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Determination of Pre-Harvest Interval for Quinalphos, Malathion, Diazinon and Cypermethrin in Major Vegetables

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Abstract

The present study was undertaken to determine the pre harvest interval (PHI) for quinalphos in Eggplant, Cabbage and Yard long bean; malathion in Eggplant, Yard Long bean and Cauliflower; cypermethrin in Tomato and Yard long bean; and diazinon in Eggplant and Yard long bean depending on Maximum Residue Limit (MRL) set by FAO/ WHO. Five supervised field trials were conducted and sprayed with the field dose (2 ml/L of water) of each pesticide except cypermethrin (1 ml/L of water). Samples were collected at 0, 1, 3, 5, 7, 10, 12, 15 and 18 days after spray. The collected samples were analyzed using Gas Chromatography (GC) coupled with Flame Thermionized Detector (FTD) and Electron Capture Detector (ECD) for the determination of pesticide residues. The level of residues were above MRL up to 10 DAS for quinalphos in Cabbage, 7 DAS in Eggplant, 5 DAS in Yard long bean; for malathion 5 DAS in Yard long bean and Eggplant, 7 DAS in cauliflower; for diazinon 5 DAS in Yard long bean and Eggplant; and 3 DAS for cypermethrin in Yard long bean and Tomato. The determined PHI for quinalphos were 12 DAS in Cabbage and 10 DAS in Eggplant and 7 DAS in Yard long bean; For malathion 7 DAS in Yard long bean and Eggplant and 10 DAS in cauliflower; For diazinon 7 DAS in Yard long bean and Eggplant; For cypermethrin 5 DAS in Yard long bean and Tomato.

Keywords: Vegetables; Pesticide residues; PHI determination; GC-FTD; GC-ECD

Introduction

Pesticides are considered to be indispensable for the production of an adequate food supply for an increasing world population. The remaining residues of pesticides on harvested crops could have a deleterious effect on humans and the environment [1-3]. On the other hand, pesticides play a key role to control the insect pests and diseases. Production of fruits and vegetables is seriously affected by insect pests and diseases. Due to plant pests and diseases 20 to 40 percent of the crop yields are reduced globally [4]. To overcome these situations farmers are using pesticides as it is the most convenient and economical way to control the insect pests and diseases. The population of the world is increasing day by day; the world will need to produce 60 percent more food for the over increasing world population by 2050 [4]. To ensure this demand control of insect pests and diseases plays a key role in order to increase the production.

The majority of people were indirect consumers of pesticides through food intake. Due to lack of education, the farmers of our country do not follow the prescribed dosages and use pesticides at any stage of the crop without any awareness of the residues and their ill effects on human health. The treated fruits and vegetables are picked/ harvested without taking into account of the withholding period. Every pesticide has a withholding period or pre-harvest interval (PHI), which is defined as the number of days required to lapse, between the date of final pesticide application and harvest, for residues to fall below the tolerance level established for that crop or for a similar food type. Food products become safe for consumption only after withholding period has lapsed. By this time, the pesticide residues get dissipated. However, the extent and rate of dissipation depends on the nature of the pesticide, crop, cultural practices and various environmental conditions under which the crop is grown, or a treated commodity is stored [5]. The PHI differs from pesticide to pesticide and crop to crop. So, we have to determine the pre harvest interval on the consideration of our environmental conditions. With this view this experiment was initiated to determine the PHI for quinalphos, diazinon, malathion and cypermethrin in major vegetables grown in Bangladesh.

Materials and Methods

The standard for the concerned pesticides were obtained from Sigma-Aldrich Laborchemikalien, Gmbh P O Box-100262 D-30918, Seelze, Germany via Bangladesh Scientific Pvt. ltd. Dhaka, Bangladesh. Standards of all pesticides contained 99.6% purity. Marketable size of concerned vegetables (i.e., Tomato, eggplant, yard long bean, cabbage and cauliflower) were collected from supervised field trials and sprayed with the field dose (2 ml/L of water) of each pesticide except cypermethrin (1 ml/L of water). Samples were collected at 0, 1, 3, 5, 7, 10, 12, 15 and 18 days after spray. The formulated products of those were Kinalux 25EC, Hilthion 57EC, Ripcord 10EC and Rison 60EC respectively. The purity of all formulated insecticides was tested in the laboratory and found 100% pure.

Extraction and separation

The methodology prescribed by William and George (2005) with necessary modification was adopted for extraction, separation and clean-up of the sample [6]. Collected field samples (≥ 250 g) were grounded thoroughly with the meat grinder (Handmixer M-122, Bamix, Switzerland). A sub sample of 20 g was taken into a wide mouth jar then 100 ml of hexane was added to it. Sodium sulphate (Na_2SO_4) was also added with sample until water was removed from the sample. The mixture was then macerated with high-speed homogenizer (Ultraturax, IKA T18 basic, Germany) for 2 minutes. The homogenized material was then poured into 250 ml conical flask and placed into the shaker (Orbital

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Shaking Incubator, Rexmed, Sweden) for 12 hrs continuous shaking. After shaking, the slurry was filtered through a Buchner funnel with suction. The flask and filter cakes were rinsed with 25 ml of hexane each. The filtrate was then transferred into 250 ml round bottom flask and was dried to 5 ml by evaporation using a rotary vacuum evaporator (Laborota-4001, Heidolph, Germany). The concentrated filtrate was then transferred into 500 ml separatory funnel making 10 ml in volume. Around 20 ml methanol was added with 10 ml filtrate and shaked vigorously for 5 minutes. After shaking, the separatory funnel was set on stand and kept undisturbed for 5 minutes. Then the clear part of the solution from the bottom of the separatory funnel was collected in a vial which was then centrifuged at 1200 rpm for 5 minutes (Laboratory Centrifuges, Sigma-3K30, Germany). After centrifuge, supernatant was collected for injection.

Operating condition of GC-FTD

A Gas Chromatograph (GC-2010 Shimadzu) coupled with Flame Thermionized Detector (GC-FTD) was used for the identification and quantification of quinalphos, diazinon and malathion. Separation was done by ATTM-1 capillary column (30 m long, 0.25 mm i.d and 0.25 µm film thicknesses), nitrogen was used as carrier (column flow 1.5 mL/min.) and make up gas as well. The injector and detector temperatures were set to 250°C and 280°C, respectively and the column oven temperature was programmed, which was started from 150°C (1 min hold) and went upto 220°C with incremental rate of 10°C (2 min hold). All the injections (1 µL) were done in spit mode. The total run time was 10 min. Identification of the analyte in the samples was done by comparing the retention time of the corresponding calibration standard and quantification was done by external calibration curves maid with 5 point calibration standard.

Operating condition of GC-ECD

A Gas Chromatograph (GC-2010 Shimadzu) coupled with Electron Capture detector (GC-ECD) was used for the identification and quantification of cypermethrin. Separation was done by ATTM-1 capillary column (30 m long, 0.25 mm i.d and 0.25 µm film thicknesses), nitrogen was used as carrier (column flow 1.5 mL/min.) and make up gas as well. The injector and detector temperatures were set to 250°C and 280°C, respectively and the column oven temperature was programmed, which was started from 160°C (1 min hold) and went upto 190°C with incremental rate of 10°C, then it raised to 240°C with incremental rate of 2°C. All the injections (1 µL) were done in spit mode. The total run time was 29 min. Identification of the analyte in the samples was done by comparing the retention time of the corresponding calibration standard and quantification was done by external calibration curves maid with 5 point calibration standard.

Prior to the injection of the sample extract, standard solutions of different concentrations of all pesticide groups were prepared and injected with the above instrument parameters. The samples were calibrated (retention time, peak area etc.) against four pointed calibration curve of standard solution of concerned pesticide. Each peak was characterized by its retention time. Sample results were expressed in mg/kg automatically by the GC software which represented the concentration of the final volume injected.

Determination of pre harvest interval

At first the level of residues in all of the collected samples for every pesticide and every vegetable were calculated following the described procedures. Then the sampling day which was next following MRL was selected. That selected day was chosen as PHI, since the level of residue on that day was below MRL.

Results and Discussion

Level of residue of quinalphos estimated from yard long bean, cabbage and eggplant

The Yard long bean, Cabbage and Eggplant samples containing quinalphos residues were analyzed using GC-FTD. The results obtained from this analysis have been summarized in Tables 1-3. Residue of quinalphos in yard long bean was detected up to 10 DAS and the quantities were above MRL up to 5 DAS and these were 2.012 mg/kg, 1.193 mg/kg, 0.986 mg/kg and 0.347 mg/kg at 0, 1, 3 and 5 DAS, respectively. Sample of 7 DAS and 10 DAS contained 0.086 mg/kg and 0.028 mg/kg quinalphos residue, respectively which were below MRL set by FAO-WHO [7]. No residue was detected at 12 DAS. So, the PHI of quinalphos for Yard long bean can be selected as 7 DAS. Residue of quinalphos was detected up to 15 DAS and the quantities were above MRL up to 10 DAS and these were 3.274 mg/kg, 2.325 mg/kg, 2.012 mg/kg, 1.687 mg/kg, 1.006 mg/kg and 0.628 mg/kg at 0, 1, 3, 5, 7 and 10 DAS, respectively. Sample of 12 DAS and 15 DAS contained 0.071 mg/kg and 0.033 mg/kg quinalphos residue, respectively which were below MRL set by FAO-WHO [7]. No residue was detected at 18 DAS. So, the PHI of quinalphos for Cabbage can be selected as 12 DAS. Residue of Quinalphos was detected up to 12 DAS and the quantities were above MRL up to 7 DAS and these were 1.924 mg/kg, 1.552 mg/kg, 1.057 mg/kg, 0.762 mg/kg and 0.469 mg/kg at 0, 1, 3, 5 and 7 DAS, respectively. Sample of 10 DAS and 12 DAS contained 0.110 mg/kg and 0.052 mg/kg quinalphos residue, respectively which were below MRL set by FAO-WHO [7]. No residue was detected at 15 DAS. So, the PHI of quinalphos for Eggplant can be selected as 10 DAS.

Level of residue of malathion estimated from yard long bean, cauliflower and eggplant

The Yard long bean, Cauliflower and Eggplant samples containing

Days after spraying	Application rate (ml/L)	Sample weight (g)	Total volume prepared (ml)	Injected volume (µl)	Concentration obtained in final volume (mg/kg)	Level of Residue (mg/kg)	Maximum Residue Limit; MRL (mg/kg)
0	2	20	10	2	4.024	2.012	0.2
1	2	20	10	2	3.386	1.193	
3	2	20	10	2	1.972	0.986	
5	2	20	10	2	0.694	0.347	
7	2	20	10	2	0.172	0.086	
10	2	20	10	2	0.056	0.028	
12	2	20	10	2	ND	ND	

Table 1: Level of residue of quinalphos estimated from Yard Long Bean.

Days after spraying	Application rate (ml/L)	Sample weight (g)	Total volume prepared (ml)	Injected volume (µl)	Concentration obtained in final volume (mg/kg)	Amount of Residue (mg/kg)	Maximum Residue Limit; MRL (mg/Kg)
0	2	20	10	2	6.548	3.274	0.1
1	2	20	10	2	4.650	2.325	
3	2	20	10	2	4.024	2.012	
5	2	20	10	2	3.374	1.687	
7	2	20	10	2	2.012	1.006	
10	2	20	10	2	1.256	0.628	
12	2	20	10	2	0.142	0.071	
15	2	20	10	2	0.066	0.033	
18	2	20	10	2	ND	ND	

Table 2: Level of residue of quinalphos estimated from Cabbage.

Days after spraying	Application rate (ml/L)	Sample weight (g)	Total volume prepared (ml)	Injected volume (µl)	Concentration obtained in final volume (mg/kg)	Amount of Residue (mg/kg)	Maximum Residue Limit; MRL (mg/Kg)
0	2	20	10	2	3.848	1.924	0.2
1	2	20	10	2	3.104	1.552	
3	2	20	10	2	2.114	1.057	
5	2	20	10	2	1.524	0.762	
7	2	20	10	2	0.938	0.469	
10	2	20	10	2	0.220	0.110	
12	2	20	10	2	0.104	0.052	
15	2	20	10	2	ND	ND	

Table 3: Level of residue of quinalphos estimated from Eggplant.

malathion residues were analyzed using GC-FTD. The results obtained from this analysis have been summarized in Tables 4-6. Residue of malathion was detected up to 10 DAS and the quantities were above MRL up to 5 DAS and these were 2.426 mg/kg, 1.702 mg/kg, 0.896 mg/kg and 0.562 mg/kg at 0, 1, 3 and 5 DAS, respectively. Sample of 7 DAS and 10 DAS contained 0.162 mg/kg and 0.063 mg/kg residue, respectively which are below MRL set by FAO-WHO [7]. No residue was detected at 12 DAS. So, the PHI of malathion for Yard long bean can be selected as 7 DAS.

Residue of malathion was detected up to 10 DAS and the quantities were above MRL up to 5 DAS and these were 2.781 mg/kg, 1.502 mg/kg, 0.908 mg/kg and 0.593 mg/kg at 0, 1, 3, and 5 DAS, respectively. Sample of 7 and 10 DAS contained 0.127 mg/kg and 0.029 mg/kg residue which were below MRL set by FAO-WHO [7]. No residue was detected at 12 DAS. So, the PHI of malathion for Eggplant can be selected as 7 DAS.

Residue of malathion was detected up to 10 DAS and the quantities were above MRL up to 7 DAS and these were 5.703 mg/kg, 4.311 mg/kg, 1.928 mg/kg, 0.901 mg/kg and 0.540 at 0, 1, 3, 5 and 7 DAS, respectively. Sample of 10 DAS contained 0.084 mg/kg residue which was below MRL set by FAO-WHO [7]. No residue was detected at 12 DAS. So, the PHI of malathion for Cauliflower can be selected as 10 DAS.

Level of residue of diazinon estimated from yard long bean and eggplant

The Eggplant and Yard long bean samples containing diazinon residues were analyzed using the GC-FTD. The results obtained from this analysis have been summarized in Tables 7 and 8. Residue of diazinon was detected up to 10 DAS and the quantities were above MRL up to 5 DAS and these were 2.066 mg/kg, 1.525 mg/kg, 1.116 mg/kg and 0.729 mg/kg at 0, 1, 3 and 5 DAS, respectively. Sample of 7 and 10 DAS contained 0.059 mg/kg and 0.041 mg/kg residue, respectively which are below MRL set by FAO-WHO [7]. No residue was detected at 12 DAS. So, the PHI of diazinon for Eggplant can be selected as 7 DAS.

Residue of diazinon was detected up to 10 DAS and the quantities were above MRL up to 5 DAS and these were 2.765 mg/kg, 1.925 mg/kg, 0.980 mg/kg and 0.506 mg/kg at 0, 1, 3 and 5 DAS, respectively. Sample of 7 and 10 DAS contained 0.060 mg/kg and 0.039 mg/kg residue, respectively which are below MRL set by FAO-WHO [7]. No residue was detected at 12 DAS. So, the PHI of diazinon for Yard long bean can be selected as 7 DAS.

Level of residue of cypermethrin estimated from yard long bean and tomato

The Yard long bean and Tomato samples containing cypermethrin residues were analyzed using GC-ECD. The results obtained from this analysis have been summarized in Tables 9 and 10. Residue of cypermethrin was detected up to 7 DAS and the quantities were above MRL up to 3 DAS and these were 1.806 mg/kg, 0.954 mg/kg and 0.670 mg/kg at 0, 1 and 3 DAS, respectively. Sample of 5 and 7 DAS contained 0.121 mg/kg and 0.040 mg/kg residue, respectively which are below MRL set by FAO-WHO [7]. No residue was detected at 10 DAS. So, the PHI of cypermethrin for yard long bean can be selected as 3 DAS (Table 11). Residue of cypermethrin was detected up to 7 DAS and the quantities were above MRL up to 3 DAS and these were 1.463 mg/kg, 0.875 mg/kg and 0.603 mg/kg at 0, 1 and 3 DAS, respectively. Sample of 5 and 7 DAS contained 0.094 and 0.043 mg/kg residue, respectively which are below MRL set by FAO-WHO [7]. No residue was detected at 10 DAS. So, the PHI of cypermethrin for Tomato can be selected as 5 DAS (Table 11).

Days after spraying	Application rate (ml/L)	Sample weight (g)	Total volume prepared (ml)	Injected volume (µl)	Concentration obtained in final volume (mg/kg)	Amount of Residue (mg/kg)	Maximum Residue Limit; MRL (mg/Kg)
0	2	20	10	2	4.852	2.426	0.3
1	2	20	10	2	3.404	1.702	
3	2	20	10	2	1.792	0.896	
5	2	20	10	2	1.124	0.562	
7	2	20	10	2	0.324	0.162	
10	2	20	10	2	0.126	0.063	
12	2	20	10	2	ND	ND	

Table 4: Level of residue of malathion estimated from Yard long bean.

Days after spraying	Application rate (ml/L)	Sample weight (g)	Total volume prepared (ml)	Injected volume (µl)	Concentration obtained in final volume (mg/kg)	Amount of Residue (mg/kg)	Maximum Residue Limit; MRL (mg/Kg)
0	2	20	10	2	5.562	2.781	0.3
1	2	20	10	2	3.004	1.502	
3	2	20	10	2	1.816	0.908	
5	2	20	10	2	1.186	0.593	
7	2	20	10	2	0.254	0.127	
10	2	20	10	2	0.058	0.029	
12	2	20	10	2	ND	ND	

Table 5: Level of residue of malathion estimated from Eggplant.

Days after spraying	Application rate (ml/L)	Sample weight (g)	Total volume prepared (ml)	Injected volume (µl)	Concentration obtained in final volume (mg/kg)	Amount of Residue (mg/kg)	Maximum Residue Limit; MRL (mg/Kg)
0	2	20	10	2	11.406	5.703	0.1
1	2	20	10	2	8.622	4.311	
3	2	20	10	2	3.856	1.928	
5	2	20	10	2	1.802	0.901	
7	2	20	10	2	1.040	**0.540**	
10	2	20	10	2	0.168	0.084	
12	2	20	10	2	ND	ND	

Table 6: Level of residue of malathion estimated from Cauliflower.

Days after spraying	Application rate (ml/L)	Sample weight (g)	Total volume prepared (ml)	Injected volume (µl)	Concentration obtained in final volume (mg/kg)	Amount of Residue (mg/kg)	Maximum Residue Limit; MRL (mg/Kg)
0	2	20	10	2	4.132	2.066	0.2
1	2	20	10	2	3.050	1.525	
3	2	20	10	2	2.232	1.116	
5	2	20	10	2	1.458	0.729	
7	2	20	10	2	0.118	0.059	
10	2	20	10	2	0.082	0.041	
12	2	20	10	2	ND	ND	

Table 7: Level of residue of diazinon estimated from Eggplant.

Days after spraying	Application rate (ml/L)	Sample weight (g)	Total volume prepared (ml)	Injected volume (µl)	Concentration obtained in final volume (mg/kg)	Amount of Residue (mg/kg)	Maximum Residue Limit; MRL (mg/Kg)
0	2	20	10	2	5.530	2.765	0.2
1	2	20	10	2	3.850	1.925	
3	2	20	10	2	1.960	0.980	
5	2	20	10	2	1.012	0.506	
7	2	20	10	2	0.120	0.060	
10	2	20	10	2	0.078	0.039	
12	2	20	10	2	ND	ND	

Table 8: Level of residue of diazinon estimated from Yard long bean.

Days after spraying	Application rate (ml/L)	Sample weight (g)	Total volume prepared (ml)	Injected volume (µl)	Concentration obtained in final volume (mg/kg)	Amount of Residue (mg/kg)	Maximum Residue Limit; MRL (mg/Kg)
0	2	20	10	2	3.612	1.806	0.5
1	2	20	10	2	1.908	0.954	
3	2	20	10	2	1.340	0.670	
5	2	20	10	2	0.242	0.121	
7	2	20	10	2	0.080	0.040	
10	2	20	10	2	ND	ND	

Table 9: Level of residue of cypermethrin estimated from Yard long bean.

Days after spraying	Application rate (ml/L)	Sample weight (g)	Total volume prepared (ml)	Injected volume (µl)	Concentration obtained in final volume (mg/kg)	Amount of Residue (mg/kg)	Maximum Residue Limit; MRL (mg/Kg)
0	2	20	10	2	2.926	1.463	0.5
1	2	20	10	2	1.750	0.875	
3	2	20	10	2	1.206	0.603	
5	2	20	10	2	0.188	0.094	
7	2	20	10	2	0.086	0.043	
10	2	20	10	2	ND	ND	

Table 10: Level of residue of cypermethrin estimated from Tomato.

Name of Insecticide	Name of Vegetables	PHI (DAS)
Quinalphos	Cabbage	12
	Eggplant	10
	Yard long bean	07
Malathion	Cauliflower	10
	Eggplant	07
	Yard long bean	07
Diazinon	Yard long bean	07
	Eggplant	07
Cypermethrin	Yard long bean	05
	Tomato	05

Table 11: Selected PHI for quinalphos, malathion, diazinon and cypermethrin in major vegetables.

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