apple for all the pesticides under investigation were found to fall within the acceptable limits. The levels of Chlorpyrifos and Dimethoate in cucumber and Dimethoate in garden egg were found to slightly exceed the Maximum Residue Limits (0.1 mg kg^{-1}) of Codex Alimentarius Commission of Food and Agricultural Organization for residue pesticides in fruits. Monitoring residue pesticide level in different fruit samples is important for their safe consumption and the distribution of fruits containing unacceptable levels of residue pesticides in respect of WHO/FAO standards should be discouraged.

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