

Research Paper

Pesticide Use by Rice Farmers and the Presence of Residues in the Rice Grain: an Evidence-Based Study in Selected Rice-Growing Districts in Sri Lanka



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Abstract

Rice is the major constituent in the Sri Lankan diet and the development of an analytical method for the analysis of the pesticide residues present in rice grain is important to ensure consumer safety in rice. This study attempted to investigate the use of pesticides by farmers and a random multi-pesticide residue analysis in rice grain samples. Overall, 57 pesticides in rice grain were validated according to the SANTE/12682/2019 using QuEChERS, as per AOAC official method 2012, and quantified by the Liquid chromatography separation with heated electrospray ionization and Triple Quadrupole Tandem Mass Spectrometry (LC-MS/MS). LOD was 10 ppb while, recovery studies at three spiking concentration levels of 1 LOQ, 5 LOQ, and 10 LOQ showed recovery of 70-120% with RSD of <20% and R² of ≥0.995. Pre-tested questionnaires distributed among 60 farmers in Anuradhapura, Polonnaruwa, Kurunagala, Hambantota, and Ampara Districts were evaluated. Of all the farmers, 56.7% used pretilachlor as a weedicide while 26.3% used Carbosulfan and Thiamethoxam as insecticides. For real sample analysis, 62 rice grain samples grown in the above Districts were collected randomly from farmers from January to March 2020 and were evaluated against the 57 pesticides using LC-MS/MS. The harvested rice samples were extracted and cleaned using QuEChERS and AOAC 2012. Of 57 pesticides, only six pesticide residues were detected with 4.8%, 3.2%, 3.2%, 4.8%, 1.6%, and 1.6% for Thiamethoxam, Imidacloprid, 3-hydroxycarbofuran, Profenophos, Buprofezin, and Tebuconazole respectively. The highest contamination was reported as 108 ppb for Imidacloprid harvested at Ampara District and the total detection percentage was 0.33% while not exceeding the FAO MRL's or Sri Lankan MRL's. The results revealed that the presence of pesticide residues in rice is low.

Keywords: LC/MS/MS, LOQ, Pesticide Residues, QuEChERS, Rice

Introduction

Rice is the major constituent of the Sri Lankan diet and it is the source of energy and carbohydrates. According to the records of the Senses and Statistics Department, the annual per capita consumption of rice in Sri Lanka is 107 kg year⁻¹. The total rice production in 2018/2019 *Maha* and *Yala* seasons have been 3,072,581 metric tons (Mt) and 1,532,905 Mt respectively. The total rice production in Anuradhapura, Kurunagala, Ampara, Polonnaruwa, and Hambantota districts where samples were taken in 2018, 2019 season were 475,637 Mt, 377,199 Mt, 367,085 Mt, 292,645 Mt, and 197,524 Mt respectively.

Farmers cultivate their crops mainly focusing on increased profit with little concern about the adverse effects of agricultural inputs, especially due to the overuse of pesticides. The majority of the farmers in Sri Lanka are unaware of the suitable pesticides for specific crops, their effective dosages, and potential hazards to the crop, human and environmental health. Monitoring of pesticide residue is essential for the supply of safe food and maintain good health and environmental resources.

This study analyzed the fifty-seven pesticide residues in sixty-two rice grain samples grown in Anuradhapura, Polonnaruwa, Kurunagala, Hambantota, and Ampara districts in Sri Lanka. Overall, the study launched as an initial study aiming the method validation of pesticide residue analysis according to SANTE guideline (SANTE, 2019), farmer survey, and random

pesticide residue analysis to ensure the food safety in Sri Lanka and method validation has implemented the establishment of the pre harvest interval and MRL's to Sri Lanka.

Materials and Methods

Quantification of selected pesticides

Method validation

Certified Reference Materials (CRM) were purchased from Sigma Aldrich® and the purity of the standards ranged between 98.6% to 99.4%. However, working standards of 1 ppb - 50 ppb were prepared using the stock solutions and LC/MS grade acetonitrile. Traceability standards were used for matrix spiked calibration.

All the solvents used for the study, namely, acetone, acetonitrile, and glacial acetic acids were of LC/MS/MS grade and purchased from VWR®. The QuEChERS pack for extraction, *i.e.* anhydrous magnesium sulphate (6.00 g) with 1.5 g of sodium acetate or 6.00 g of magnesium sulphate with 1.5 g of sodium chloride, QuEChERS pack for clean-up, *i.e.* 400 mg of primary secondary amine with 1200 mg of magnesium sulphate were procured from Agilent Technologies®. Dry nitrogen for nitrogen purge and high purity argon gas were procured from Ceylon Oxygen® Ltd.

Other apparatus used for the study are centrifuge machine (Hermlelabortechnik®, GmbH, Germany), analytical balance (Axis®, Poland), blender freezer, micropipettes (10-100 µl and 100-1000 µl), volumetric flask (glass Pyrex), and Teflon tubes.

The following sections detailed out the Instrument details and operating parameters as Liquid Chromatography Triple Quadrupole Tandem Mass Spectrometry (LC/MS/MS) which enables highly selective, targeted, and sensitive quantitation and combination of a mixture of target pesticides in a single run. (Melo *et al.*, 2020). A multi-residue method which was developed for screening and quantitation of the mixture of 57 pesticides in 30 minutes run using Thermo Chromatographic UHPLC and Thermo Scientific Trace finder software and a Thermo Scientific TSQ series LC/MS/MS system. At least one and often two or three ion ratios were used to confirm

each analyte as illustrated in Table 4. Chromatographic analysis was performed using the Thermo Scientific UHPLC system. The Chromatographic conditions were as Table 1.

All samples were analyzed on the Thermo Scientific TSQ endure quadrupole mass spectrometer with a heated electrospray ionization source. In addition, quantitation - enhanced data - dependent scanning was used for structural confirmations. Alternating positive and negative polarity switching was utilized in the method. The MS conditions as shown in Table 2.

Table 1. UHPLC details

Column	Thermo Scientific Hypersil GOLD aQ column (100 x 2.1 mm, 1.9 µm particle size)		
Mobile Phase A	Water with 0.1% formic acid and 4 mM ammonium formate		
Mobile phase B	Methanol with 0.1% formic acid and 4 mM ammonium formate		
Flow rate	300 µL/min		
Column Temperature	40 °C		
Sample injection volume	5 µL		
Gradient	Gradient Time (min)	% A	% B
	0.00	98	2
	0.25	70	30
	20.00	0	100
	25.00	0	100
	25.01	98	2
	30.00	98	2

Table 2. MS details

Sheath gas flow rate	55 units
Aux gas flow rate	15 units
Spray voltage	3500 v
Capillary temp	280 °C
Heater Temp	295 °C
Cycle Time	0.20 S

Method development, data acquisition, and data processing were performed with trace finder software.

In the matrix calibration procedure, grains were spiked with a mixture of 57 pesticides to give a solution containing 1 ppb and 50 ppb of each pesticide. Matrix spiked standards were prepared at six concentrations for each of the pesticides. Only those pesticides that showed analytical results within the lowest and the highest calibration standards, having a linear correlation(R^2) of more than 0.995, were accepted for the study (SANTE (2019)).

Samples were extracted according to the quick, easy, cheap, efficient, rugged, and safe (QuEChERS), as per AOAC official method 2012 (AOAC, 2012) by application of a single-step buffered acetonitrile extraction, salting out liquid-liquid partitioning from water in the sample with $MgSO_4$ and clean-up were done by dispersive solid-phase extraction. Analytical quality control and method validation were in accordance with the SANTE/12682/2019 guideline (SANTE, 2019) and quantified by the LC/MS/MS. The chromatographic separation by the UHPLC system and the electron spray ionization and mass spectra were used for structural confirmation while, recovery studies at three spiking concentration levels, *i.e.* 1

LOQ, 5 LOQ, and 10 LOQ were evaluated for 57 No's of pesticides as illustrated in Table 4.

Farmer survey and sampling selection of area

Five districts in Sri Lanka, namely, Anuradhapura, Kurunagala, Ampara, Polonnaruwa, and Hambantota districts were selected depending on the harvested yield in 2019. Areas of the districts and the farmers were selected on a random basis. The sample size was 62 including 12 samples from each district and 14 samples from Hambantota District. A pre-tested questionnaire was distributed among 60 farmers including 12 farmers from each district to collect information on the usage of insecticides, fungicides, and herbicides, and evaluated the various types of farmer practices among them. Samples were collected during the period of January to March 2020. The details of the selected areas are shown in Table 3.

Sampling

The procedure adapted to the sampling was mainly based on the method recommended by the Codex Alimentarius Commission of the Food and Agriculture Organization (FAO) of the United Nations and ISO 874:1980 (Areas in each district and farmers were selected on a random basis). Accordingly, samples of freshly harvested paddy were taken from the farmers. Each sample size was 1 Kg and the harvests were then divided into four parts and each part was mixed well. Each part was divided into two portions and one portion was kept in the refrigerator at 4 - 8 °C (AOAC, 2007) and the other was used for the analysis

(Composite sampling). While harvesting, handling, milling, packing, and preparation, necessary precautions were taken to avoid any removal of surface residues in paddy, and cross contaminations. The samples were stored in large zip lock polyethylene bags or foil-lined paper bags at 10 °C. Each sample was properly labeled (ISO 874:1980). (<http://www.fao.org/fao-who-codexalimentarius>).

Sample analysis

A total of 62 paddy samples collected from five districts were milled separately and blended using a mechanical blender. The blended samples were placed separately in clean plastic containers, labeled, and frozen overnight (AOAC, 2012). For each rice sample, 5 g $\pm$ 0.1 g of was then transferred into a 50 ml Teflon tube and 6 g of anhydrous magnesium sulfate, 1.5 g of anhydrous sodium acetate or 1.5 g of sodium chloride were added (Michelangelo *et al.*, 2003). 10 ml water was added and leaves it for 1 hour and 10 ml of 1% acetic acid in acetonitrile was added into the sample tube, vortex for 1 min and centrifuged at 3000 rpm for 3 min. An aliquot from the supernatant layer was transferred into the dispersive 15 ml SPE tube containing 400 mg Primary Secondary

Amine (PSA) and 1200 mg magnesium sulphate. The Solid Phase Extraction (SPE) tubes were also Vortex for 1 min and centrifuged for 3 min at 3000 rpm (Lesueur *et al.*, 2008). Finally, the supernatant layer was passed through a 0.45 μ m HDPE filter by using a plastic syringe, and the extract was transferred to an LC vial. The extract was subjected to LC/MS/MS autosampler for quantitative analysis (AOAC, 2012) (Pareija and Fernandez, 2010).

Linearity and recovery

All calibration curves were prepared with multi-pesticide standard solutions, including the blank standard solution. The correlation coefficient (r^2) values were calculated for each curve. The analytical calibration extended over a range appropriate to the lowest and the highest concentration of the analyte, and the linearity criteria of $r^2 \geq 0.995$ had to be achieved. For determination of the recovery percentage replicates of high-spiked and low-spiked samples were analyzed using the candidate method and the recovery percentage was estimated. The mean recoveries for 1 LOQ, 5 LOQ, and 10 LOQ should be in the range of 70 - 110% with an acceptability RSD $\leq$ 20%.

Table 3. Selected study areas for sampling

District	Area	Agro Ecological Region
Anuradhapura	Rajanganaya, Nachchduwa, Galenbidunu wawa	Low country Dry Zone (DL _{1b})
Kurunagala	Ibbagamuwa, Mahawa, Wariyapola	Low country intermediate Zone (IL _{1a})
Ampara	Nindawur, Akkareipattuwa, Mayadunna	Low Country Dry Zone (DL _{2b})
Polonnaruwa	Giritale, Higurakgoda, Madirigiriya	Low Country Dry Zone (DL _{1c})
Hambantota	Weeravila, Yodakandiya, Beralihela	Low Country Dry Zone (DL _{2b})

Data analysis

CHROMELEON 8 Thermo licenced inbuilt software has used for the data analysis and SAS software has used for the farmer survey evaluation.

Results and Discussion**Quantification of selected pesticides**

The precursor ion, product ion, and the retention times of the selected pesticides are presented in Table 4 (Muhammed *et al.*, 2021).

Table 4. Precursor ion, product ion and the retention times of the selected pesticides

	Compound	RT	Precursor ion		Product ions
1	Acephate	2.82	184.08	143.05	95.17
2	Omethoate	3.20	214.07	125.07	155.04
3	Pymetrozine	3.29	218	78.29	51.41
4	Dinotefuran	3.26	203.02	129.19	112.24
5	Nitenpyram	3.58	271.22	126.10	224.10
6	Methomyl	3.71	163.05	88.3	73.3
7	Thiamethoxam	3.82	292.15	181.1	132.04
8	Carbendazim	3.89	192.1	160.13	132.15
9	Monocrotophos	3.87	224.08	193.01	127.11
10	Imidacloprid	4.24	256.12	209.1	175.14
11	Acetamiprid	4.65	223.1	126.13	90.23
12	Thiacloprid	5.14	253.13	126.11	99.15
13	Aldicarb [M+NH ₄]	5.31	208.1	89.26	41.52
14	Tricyclazole	5.73	190.01	163	136
15	Paraoxon-methyl	5.72	230.01	201.93	90.17
16	Phosphamidon	5.79	300.07	127.13	76.26
17	Carbofuran	6.33	22.14	165.13	123.16
18	Bendiocarb	6.34	224.16	167.13	109.17
19	Malaoxon	6.53	315.06	99.16	71.28
20	Carboxin	6.94	235.95	143.1	87.22
21	Carbaryl	7.11	202.08	145.11	127.15
22	Thiodicarb	7.85	355.21	88.23	73.29
23	Flutriafol	8.07	302.16	70.33	123.11
24	Metalaxyl	8.23	280.11	220.15	192.18
25	Metalaxyl-M	8.24	280.1	220.13	160.17
26	Chlorantraniliprole	9.07	482.13	452.93	285.89
27	Azoxystrobin	9.99	404.1	372.07	344.08
28	Fenamidone	10.02	312.20	236.12	92.25
29	Ethiprole	10.10	397.12	350.94	254.98
30	Flutolanil	10.68	324.21	262.06	242.08
31	Iprovalicarb	11.18	321.16	119.30	91.40

Table 4. cont.

	Compound	RT	Precursor ion		Product ions
32	Fipronil	12.56	437.2	329.7	317.8
33	Kresoxim-methyl	12.59	314.1	222.12	235.1
34	Phenthoate	12.67	320.9	246.8	135.12
35	Tebuconazole	12.96	308.2	70.34	125.11
36	Flubendiamide	13.06	681	408.20	274.10
37	Edifenfos	13.08	311	282.97	109.16
38	Diazinon	13.13	305.03	169.16	97.13
39	Fenthion	13.14	278.95	169.02	153.07
40	Propiconazole	13.28	342.2	159.02	172.99
41	Pyraclostrobin	13.82	388.2	194	163
42	Pencycuron	14.16	329	125.14	261.12
43	Spinosad A	14.30	732.5	142.21	98.27
44	Difenoconazole	14.48	406.17	251.02	188.10
45	Trifloxystrobin	14.68	409.3	186.09	145.09
46	Indoxacarb	14.80	528.3	150.06	203.02
47	Spinosad D	15.14	746.5	142.20	98.27
48	Profenophos	15.20	372.9	304.84	346.93
49	Buprofezin	15.22	306.21	106.22	57.45
50	Emamectin-B1b-benzoate	15.95	872.4	158.18	82.28
51	Chlorpyrifos	16.34	350	197.96	97.13
52	Emamectin-B1a-Benzozate	15.95	936.53	158.18	82.28
53	Lufenuron	16.59	509.2	158.11	141.13
54	Flufenoxuron	17.19	489.04	158.09	141.09
55	Fenpyroximate	17.53	422.21	366.13	214.14
56	Fenazaquin	18.55	307.2	161.19	57.45
57	Etofenprox [M+NH ₄] ⁺	19.17	394.15	359.17	135.16

The mixture of 57 pesticides representing a broad spectrum of chemical classes was separated and detected within 30 minutes as shown in Table 2. The concentration range studied was 10 ppb to 1000 ppb and limits of detection (LOD) were estimated at 10 ppb. Matrix spiked calibrations were recorded $R^2 > 0.995$ while, recoveries for 1 LOQ, 5 LOQ, and 10 LOQ ranged 70 - 120

% with RSD <20 %. The chromatogram for the selected pesticides is illustrated in Figure 1 and the confirmation of the presence of imidacloprid was illustrated in Figure 2. Matrix spiked calibration curves for Acephate, Pymetrozine, Thiamethoxam, Carbendazim, and Imidacloprid were illustrated in Figures 3, 4, 5, 6, and 7 respectively.

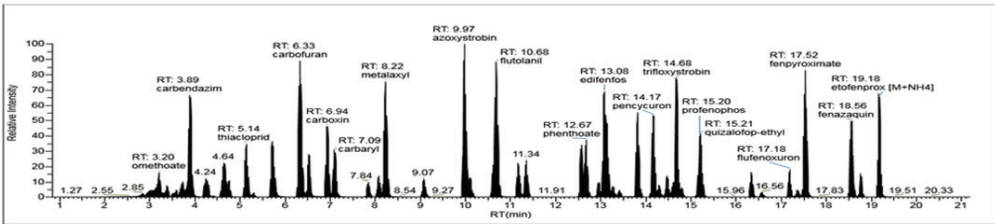


Figure 1. Chromatogram for selected pesticides

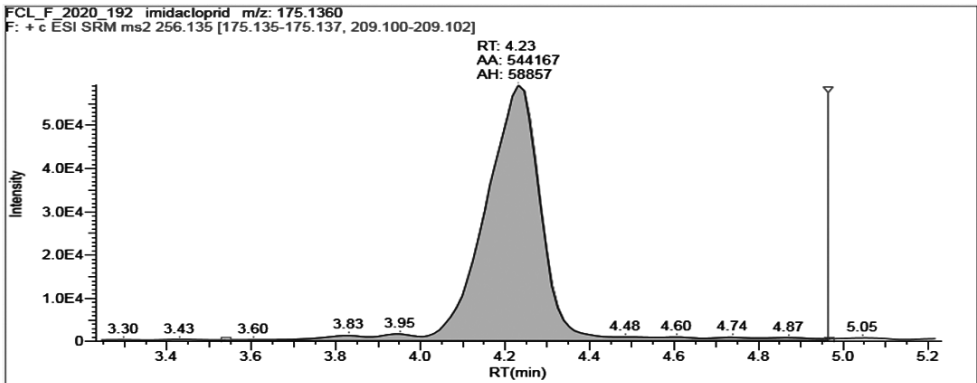


Figure 2. Confirmation of the imidacloprid presence in the sample

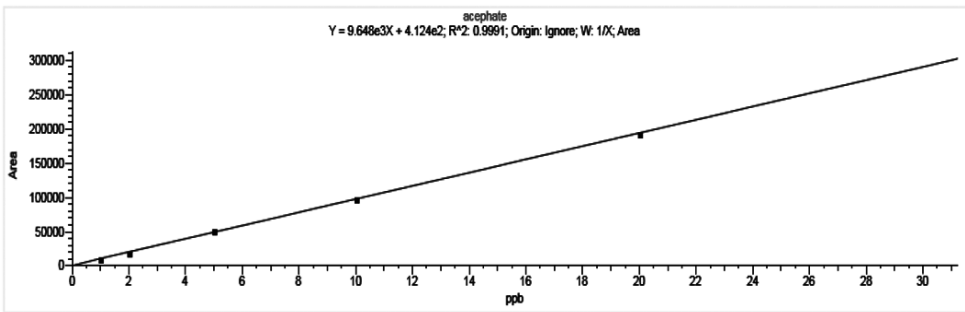


Figure 3. Calibration curve for acephate

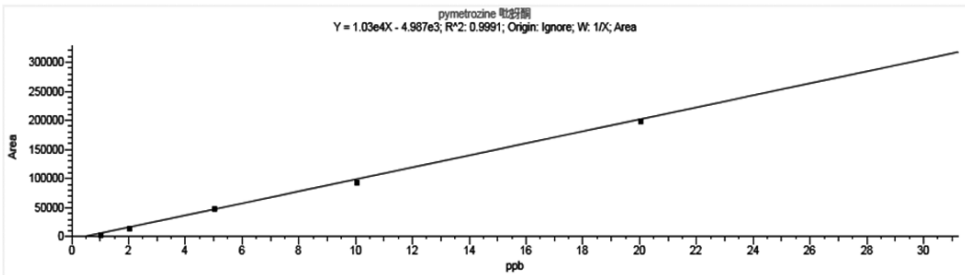


Figure 4. Calibration curve for pymetrozine

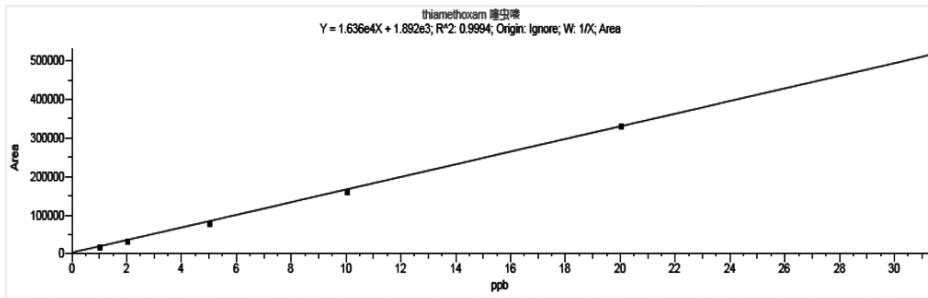


Figure 5. Calibration curve for thiamethoxam

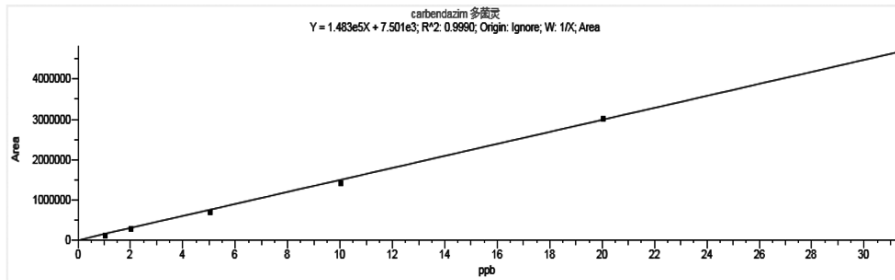


Figure 6. Calibration curve for carbendazim

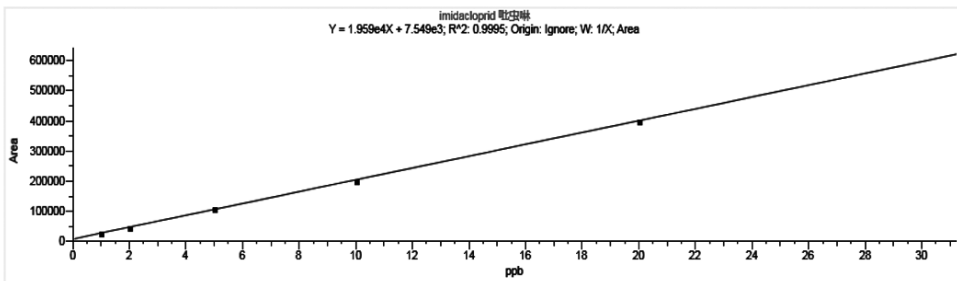


Figure 7. Calibration curve for imidacloprid

Limit of Detection (LOD)

The limit of detection (LOD) for pesticide residue analysis in rice was 10 ppb

Results of the survey of farmers in the selected districts

A pre-tested questionnaire, based on the information concerning the education background, usage of pesticide (weedicide, insecticide, and fungicide), source of pest

identification, pesticide mixing practice, stage of application of the pesticide, usage of tank and nozzles were collected from 60 farmers.

Educational background of farmers

The education level of the farmers interviewed was 60% with primary education, 35% with guiding education (1-3 years after primary education), and only

5% with secondary education. The average age and agricultural experiences were 65 and 35 years respectively. Out of the total participants, 90% were male household heads and 5% were the second generation of the farm family. The involvement of farming has been reduced accordingly. This reflects the current situation of the farm families which needs an intervention.

Pesticide usage

The survey results revealed that all farmers in each district use synthetic pesticides to control pests.

Usage of weedicide

Weedicide usage in five districts and average use of weedicide as illustrated in Figure 8.

The results revealed that 60 farmers used 13 generic pesticide formulations to control weeds. Pretilachlor was used by 56.7% of farmers. In addition, about 11.7% of farmers used MCPA, and Propanil with Clomazone and Bisphyribac Sodium was used by 15.0% of farmers. Furthermore, Pretilachlor with Pyribenzoxim was used

by about 13.3% of farmers in survey districts. Carfentrazone ethyl was used by 5.0% of farmers while about 3.3% of farmers were sprayed with Matamifop and Quinclorac. However, about 1.7% of farmers sprayed Propanil with Pretilachlor, Cyhalofop Butyl, 3,4-DPA, Propanil with MCPA, and Thiobencarb with Propanil to control weeds.

Usage of insecticides

The mean usage of insecticide were shown in Figure 9. The results revealed that from 60 farmers only 38 farmers used 11 generic insecticide formulations to control insects as Carbosulfan, Tebufenazoide, imidacloprid, Abamectin, Thiamethoxam, Chlorantraniliprole with Thiamethoxam, Diazinon Abamectin, Diazinon, Fipronil, Fenobucarb, Pymetrozine, and Profenophos. 26.3% of farmers used Carbosulfan and Thiamethoxam and about 10.5% of farmers used imidacloprid while 7.8% of farmers used Tebufenazoide in the surveyed area. In addition to that, each 5.2% of farmers used Abamectin and Profenaphos to control rice pests. 2.6% of farmers used Diazinon, Fipronil, Fenobucarb and pymetrozine.

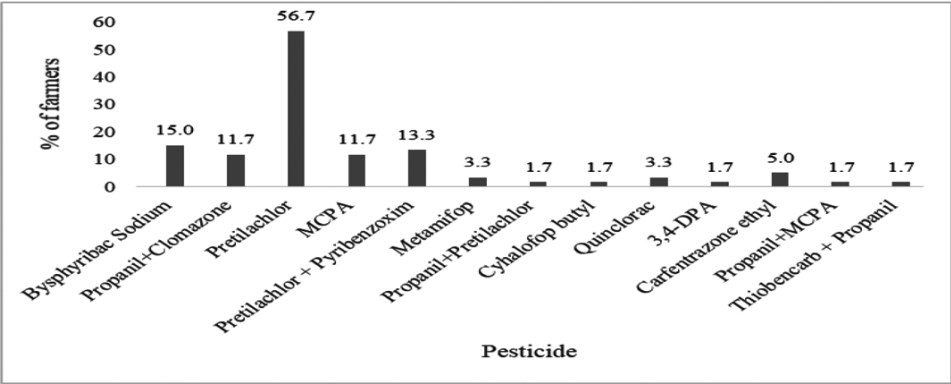


Figure 8. Mean weedicide usage of farmers

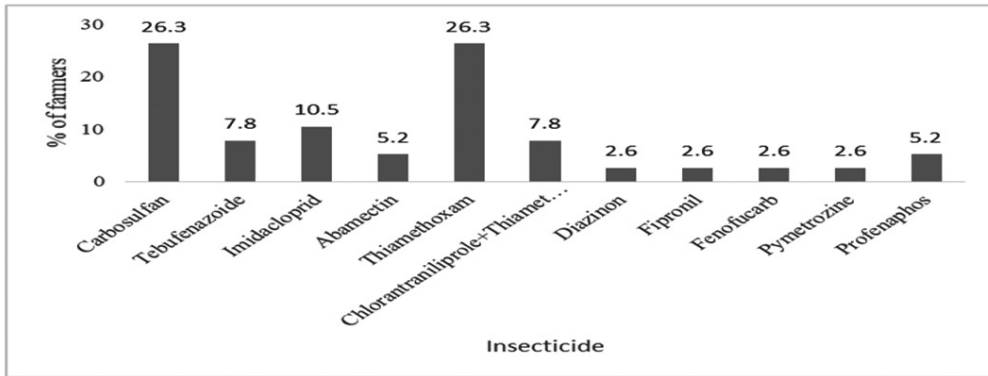


Figure 9. Mean usage of insecticide among farmers

Usage of fungicides

The mean usage of fungicide among farmers is shown in Figure 10. Out of 60 number of farmers only 6 farmers used fungicide and popular generic fungicides were Tebucanazole, Carbendazim, Hexaconazole, Pencycuron and Flutolanil. The survey results revealed that Tebuconazole 250 gL⁻¹ EW was the most popular fungicide used by farmers.

Identification of pests by the farmers

The source of information and instructions received by the farmers is illustrated in

Figure 11. The results revealed that about 56.6% of farmers followed the instructions given by the Agriculture Instructor (AI) of the area and followed the label instructions, of the pesticide container. About 10% of farmers were aware of the instructions given on the pesticide label and 25% of farmers get the instructions from Agriculture Instructor while 3.3% of farmers used Instructions given by the retailer of the Agrochemical shop and 93.3% of farmers followed the correct instruction for pest control.

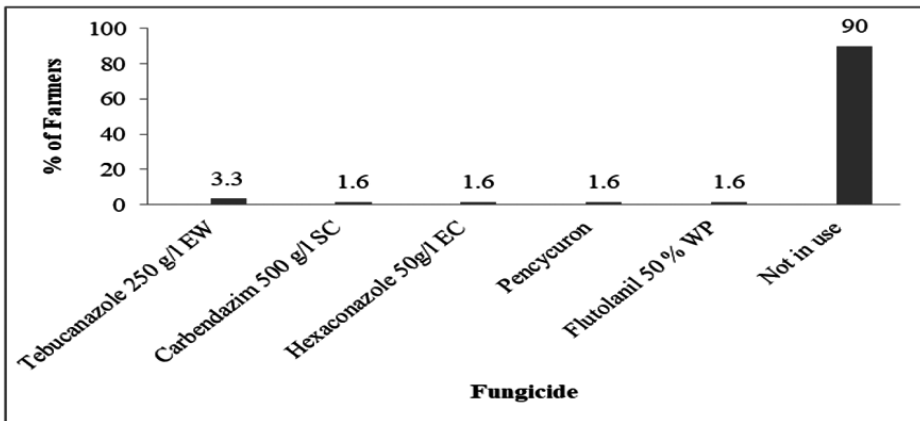


Figure 10. Mean usage of fungicide among farmers

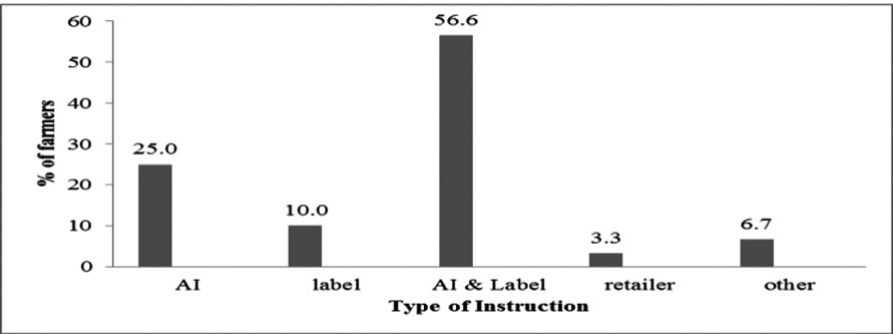


Figure 11. Source of instructions receiving by the farmers

The distribution pattern of the instructions varied from farmer to farmer among the different districts. Therefore, a significant relation was observed between different districts and the p value is 0.00001.

Pesticide mixing practice among farmers

Pesticide mixing practices among different farmers in five districts were illustrated as Figure 12. About 33.3% of farmers in Hambanthota, 16.6% in Polonnaruwa, and 8.33% in Anuradhapura applied mixtures of pesticides to control pests in paddy. A large number of farmers mixed different types of weedicides together and applied them to the paddy land. About 25% of farmers in Hambanthota district, and 16.6% of farmers in Anuradhapura, Polonnaruwa, and Ampara districts applied tank mixture

of pesticides to control pests. However, a majority of the farmers in Kurunegala used individual pesticides to control pests in paddy cultivation. From 60 number of farmers only, 73.3% of farmers were not practiced neither tank mix nor pre mix.

Stage of application the pesticides

The position of the farmers regarding the application of pesticides was illustrated in Figure 13. Results revealed that, no significant relationship between the different districts and the position of the pest damage was observed and the P value is 0.2645. However, about 53.4% of farmers tend to apply pesticides after observing the pest incidence while 46.6% of farmers apply pesticides before the appearance of pest incidence.

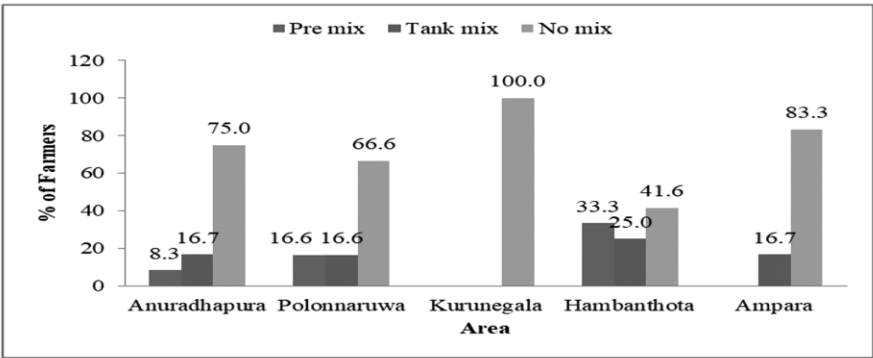


Figure 12. Pesticide mixing practice among farmers

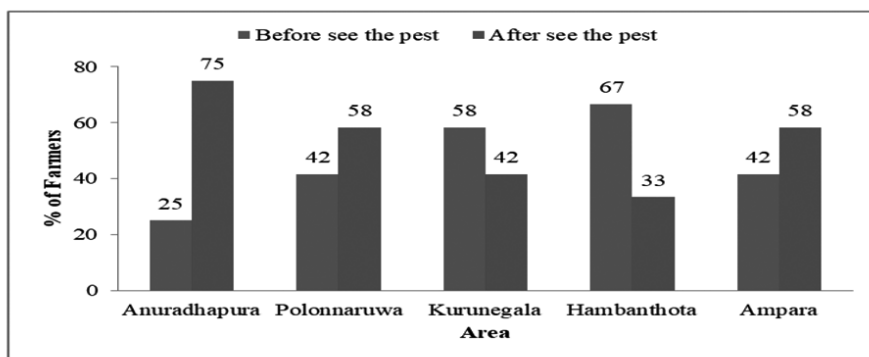


Figure 13. Stage of the application by farmers

Usage of the tank and the nozzles

The results revealed that 75% of farmers did not use separate tanks and 25% of farmers used separate tanks and nozzles. Farmers in Ampara, Kurunegala, and Anuradhapura districts did not use a separate tank for pesticide spraying. However, the farmers in Hambantota district (50%) used separate tanks. Further, 100% of the farmers in Girithale and Weeravila used separate tanks.

Sample analysis

Out of 62 samples including 12 each samples from Anuradhapura, Polonnaruwa, Kurunagala, Ampara, and 14 samples from Hambantota, only 9 samples showed 12 detections leading to 0.33% of detections from the total detections. Out of 57 pesticides, six pesticides, Thiamethoxam, Imidacloprid, Carbofuran - 3 - hydroxy, Profenaphos, Buprofezin and Tebuconazole showed detection. Only 3 samples from Ampara district (Akkareipaththuwa) contaminated with Thiomethoxam range from 13.26 ppb to 21.69 ppb while, 2 samples from Hambantota and Ampara contaminated with Imidacloprid about

28.57 ppb and 108.73 respectively. Two samples from Anuradhapura district contaminated with carbofuran-3-hydroxy derivative at about 12.34 ppb and 13.64 ppb respectively. About 1 sample from Anuradhapura and two samples from Ampara were contaminated by Profenofos with a range of 14.30 ppb to 36.73 ppb. About 33.80 ppb of Buprofezin was contaminated in one sample from Ampara and 31.25 ppb of Tebuconazole was contaminated in one sample from Ampara district. The detection percentage of the detected pesticides in different locations and the mean detection of each pesticide were illustrated in Figure 14. Overall, the mean detected percentage of Thiomethoxam, Imidacloprid, Profenaphos, Buprofezin and Tebuconazole in all district are 4.8%, 3.2%, 3.2%, 4.8%, 1.6%, and 1.6% respectively. No pesticides detected in samples available in Polonnaruwa and Kurunegala districts. The highest contamination detected in the rice sample available in Ampara district was 108 ppb for Imidacloprid and does not exceeding the stated maximum residue limit.

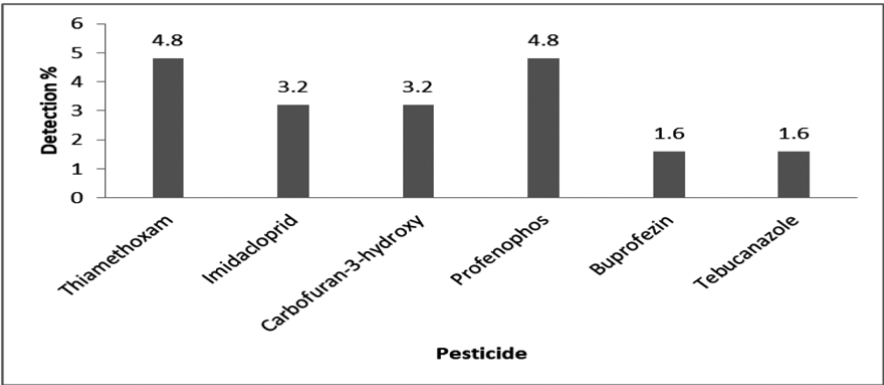


Figure 14. Overall pesticide detections among farmers

The details of the MRL's as shown in table 5. Out of 62 samples, neither any sample exceeded the FAO MRL's (CODEX Alimentarius.) nor Sri Lankan MRL's (2023/34 gazette).

Table 5. Details of MRL's for the detected pesticide

Pesticide	FAO MRL's (ppm)	Sri Lankan MRL (ppm)
Thiamethoxam	-	0.3
Imidacloprid	0.05 (cereal grains)	-
Carbofuran-3-hydroxy	1 (rice for carbofuran)	-
Profenaphos	-	-
Buprofezin	-	0.05
Tebucanazole	1.5 (Rice)	1.5

Conclusion

A farmer survey revealed that about 56.7% of farmers used Pretilachlor as weedicide while, 26.3% used Carbosulfan and Thiomethoxam as insecticides. However, 90% of farmers were not using fungicides. About 93% of farmers used information from Agriculture Instructor and label while

73.3% of farmers do not practicing either tank mix or pre-mix during the application. Pesticide application before and after the pest attack was 46.6 and 53.4% respectively and about 75% of farmers do not used separate tanks and nozzles for different pesticide application. Therefore the farmer survey results can apply to the the risk assements of the mentioned pesticides to minimize the potential health risk.

This study was covered only for pest management from seedling stage to harvesting stage of rice and not for control of post-harvest pests. About 0.33% of total detections were ranged between 10 ppb to 100 ppb while, the highest contamination was reported as 108 ppb for imidacloprid in rice samples from Ampara district .Thus, the sample was not exceeding the EU MRLof 1500 ppb. Out of 62 rice grain samples, non of the detections were reported for the samples available in Polonnaruwa and Kurunagala districts. The detection percentage in Anuradhapura, Hambantota, and Ampara was 0.14%, 0.12%, and 1.16% respectively and none of the samples were exceeding the FAO MRL's or Sri Lankan MRL's.

Overall, the detections and the detection percentages are very low. However, two samples found at Anuradhapura district were contaminated with the 3-carbofuran hydroxy which is a metabolite of carbofuran. Consequently, the detections of 13.64 ppb and 12.34 ppb does not exceed the FAO MRL's for the Carbofuran.

This study clearly indicates the necessity of a comprehensive monitoring program to safeguard the quality of the rice in Sri Lanka and need of extensive farmer awareness programs on the safe margins in the use of agro-chemicals on rice production programs across the entire island.

It is recommended to expand monitoring studies to other pesticides including weedicides and storage pest control pesticides and other Districts with frequency. Studies will serve as a basis for future policy regarding the standards and quality control for rice available at the local market.

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References

Anastassiades, M., Lehotay, S. J., Štajnbaher, D., & Schenck, F. J. (2003). Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. *Journal of AOAC international*,

86(2), 412-431.

AOAC International. (2012). AOAC Official Method 2012, Pesticide Residues in Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulfate. Official Methods of Analysis of AOAC International 90(2), 17-26.

Gazette Extraordinary of the Democratic Socialist Republic of Sri Lanka No 2023/34 on 14.06.2017

Hussain, S. Z., & Maqbool, K. (2014). GC-MS: Principle, Technique and its application in Food Science. *International Journal of Current Science*, 13, 116-126.

International Organization for Standardization. (1980). *Fresh fruits and vegetables - Sampling* (ISO Standard No. 874:1980). <https://www.iso.org/standard/5259.html>

Joint FAO/WHO Food Standards Programme (1999). Recommended methods of sampling for the determination of pesticide residues for compliance with MRLs (CAC/GI 33-1999) <http://www.fao.org/fao-who-codexalimentarius>. 8. (Accessed on 10.05.2019)

Lehotay, S.J., de Kok, A., Hiemstra, M., Van Bodegraven, P. (2005) Validation of a fast and easy method for the determination of residues from 229 pesticides in fruits and vegetables using gas and liquid chromatography and mass spectrometric detection. *Journal of AOAC International*, 88(2), 595-614.

Lesueur, C., Knittl, P., Gartner, M., Mentler, A., & Fuerhacker, M. (2008). Analysis of

140 pesticides from conventional farming foodstuff samples after extraction with the modified QuEChERS method. *Food Control*, 19(9), 906-914.

Melo, M. G., Carqueijo, A., Freitas, A., Barbosa, J., & Silva, A. S. (2019). Modified QuEChERS extraction and HPLC-MS/MS for simultaneous determination of 155 pesticide residues in rice (*Oryza sativa* L.). *Foods*, 9(1), 18.

Pareja, L., Fernández-Alba, A. R., Cesio, V., & Heinzen, H. (2011). Analytical methods for pesticide residues in rice. *TrAC Trends in Analytical Chemistry*, 30(2), 270-291.

SANTE (2019). SANTE/12682/2019. Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed. EU Reference Laboratories for Residues of Pesticides.

Tauseef, M., Rafique, N., Ahmad, I., Ishtiaq, M., Samad, A., Saba, S., Ahad, K., Mehboob, F. (2021). Analysis of multiple pesticide residues in rice by LC-MS/MS. *Chemical Papers*, 75(6), 2871-2879.