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Article

Determination of pre-harvest interval for dimethoate and quinalphos in selected vegetables

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Abstract: The study was undertaken to determine the pre-harvest interval (PHI) for dimethoate and quinalphos in cauliflower, eggplant and hyacinth bean depending on Maximum Residue Limit (MRL) set by European Union. Six supervised field trials were conducted and sprayed with the recommended dose (2 ml/L of water) of each pesticide. Samples were collected at 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 days after spray (DAS). The collected samples were analyzed using Gas Chromatography (GC) with Flame Thermionized Detector (FTD) for the determination of pesticide residue. The quantities of residue were above MRL up to 9 DAS for quinalphos in cauliflower, 7 DAS in hyacinth bean, 8 DAS in eggplant; 11 DAS for dimethoate in cauliflower, 10 DAS in hyacinth bean, and 9 DAS in eggplant. At 11 DAS, no residue was detected from any of the tested samples except dimethoate in cauliflower. The determined PHI for quinalphos was 10 DAS in cauliflower, 8 DAS in hyacinth bean and 9 DAS in eggplant. In case of dimethoate it was 12 DAS in cauliflower, 11 DAS in hyacinth bean and 10 DAS in eggplant.

Keywords: pesticide residue; PHI determination; cauliflower; hyacinth bean; eggplant

1. Introduction

Cauliflower, eggplant and hyacinth bean are commercial crop in Bangladesh. These vegetables are attacked by many insect pests. Insecticides are one of the major components of plant protection for the farmers of Bangladesh. Dimethoate (M.f.$C_6H_{12}NO_3PS_2$) and quinalphos (M.f. $C_{10}H_5Cl_2NO_2$) are an organophosphorus insecticide and acaricide. These are plays an important role for the control of chewing, sucking and some borer pests of vegetables. The pattern of insecticide usage in vegetables led to assume that major vegetable growing areas of Bangladesh should be overloaded with insecticide residue, since insecticides are being used by vegetable farmers irrationally, in some occasions whimsically. It was understood from farmers' interview that they use insecticides irrationally and indiscriminately (Anonymous, 2001; Ahmed *et al.*, 2005). A considerable number of farmers sell vegetables immediate after spray or at an interval of 0-2 days after spray (Anonymous, 2000). This led to assume that over-sprayed vegetable consumers might face health hazards and environment might be over loaded with insecticide residue. Pesticide being toxic can become a potential hazard to the manufacturers, the user, the public at large and the environment. Pesticide can produce negative impacts, both social and private (Antle and Pingali, 1994). 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 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. The PHI differs from pesticide to pesticide and crop to crop. So, we have to re-set the pre harvest interval on the consideration of our environmental conditions.

Considering these, the present study was undertaken to re-set the PHI for dimethoate and quinalphos in selected vegetables grown in Bangladesh.

2. Materials and Methods

The standard for dimethoate and quinalphos were obtained from Sigma-Aldrich Laborchemikalien, Gmbh P O Box-100262 D-30918, Seelze, Germany via Bangladesh Scientific Pvt. ltd. Dhaka, Bangladesh. Standards of both the insecticides contained 99.6% purity. Marketable size of cauliflower, hyacinth bean and eggplant were collected from supervised field trials at 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 days after spray (DAS) which (dimethoate and quinalphos) were sprayed with @ 2 ml/L of water. The formulated product of dimethoate was Tafgor 40EC and quinalphos was Kinalux 25EC. The purity of formulated insecticides were tested in the pesticide analytical laboratory and found to be 100% pure.

2.1. Extraction, separation and cleanup

Field collected 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 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 in Gas Chromatography.

2.2. Operating condition of GC-FTD

The concentrated extracts were subjected to analysis by Gas Chromatography (GC-2010 Shimadzu). For Organophosphorus insecticide (dimethoate and quinalphos), FTD (Flame Thermionized Detector) was used. Separation was done by ATTM-1 capillary column (30 m length, 0.25 mm inner diameter and 0.25 µm film thickness). Helium was used as carrier and make up gas. Injection temperature was 260^0C and detector temperature was 280^0C, respectively and the column oven temperature was programmed. The column oven initial temperature was 160^0C which went upto 240^0C following 8 min incremental time. Current was 0.5 pA, Makeup flow was 30 ml/min, H_2 Flow was 1.5 mL/min and Air flow was 145 ml/min, respectively. All the injections (2 µL) were done in split mode. The total run time was 12 min. Identification of the analyte in the sample was done by compering the retention time of the corresponding calibration standard and quantification was done by external calibration curves maid with 5 point calibration standard.

Previous to the injection of the sample extract, standard solutions of different concentrations of both pesticide groups were prepared and injected with the above instrument parameters. The samples were calibrated (retention time, peak area etc.) against three to 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.

2.3. Determination of pre-harvest interval

The amount of residues in all of the collected samples for both the 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.

3. Results

3.1. Amount of residue of quinalphos estimated from cauliflower, hyacinth bean and eggplant

The cauliflower, hyacinth bean and eggplant samples containing quinalphos residues were analyzed using the GC-FT D with set parameters. The results obtained from this analysis are summarized in Table 1-3.

Table 1. Quantity of residue of quinalphos (Kinalux 25EC) estimated from cauliflower.

Days after spraying	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	20	10	2	13.380	6.690	0.01
1	20	10	2	10.256	5.128	
2	20	10	2	8.640	4.320	
3	20	10	2	5.810	2.905	
4	20	10	2	2.864	1.432	
5	20	10	2	1.734	0.867	
6	20	10	2	0.924	0.462	
7	20	10	2	0.460	0.230	
8	20	10	2	0.130	0.065	
9	20	10	2	0.046	0.023	
10	20	10	2	ND	ND	

The residue of quinalphos was detected up to 9 DAS. The quantities of residues were 6.690 mg/kg, 5.128 mg/kg, 4.320 mg/kg, 2.905 mg/kg, 1.432 mg/kg, 0.867 mg/kg, 0.462 mg/kg, 0.230 mg/kg 0.065 mg/kg and 0.023 mg/kg at 0, 1, 2, 3 4, 5, 6, 7, 8 and 9 DAS, respectively. All of the tested samples had quinalphos residues which were above MRL set by European Union. No residue was detected at 10 DAS. So, the PHI of quinalphos for cauliflower can be selected at 10 DAS.

Table 2. Quantity of residue of quinalphos (Kinalux 25EC) estimated from hyacinth bean.

Days after spraying	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	20	10	2	7.520	3.760	0.01
1	20	10	2	2.960	1.480	
2	20	10	2	1.316	0.658	
3	20	10	2	0.792	0.396	
4	20	10	2	0.402	0.201	
5	20	10	2	0.184	0.092	
6	20	10	2	0.112	0.056	
7	20	10	2	0.058	0.029	
8	20	10	2	ND	ND	

Residue of quinalphos in hyacinth bean could be detected up to 7 DAS and all of the quantities were above MRL which were 3.760 mg/kg, 1.480 mg/kg, 0.658 mg/kg, 0.396 mg/kg, 0.201 mg/kg, 0.092 mg/kg, 0.056 mg/kg and 0.029 mg/kg at 0, 1, 2, 3, 4, 5, 6 and 7 DAS, respectively. Sample of 8 DAS contained no detectable residue. So, the PHI of quinalphos for hyacinth bean can be selected at 8 DAS.

Table 3. Quantity of residue of quinalphos (Kinalux 25EC) estimated from eggplant.

Days after spraying	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	20	10	2	14.032	7.016	0.01
1	20	10	2	8.764	4.382	
2	20	10	2	5.520	2.760	
3	20	10	2	3.608	1.804	
4	20	10	2	1.912	0.956	
5	20	10	2	1.362	0.681	
6	20	10	2	0.816	0.408	
7	20	10	2	0.458	0.229	
8	20	10	2	0.056	0.028	
9	20	10	2	ND	ND	

The results revealed that residues of quinalphos were detected up to 8 DAS in eggplant. The detected quantities were 7.016 mg/kg, 4.382 mg/kg, 2.760 mg/kg, 1.804 mg/kg, 0.956 mg/kg, 0.681 mg/kg, 0.408 mg/kg and 0.229 mg/kg and 0.028 mg/kg at 0, 1, 2, 3, 4, 5, 6, 7 and 8 DAS, respectively. All the tested samples which had quinalphos residues were of above the MRL set by European Union. No residue was detected at 9 DAS. So, the PHI of quinalphos for eggplantl can be selected at 9 DAS.

3.2. Amount of residue of dimethoate estimated from cauliflower, hyacinth bean and eggplant

The cauliflower, eggplant and hyacinth bean samples containing dimethoate residues were analyzed using the GC-FTD with set parameters. The results obtained from this analysis are summarized in Table 4-6.

Table 4. Quantity of residue of dimethoate (Tafgor 40EC) estimated from cauliflower.

Days after spraying	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	20	10	2	36.058	18.029	0.01
1	20	10	2	31.812	15.906	
2	20	10	2	24.196	12.098	
3	20	10	2	18.804	9.402	
4	20	10	2	13.986	6.993	
5	20	10	2	8.638	4.319	
6	20	10	2	3.410	1.705	
7	20	10	2	0.938	0.469	
8	20	10	2	0.612	0.306	
9	20	10	2	0.280	0.140	
10	20	10	2	0.124	0.062	
11	20	10	2	0.036	0.018	
12	20	10	2	ND	ND	

Residue of dimethoate was detected up to 11 DAS in cauliflower. The detected quantities were 18.029 mg/kg, 15.906 mg/kg, 12.098 mg/kg, 9.402 mg/kg, 6.993 mg/kg, 4.319 mg/kg, 1.705 mg/kg, 0.569 mg/kg and 0.306 mg/kg, 0.140 mg/kg, 0.062 mg/kg and 0.018 mg/kg, at 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11 DAS, respectively. All of the quantities were above MRL set by European Union. No residue was detected at 12 DAS. So, the PHI of dimethoate for cauliflower can be selected at 12 DAS.

Table 5. Quantity of residue of dimethoate (Tafgor 40EC) estimated from hyacinth bean.

Days after spraying	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	20	10	2	22.522	11.261	0.01
1	20	10	2	19.900	9.950	
2	20	10	2	14.136	7.068	
3	20	10	2	10.024	5.012	
4	20	10	2	7.018	3.509	
5	20	10	2	2.520	1.260	
6	20	10	2	1.092	0.546	
7	20	10	2	0.308	0.154	
8	20	10	2	0.128	0.064	
9	20	10	2	0.078	0.039	
10	20	10	2	0.024	0.012	
11	20	10	2	ND	ND	

Form the Table 5, it was observed that dimethoate residue was detected in the hyacinth bean sample up to 10 DAS and the quantities were 11.261 mg/kg, 9.950 mg/kg, 7.068 mg/kg, 5.012 mg/kg, 3.509 mg/kg, 1.260 mg/kg and 0.546 mg/kg, 0.154 mg/kg, 0.064 mg/kg, 0.039 mg/kg and 0.012 mg/kg at 0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 DAS, respectively. The quantities decreased down gradually from 0 DAS to 10 DAS and all the detected residue

levels were above MRL set by European Union. No residue was detected at 11 DAS. So, the PHI of dimethoate for hyacinth bean can be selected at 11 DAS.

Table 6. Quantity of residue of dimethoate (Tafgor 40EC) estimated from eggplant.

Days after spraying	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	20	10	2	13.842	6.921	0.01
1	20	10	2	10.602	5.301	
2	20	10	2	7.928	3.964	
3	20	10	2	3.340	1.670	
4	20	10	2	1.522	0.761	
5	20	10	2	1.058	0.529	
6	20	10	2	0.494	0.247	
7	20	10	2	0.208	0.104	
8	20	10	2	0.106	0.053	
9	20	10	2	0.044	0.022	
10	20	10	2	ND	ND	

The results revealed that residue of dimethoate could be detected up to 9 DAS in eggplant. All of the detected quantities were above MRL and these were 6.921 mg/kg, 5.301 mg/kg, 3.960 mg/kg, 1.670 mg/kg, 0.761 mg/kg, 0.529 mg/kg, 0.247 mg/kg, 0.104 mg/kg, 0.053 mg/kg and 0.022 mg/kg at 0, 1, 2, 3, 4, 5, 6, 7, 8 and 9 DAS, respectively. But the sample of 10 DAS, no residue was detected. So, the PHI of dimethoate for eggplant can be selected at 10 DAS.

4. Discussion

The residue of quinalphos was detected up to 9 DAS in cauliflower, 7 DAS in hyacinth bean and 8 DAS in eggplant. The tested samples had quinalphos residue ranged from7.016-0.023mg/kg which were above MRL set by European Union. No residue was detected at 10 DAS in cauliflower, 8 DAS in hyacinth bean and 9 DAS in eggplant. The PHI can be selected for quinalphos at 10 DAS in cauliflower, 8 DAS in hyacinth bean and 9 DAS in eggplant. Residue of dimethoate was detected up to 11 DAS in cauliflower, 10 DAS in hyacinth bean and 9 DAS in eggplant. The levels of dimethoate residue ranged from 18.029-0.012 mg/kg which were above MRL set by European Union. Sample of 12 DAS in cauliflower, 11 DAS in hyacinth bean and 10 DAS in eggplant did not show any detectable residue. The PHI for dimethoate at 12 DAS in cauliflower, 11 DAS in hyacinth bean and 10 DAS in eggplant. The PHI of tested pesticides were varied in crop to crop because of the plant behavior might be related to physic-chemical properties of pesticide degradation (Virgina and Bajet, 1996). Ahmed *et al.* (2011) reported that quinalphos residue detected up to 10 DAS in cauliflower and brinjal and 7 DAS in bean and the quantities were above MRL up to 7 DAS. The PHI for quinalphos might be selected 10 DAS in cauliflower, bean and brinjal. But it differed from Kabir *et al.* (2008) who observed the residue of quinalphos detected up to 6 DAS in yard long bean and the quantity was above MRL at 4 DAS. The findings of the study also agreed with the observation of Prodhan *et al.* (2018) they found PHI for quinalphos at 7 DAS in yard long bean, 10 DAS in eggplant and 12 DAS in cabbage.

5. Conclusions

The present study selected the pre-harvest interval (PHI) of dimethoate and quinalphos in three different vegetables. The determined PHI for quinalphos was 10 DAS in cauliflower, 8 DAS in hyacinth bean and 9 DAS in eggplant. But for dimethoate it was 12 DAS in cauliflower, 11 DAS in hyacinth bean and 10 DAS in eggplant. The results of the study will help the farmers for safe food production.

Conflict of interest

None to declare.

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