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Quantification of Pesticide Residues in Selected Vegetables using the QuEChERS Method

Meragal Kulathilakage Lasanthi Kumari Rajapakse[1] Nimsha Sevwandika Weerakkody[1*] Pulippu Widana Yoshida Lakshani[2]

[1]Department of Agricultural and Plantation Engineering, Faculty of Engineering Technology, The Open University of Sri Lanka, Nawala, Sri Lanka
[2]Office of Registrar of Pesticides, Gatambe, Peradeniya, Sri Lanka

Abstract

Pesticide residues in fruits and vegetables have become a major problem in Sri Lanka. Therefore, there is a need to optimize the Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method to determine pesticide residues in fruits and vegetables and assure the safety of food. The objectives of this study were to optimize the method for multi-residue pesticide analysis, to develop calibration curve to detect concentration of pesticides and to determine prevalence of five pesticide residues in locally grown vegetables tomato, cabbage and capsicum in Puttalum, Dambulla and Nuwara Eliya districts. Pesticide residues were determined by Gas Chromatography with Mass Spectrometry after multi residue extraction procedure (QuEChERS method). The QuEChERS method was validated using five pesticides named Diazinon, Chlopyrifos, Fipronil, Prothiofos and Tebuconazole and their retention times in minutes were15.948, 19.566, 20.342, 22.308, and 26.201 respectively. Coefficient of detection was obtained near 0.99 for all

**Correspondence should be addressed to Dr. N. S. Weerakkody*
Email: *nweer@ou.ac.lk*
https://orcid.org/0000-0003-3351-1889

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tested standard pesticides confirming the accuracy of the test method. Out of 45 vegetables samples, 15 samples were detected with pesticide residues, either Chlopyrifos, Prothiofos or Tebuconazole. However, pesticide residual values were less than Maximum Residual Levels for all the tested pesticides. Tebuconazole was the mostly detected pesticide residue with 0.128 ppm and 0.052 ppm in tomato and cabbage collected from Matale and Puttlum districts respectively. Therefore, it is important to collect samples while obtaining farmer details including the type of pesticide applied, harvesting interval and frequency and application rate of pesticide for further study.

Key Words: Pesticide residues, vegetables, Gas Chromatography-Mass Spectrometry, QuEChERS

Introduction

Vegetables are cultivated as seasonal and non-seasonal crops, mainly in the Yala and Maha seasons in Sri Lanka. Some areas of Nuwara Eliya and Kalpitiya grow vegetables in more than two seasons practicing intensive cultivation methods. Fresh vegetables are good a source of vitamins, minerals, fiber, and antioxidants. Therefore, vegetables have high demand throughout the year. With the green revolution, farmers are shifting from traditional varieties to cultivate high-yielding new-improved and hybrid varieties. Most of these varieties are highly vulnerable to pest and diseases. Therefore, farmers tend to use more pesticides. Most pest control strategies heavily depend on the type of pesticides used. Pesticides are chemical substances applied to crops at various stages of cultivation and during the post-harvest storage of crops. The use of pesticides is intended to prevent the destruction of food crops by controlling agricultural pests or unwanted plants and to improve plant quality (Gözde *et al*, 2014). Pesticides used in agriculture include insecticides, fungicides and herbicides. Pesticides are applied to crops throughout the world but they can be toxic and can thus be harmful to human health. More than 800 pesticides belonging to over 100 different chemical classes are used (Camino *et al*, 2011). In vegetable production, insecticides are used to control pest and fungicides to control diseases. In the Sri Lankan context, pesticides are directly applied to crops and some may still be present as residues in the vegetables after their harvest.

Human intake of toxic substances due to pesticide residues in food commodities can be much higher than the intake of pesticide substances related to water consumption and air inhalation (Ewa *et al*. 2015). As food safety is among the first priorities in many countries, there is an increasing need for the determination of pesticide residues in various food commodities. The detection of pesticide residues in conventional food has important implications in the rational development and proper use of chemical pesticides, protecting the environment, human health, improving the quality and assuring the safety of agricultural produce by avoiding international trade disputes (Yan-Fei *et al*, 2014). A pesticide residual level in food has become a major problem worldwide due to their direct implication on human health and international trade (Blankson *et al*, 2016). The residual analysis of fruits and vegetables is an important requirement and responsibility for all food authorities to prevent toxic chemicals entering our bodies through the food chain. For toxic residual levels detection of pesticides in fruits and vegetables advance spectroscopic instruments like Gas Chromatography with Mass Spectrometry (GC/MS), Liquid Chromatography with Mass Spectrometry (LC/MS) are important. The pesticide residual detection method needed to be a Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method which can be optimized for individual requirement. Yan-Fei Li *et al* (2014) developed QuEChERS with magnetic Nano particles gas chromatography tandem mass spectrometry to remove impurities and enhance the purifying effect. Further, Koesukwiwat *et al* (2011) developed the fast-low pressure gas chromatography triple quadrupole tandem mass spectrometry method. However, these sophisticated equipment are not available in Sri Lanka, hence the requirement for a quick, easy and safe methods which can be easily used in low-middle income countries.

The demand for organically grown food crops is expected to increase significantly in the years ahead as consumers become more concerned about pesticides residues in the human diet (Tietz, 1990). Diazinon, Chlopyrifos, Fipronil, Prothiofos and Tebuconazole are the most commonly used pesticides in Sri Lanka (Sumith 2005; DOA 2011, 2012, 2013, 2014, 2015). Therefore, there is a need to determine pesticide residues in fresh vegetables related to organophosphorus (OPP) mainly used in agriculture.

The aim of this study was to investigate the pesticide residues in selected vegetables which have been collected from Nuwara Eliya, Matale and Puttalum markets. Pesticide residues were determined by Gas Chromatography with Mass Spectrometry (GC/MS). A multi-residue method QuEChERS was developed and described for simultaneous determination of five pesticides commonly used in crop protection.

Materials and Method

Preparation of standards and calibration curves Stock solutions (500 mg/L) of Diazinon, Chlopyrifos, Fipronil, Prothiofos and Tebuconazole standards were prepared for the calibration of GC/MS (Sigma Aldrich, Germany). Pure standard taken out of the refrigerator (2-8 °C) and kept at room temperature till the standard reached the room temperature. Each standard 25 mg was weighted into 50 ml volumetric flask and volume was adjusted with HPLC grade acetone (Sigma Aldrich, USA). Labeled bottles were stored in the refrigerator at 4-6 °C.

Intermediate stock solution 50 mg/L was prepared by transferring 5.0 ml stock solution by using 5 ml bulb pipette into 50 ml volumetric flask and adjusted with HPLC grade acetone.

Primary working standard solution 5 mg/L was prepared by transferring 5.0 ml from each intermediate stock solution by using 5 ml bulb pipette into same 50 ml volumetric flask and the volume adjusted with HPLC grade acetone. Calibrations working standard concentrations 0.2, 0.5, 1.0, 1.5 and 2.0 mg/L were prepared into 10 ml volumetric flask. The level of detection (LOD) and recovery percentage were calculated as follows.

LOD = Lowest calibration level x final volume/weight use (per sample)

Recovery % = Calculated concentration/spiked concentration *100

Sample Collection

The locally grown vegetable sample of 1 kg was collected from local markets as presented in Table 1. All samples were immediately freeze-dried and stored in a deep freezer at - 20 °C until analysis.

Table 1: - Locations of the vegetable samples collected from different districts

District	Location	Field type	Vegetable
Nuwara Eliya	SithaEliya	Market	Cabbage, Capsicum,Tomato
	Shanthipura	Market	Cabbage, Capsicum, Tomato
	Kandapola	Market	Cabbage, Capsicum, Tomato
	Labukele	Market	Cabbage, Capsicum, Tomato
	Hanguranketha	Market	Cabbage, Capsicum, Tomato
Matale	Dambulla	Market	Cabbage, Capsicum, Tomato
		Market	Cabbage, Capsicum, Tomato
		Market	Cabbage, Capsicum, Tomato
		Market	Cabbage, Capsicum, Tomato
		Market	Cabbage, Capsicum, Tomato
Puttalam	Norochchole	Market	Cabbage, Capsicum, Tomato
	Mampuri	Market	Cabbage, Capsicum, Tomato
	Puttalim	Market	Cabbage, Capsicum, Tomato
	Kalpitiya	Market	Cabbage, Capsicum, Tomato
	Anamaduwa	Market	Cabbage, Capsicum, Tomato

Sample Preparation

The laboratory samples of freeze-dried vegetables were thoroughly homogenized. Approximately 10 g sample was taken into a polypropylene centrifuge tube (50 mL) and the 100 µl and 200 µl of the 5.0 mg/L spiking mixture was added separately. The extraction procedure was followed as Gözde*et al*, (2014) and AOAC (2011) for the determination of pesticide residues based on fruits and vegetables by acetonitrile extraction and partitioning with magnesium sulphate. Acidified acetonitrile 10 ml was added into each tube and the content was shaken using vortex. Subsequently, the content of the salt kit was added. The mixture was immediately shaken for 1 min and centrifuged at 3000 rpm for 3 min. Afterwards total amount of acetonitrile fraction was transferred to 15 ml polypropylene tube containing 1200 mg of Magnesium Sulfate, 400 mg PSA (Primary Secondary Amine) and 400 mg of GCB (Graphitized Carbon Black).

The tube was vortexed for 1 min and centrifuged at 4000 rpm for 4 min. Finally total volume aliquot of the supernatant was transferred into glass round bottom flask and totally dried under nitrogen. Acetone 2 ml was added and dissolved in all the dried compounds and filtered through 0.45 µm PTFE filter. Content was transferred into glass auto sampler vial.

GC/MS Analyses

Gaschromatography analysis was conducted on Agilent DB-35ms GC capillary Column, (30 m x 0.25 mm, 0.25 µm) with the following conditions: Helium was in constant flow mode, 2.0 ml/min; initial inlet temperature 80 °C ramp to 300 °C , with 8 min solvent delay, injection volume 1 µl with split less (20:1 split ratio), oven temperature program 80 (1 min), 10 °C/min to 160 °C (1 min), 6 °C/min to 250 °C (1 min), 10 °C/min to 300 °C (2 min). Source, Quadruple and transfer line temperature were 230 °C, 150 °C and 300 °C respectively. The Mode SIM (Selected Ion Monitoring) and Multiplier Voltage were the Auto Tune Voltage.

Standards were injected to GC/MS continuously for three days with a proper sequence for validation of GC/MS. After completing the validation process calibration curves were prepared for five pesticides. Then samples were injected to GC/MS.

Data Analysis

The quantitative residual values of Chlopyrifos, Diazinon, Fipronil, Prothiofos and Tebuconazole were reported using appropriate units as milligrams per kilograms (mg/kg) or ppm

$$\text{Amount of Pesticide} = \frac{\text{Concentration of sample solution (mg/µl)} \times 2\text{ml} \times 1000\ \mu\text{l}}{\text{Sample weight (g)} \times 1000\ (\text{mg})}$$

Results and Discussion

Validation Results

Retention times for each pesticide standard were obtained for the validation of the method. Retention times for calibration standards are shown in Table 2.

Table 2. – Retention times for calibration chemical standards

Calibration Standard	Retention Time (RT)	Coefficient of Detection (r^2)	LOD with Uncertainty (mg/kg)	Average recovery (%)
Diazinon	15.946	1.0000	0.04 ± 0.0061	85.81
Chlopyrifos	19.565	0.9980	0.04 ± 0.0067	86.58
Fipronil	20.353	0.9960	0.04 ± 0.0065	82.56
Prothiofos	22.308	0.9990	0.04 ± 0.0063	85.05
Tebuconazole	26.179	0.9980	0.04 ± 0.0064	82.91

The level of detection for all the pesticides was:
0.2x 2/10=0.04 ppm or 0.04 mg/kg.
The average recovery percentage was: 82.56 - 86.58%.

Chromatogram for the five selected pesticides is showed in Fig.1. Different retention times were obtained for 5 different standard pesticides. The following standard pesticides peaks with their retention times were considered for the analysis of pesticide residuals of market sample analysis.

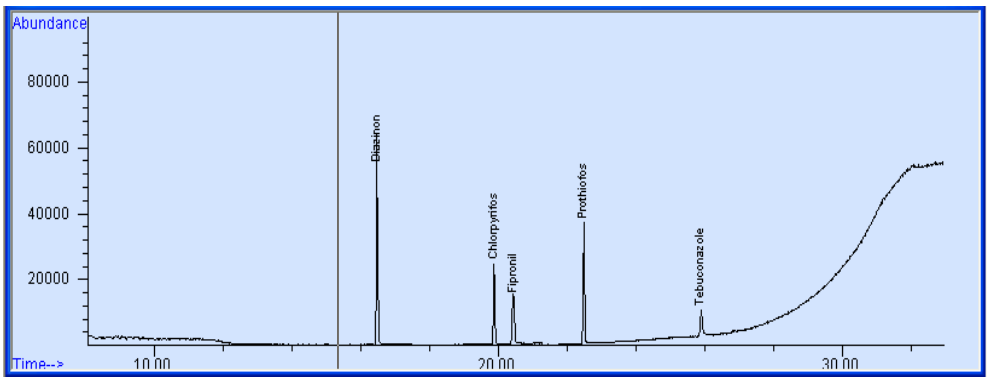

Figure1. Chromatogram for 5 selected standard pesticides

Pesticide Residue Levels in local vegetables in selected areas
Pesticide residue levels of selected vegetables from Nuwara Eliya, Matale and Puttalam districts are shown in Table 3, 4 and 5

Table 3. Pesticide residues in vegetables from the Nuwara Eliya District

Sample No.	Vegetable	Diazinon	Chlorpyrifos	Fipronil	Prothiofos	Tebuconazole
ROP/RV/16/200	Tomato	ND	ND	ND	ND	ND
ROP/RV/16/201	Tomato	ND	ND	ND	ND	ND
ROP/RV/16/202	Tomato	ND	ND	ND	ND	ND
ROP/RV/16/353	Tomato	ND	ND	ND	ND	ND
ROP/RV/16/488	Tomato	ND	ND	ND	ND	ND
ROP/RV/16/203	Cabbage	ND	ND	ND	ND	ND
ROP/RV/16/204	Cabbage Cabbage	ND	ND	ND	ND	0.052 ppm
ROP/RV/16/205	Cabbage Capsicum	ND	ND	ND	ND	0.052 ppm
ROP/RV/16/354	Capsicum Capsicum	ND	ND	ND	ND	ND
ROP/RV/16/489	Capsicum Capsicum	ND	ND	ND	ND	ND
ROP/RV/16/206		ND	ND	ND	ND	0.054 ppm
ROP/RV/16/207		ND	ND	ND	ND	ND
ROP/RV/16/208		ND	ND	ND	ND	ND
ROP/RV/16/355		ND	ND	ND	ND	ND
ROP/RV/16/490		ND	ND	ND	ND	ND

Tebuconazole was detected in only 2 cabbage samples and a capsicum sample out of 15 vegetable samples analyzed from the Nuwara Eliya district. The residue content of tebuconazole in cabbage was 0.052 ppm and 0.054 ppm in capsicum. However, MRL of cabbage for tebuconazole was 1 mg/kg /1ppm (CODEX Alimentarius).

Table 4. Pesticide residues in vegetables from the Matale District

Sample No.	Vegetable	Diazinon	Chlorpyrifos	Fipronil	Prothiofos	Tebuconazole
ROP/RV/16/370	Tomato	ND	ND	ND	ND	0.128 ppm
ROP/RV/16/371	Tomato	ND	ND	ND	0.068 ppm	ND
ROP/RV/16/372	Tomato	ND	ND	ND	ND	ND
ROP/RV/16/373	Tomato	ND	ND	ND	ND	ND
ROP/RV/16/374	Tomato	ND	ND	ND	0.068 ppm	ND
	Cabbage	ND	ND	ND	ND	ND

ROP/RV/16/375	Cabbage	ND	ND	ND	ND	ND
ROP/RV/16/376	Cabbage	ND	ND	ND	ND	ND
ROP/RV/16/377	Cabbage	ND	ND	ND	ND	ND
ROP/RV/16/378	Cabbage	ND	ND	ND	ND	ND
ROP/RV/16/379	Capsicum	ND	ND	ND	ND	ND
ROP/RV/16/380	Capsicum	ND	ND	ND	ND	0.104 ppm
ROP/RV/16/381	Capsicum	ND	ND	ND	ND	ND
ROP/RV/16/382		ND	ND	ND	0.068 ppm	ND
ROP/RV/16/383		ND	ND	ND	ND	0.108 ppm
ROP/RV/16/384						

Results showed that the prothiofos was detected in two tomato samples with 0.068 ppm and one capsicum sample having 0.068 ppm. While tebuconazole was detected in one tomato sample with 0.128 ppm and two capsicum sample with 0.104 ppm and 0.108 ppm respectively among 15 vegetable samples analyzed from the Matale district. However, MRL of tomato for tebuconazole was 0.7 mg/kg or 0.7 ppm (CODEX Alimentarius).

Table 5. Pesticide residues in vegetables from the Puttalam District

Sample No.	**Vegetable**	**Diazinon**	**Chlorpyrifos**	**Fipronil**	**Prothiofos**	**Tebuconazole**
ROP/RV/16/303	Tomato	ND	ND	ND	ND	ND
ROP/RV/16/304	Tomato	ND	ND	ND	ND	ND
ROP/RV/16/305	Tomato	ND	ND	ND	ND	ND
ROP/RV/16/306	Tomato	ND	ND	ND	ND	ND
ROP/RV/16/307	Tomato	ND	ND	ND	ND	ND
ROP/RV/16/308	Cabbage	ND	0.048 ppm	ND	ND	ND
ROP/RV/16/309	Cabbage	ND	ND	ND	ND	0.052 ppm
ROP/RV/16/310	Cabbage	ND	ND	ND	ND	0.052 ppm ND
ROP/RV/16/311	Cabbage	ND	ND	ND	ND	0.052 ppm ND
ROP/RV/16/312	Cabbage	ND	ND	ND	ND	0.052 ppm ND

ROP/RV/16/313	Capsicum	ND	ND	ND	ND	ND
ROP/RV/16/314	Capsicum	ND	0.048 ppm	ND	ND	ND
ROP/RV/16/315	Capsicum	ND	ND	ND	ND	
ROP/RV/16/316	Capsicum	ND	ND	ND	ND	
ROP/RV/16/317	Capsicum					

The data of Table 5 showed that the chlorpyrifos was detected in one cabbage sample with one capsicum sample having the same amount of 0.048 ppm. Tebuconazole content 0.052 ppm was detected in three cabbage samples and one capsicum sample among 15 vegetable samples analyzed from the Puttalam district. Interestingly, Tebuconazole in cabbage and tomato samples did not exceed the MRL 1.0 ppm and 0.7 values respectively specified by CODEXs. Similarly, Tebuconazole in tomato did not exceed the global MRL 1.3 ppm and EU MRL 0.9 ppm as specified. However, MRLs for other pesticides for cabbage, tomato and capsicum were not found in the relevant literature except as shown in Table 5 for the comparison of our data. None of the tested samples showed the presence of Diazinon chemical residue. We did not detect chlorpyrifos in our tested tomato samples from the three different districts, Amadoudiop *et al* (2016) reported the presence of higher chlorpyrifos residuals 0.037 ppm and 0.05 ppm in tomato collected from Camberena and Malika of Niayes Zone Senegal. Chlorpyrifos was only detected in 2 samples of cabbage and capsicum with a figure below MRLS 0.048 ppm level found in the Puttalam district out of 45 samples tested in our study. However, according to Blankson *et al* (2016) chlorpyrifos was reported as the most frequently identified pesticide residue in 14% of the vegetables collected from the market Accra, Ghana.

Table 6. Different MRL data

	Cordex MRL			**Global MRL**			**EU MRL**		
	Toma	**Capsi.**	**Cabb.**	**Toma.**	**Capsi.**	**Cabb.**	**Toma.**	**Capsi.**	**Cabb.**
Diazinon	0.5	-	0.5	-	-	-	0.01	-	0.05
Chlorpyrifos	-	-	1	-	-	1	0.01	-	0.01
Fipronil	-	-	0.02	-	-	-	-	-	-
Prothiofos	-	-	-	-	-	-	-	-	-
Tebuconazole	0.7	-	1.0	1.3	-	-	0.9	-	-

Most of the experiments conducted worldwide interpreted the residue levels in the tested samples up to micro or nano gram per kg or mL level. Anastassiades *et al* (2007) showed that the limit of detection was up to ppb level and Nano gram/g level using the advances GC/MS, EI/MS and CI/MS. In the present experiment we used GC/MS which has a single quadruple, and which could detect a minimum of 0.04 ppm level, even though detected residue levels in the tested samples were below than the standard MRLs.

Conclusion

Multi residue methodology showed to be very simple and rapid, requiring small sample sizes, minimizing solvent consumption resulting in low amount of hazardous waste. The utilization of Mass Spectrometric detection provided both quantitative information and confirmation of pesticide residues in cabbage. Out of 45 samples collected from three different districts, 15 samples detected significant values for Chlorpyrifos, Prothiofos and Tebuconazole. These values did not exceed MRL levels for cabbage and tomato.

For the purpose of this study samples were collected from markets where the sample origin was not known. Therefore, details of the farmers, occurrence of pest and disease and spectrum of pesticides usage, pre-harvest interval, and fertilizer usage are unknown. For further research purposes, samples should be collected from known sources where such details could be obtained. Moreover, there is a need to test samples for all possible pesticides.

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