Dissipation Pattern of Five Pesticides in Vegetable Samples

Mohammad Shoeb (shoeb71@yahoo.com)
Dhaka University https://orcid.org/0000-0002-9486-2749
Zerin Sultana Munia
University of Dhaka: Dhaka University
Nilufar Nahar
University of Dhaka: Dhaka University

Research Article

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Abstract

Pesticides are frequently used in agricultural fields in Bangladesh. Residual pesticides in vegetable samples above maximum residue limits (MRL) are illegal use of pesticides and absence of Good Agricultural Practice (GAP). The Government made Safe Food Law to ensure safe food for all citizens of the country. To assess the dissipation of pesticides in vegetable samples for consumer safety, five locally banded pesticides *i.e.*, Vitaban (chlorpyrifos), Double (mixture of imidacloprid and cypermethrin), Nitro (mixture of chlorpyrifos and cypermethrin), Acephate and Reeva (lambda cyhalothrin) were applied to eight different vegetables at the dose which farmers apply in their field in a large vegetable cultivation area. Samples were harvested from the farmer's fields at 2h (0 day) after application of pesticides and analyzed at 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 days keeping them at ambient temperature. Samples were extracted following Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method and cleaned up using primary secondary amine (PSA), and finally analysed by Gas Chromatograph Electron Captured Detector (GC-ECD. Limit of detection (LOD) and limit of quantification (LOQ) of chlorpyrifos, cypermethrin, imidacloprid, acephate and lambda cyhalothrin were 0.019 and 0.057, 0.019 and 0.057, 0.009 and 0.027, 0.019 and 0.057, and 0.009 and 0.057 μg/mL, respectively. Recoveries of these pesticides in these vegetables samples were within acceptable range of 74–110%. Level below MRL value of cypermethrin was found to be 2–5 days while chlorpyrifos, imidacloprid, acephate and lambda cyhalothrin treated vegetables were varied 3–8 days and considered to consume after these days, respectively.

1. Introduction

Bangladesh is an agricultural country with a population of 160 million in 56,000 square miles. Although the economy of the country mainly depends on the agriculture small industries for example garments, leather etc are increasing and contributing to the national GDP. The country is also facing natural disaster like cyclone, tornado, flood, thunderstorms, monsoon and heavy rain, and is vulnerable for climate change. Rice, wheat, jute, cotton, tobacco, potato, sugarcane, pulse, lentils, tea and vegetables are the major crops grown in the country [Rahman et al. 2012, Chowdhury et al. 2013]. In order to meet the demand of food supply for a huge number of populations, a large number of fertilizer and pesticides are being used in agricultural crops. Due to climatic condition of Bangladesh the widely cultivated and high-yielding variety plants are highly vulnerable to pest and other diseases and therefore, the use of pesticides is an integral part for pest control [Chowdhury et al. 2013].

Pesticides are chemical compounds which are used to control pests and diseases of plants, to eradicate weeds, to kill pests and microorganisms that spoil agricultural products, materials and articles and to control parasites and vectors of dangerous diseases of man and animals [Nahar 2006]. The use of pesticides in Bangladesh started during middle of 1950s to promote crop productions. Organochlorine pesticides including DDT, dieldrin, chlordane were extensively used for control of pests and vector diseases [Bergkvis et al. 2012, Rahman and Alam 1997]. Government encouraged farmers to use pesticides through price reduction until the 1980s. Consequently, the important of pesticides increased from 2 metric tons in 1956 to about 8000 metric tons in 1993 [Bergkvis et al. 2012]. According to statistics from the Government of Bangladesh, consumption of pesticides increased from 7,350 metric tons in 1992 to 16,200 metric tons in 2001 [Dasgupta and Huq 2007]. Since organochlorine pesticides have been banned in 1993 according to the Bangladesh Environment Conservation ACT 1995 due to their high toxicity in human health and environment after Stockholm Convention other types of pesticides such as organophosphorus, pyrethroid, carbamate have extensively been used by farmers in Bangladesh. It was reported that 64% of the crop-producing area is treated with carbamates and 35% are treated with organophosphates in 2012 [Matin et al. 1998, Chowdhury et al. 2012]. Until 2008, a total of 84 pesticides, with 299 trade name, of different groups and formulations, have been registrared in Bangladesh [Bhattacharjee et al. 2012]. During several visits to vegetable cultivation area in Jhinaidoho, Jamalpur, Comilla, Mymensing districts of Bangladesh and discussion with farmers it was revealed that currently chlorpyrifos, cypermethrin, imidacloprid, fenvalerate, abamectic, quinalphos, acephate, lamda cyhalothrin are frequently used in vegetable cultivation fields in Bangladesh either as single pesticide or mixture of pesticides called cocktail. But more than 50% farmers use pesticide in excessive amount than what they need to protect their crops and harvest immediately after application of pesticides which is harmful for human health and environment.

Chlorpyrifos (*O*,*O*-diethyl *O*-3,5,6-trichloropyridin-2-yl phosphorothioate) is an organophosphate insecticide and acts on the nervous system of insects by inhibiting acetylcholinesterase. Cypermethrin [(RS)-α-cyano-3-phenoxybenzyl(1RS, 3RS; 1RS, 3RS)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] is a synthetic pyrethroid insecticide and behaves as a fast-acting neurotoxin in insects. Imidacloprid which is N-{1-[(6-Chloro-3-pyridyl)methyl]-4,5-dihydroimidazol-2-yl}nitramide is a systematic chloronicotinyl insecticide. Lambda-cyhalothrin [3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethyl-cyano(3-phenoxyphenyl)methyl] is a synthetic pyrethroid insecticide. *N*-(Methoxy-methylsulfanylphosphoryl)acetamide. Acephate is *N*-(Methoxy-methylsulfanylphosphoryl)acetamide [Tomin et al. 2006.].

The vegetables are low in fat, high in dietary fibers; contain minerals and vitamins, possessing a very high nutritional density [Nahar et al. 2016]. However, vegetables are usually susceptible to pest attack and different kinds of pesticides are being used in cultivation around the world including Bangladesh. Use of pesticide is necessary to increase crop production. However, indiscriminate use of insecticides and without maintaining the proper pre-harvest interval can make the food unsafe, especially when tamotoes are used as salad [Nahar et al. 2012]. Pesticide residues in the agricultural products depend on the dose of application, climatic condition of each country and also on seasons like winter and summer [Nahar et al. 2014]. We earlier reported dissipation pattern of fenvalerate in tea, and cypermethrin and quinalphos in tomato, bean, cauliflower in experimental fields [Nahar et al. 2012, 2014, 2016, Munia 2018]. Now we are reporting dissipation of five locally used pesticides namely Vitaban 48 EC, Double 50 EC, Nitro 505 EC, Asataf 75 SP (acephate) and Reeva 2.5 EC in eight commonly consumed vegetable samples *i.e.*, tomato, cabbage, cauliflower, bottle gourd, sweet gourd, sponge gourd, green chili and cucumber at ambient temperature for environment and consumer safety.

2. Materials And Methods

2.1 *Reagents and materials*

The standards of chlorpyrifos, cypermethrin, imidacloprid, acephate, lambda-cyhalothrin (99% pure) were purchased from Dr. Ehrenstorfer, Germany. Primary secondary amine (PSA) from Supelco USA, was used in clean-up steps. Analytical grade magnesium sulphate, sodium chloride (anhydrous), ethyl acetate and ultra-pure GC-grade n-hexane were obtained from Merck KGaA, Germany.

2.2 *Sample collection*

Eight commonly consumed vegetable *i.e.*, cabbage, cucumber, bottle gourd, sweet gourd, sponce gourd, green chili, cauliflower and tomato were treated with five locally used pesticides namely, Vitaban 48 EC (chlorpyrifos), Double 50 EC (mix formulation of imidacloprid and cypermethrin), Nitro 505 EC (mix formulation of chlorpyrifos and cypermethrin), Asataf 75 SP (acephate) and Reeva 2.5 EC (lambda-cyhalothrin) at farmer's field in Nuritola, Comilla, Bangladesh. Vegetable were harvested 2 hours after application of pesticides and a total of 40 samples were collected to analyze the dissipation pattern and the safe level from consumer perception. Fresh and untreated (with pesticides) vegetables of all eight types were first collected in zip-locked bag before application of these pesticides, brought to the laboratory. Only control samples were kept in freezer at -20 ^{0}C and the rest of the samples were kept at ambient temperature, so that they could be in a contact with air, wind, light and heat. From these samples, working samples were chopped, homogenized by kitchen blender and then extracted and cleaned-up on consecutive 1st, 3rd, 5th, 8th and 10th day from the application day.

2.3 *Application of pesticides*

Nitro was sprayed at a dose of 1 mL L^{-1} of water/ha; Vitaban 48 EC was sprayed at a dose of 3 mL L^{-1} of water/ ha, Double 50 EC was sprayed at a dose of 800 mL/ ha, Reeva 2.5 EC was sprayed at a dose of 0.5 mL L^{-1} of water/ ha; Asataf 75 SP was used at a dose of 1gm L^{-1} of water/ ha.

2.4 *Extraction*

The extraction process followed the Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method [Anastassiades et al. 2003]. To homogenized vegetable sample, weighed of about 10g was taken in a teflon tube and 20 mL of ethyl acetate was added to it. The tube was then vortexed for about 1 minute. Then 6 g of MgSO4 and 1.5 g of NaCl were added and again vortexed for 1 minute. The mixture was then centrifuged for 5 minutes at 5,000 rpm maintaining temperature 20 ^{0}C. About 10 mL of supernatant was taken in a round bottom flask and dried to dryness. 5 mL n- hexane was added to the dried mass and from there; 2 mL solution was taken in a test tube.

For clean-up, 150 mg primary secondary amine (PSA) and 750 mg $MgSO_4$ were added and the test tube vortexed for about 1 minute. It was then centrifuged for another 5 minutes and then the extract was passed through pipette with cotton plugged inside which was washed successively with methanol, acetone and finally with n- hexane.

Pesticide residues were identified and quantified using a Shimadzu 2010 gas chromatograph (GC) equipped with a ^{63}Ni electron capture detector (ECD). Separation was on an ultra-performance quartz capillary column (HP 5MS, 30 m, 250 μm internal diameter, 0.25 μm film thickness, Agilent, USA). The injector and detector temperatures were 250°C and 260°C, respectively. For determination of chlorpyrifos, lambda-cyhalothrin and acephate, the oven temperature was programmed as: initial temperature of 140°C hold for 1 minute; increased at 15°C min^{-1} to 260°C; hold for 2 minutes but for determination of cypermethrin and imidacloprid, the oven temperature was programmed as: initial temperature of 120°C held for 1 minute; increased at 14°C min^{-1} to 260°C; held for 3 minutes. Nitrogen gas was used as carrier and make up gas, and the flow rate was 1.92 mL min^{-1}. Samples were injected manually in the splitless (1 min)/split mode.

The recovery experiments of pesticides in spiked control vegetable samples were carried out in two different concentrations levels and were extracted and cleaned up following the same procedure as described above.

Storage ability

The storage stability was determined by spiking the control vegetable samples with the five pesticides and then storing them in a freezer at -20 ^{0}C. The control vegetables were spiked with chlorpyrifos, cypermethrin and imidacloprid at a concentration level of 1.0 μg mL^{-1} and with lambda-cyhalothrin and acephate at a concentration level of 0.5 and 2.0 μg mL^{-1}, respectively. Then these spiked samples were stored in freezer for 35 days and extracted, cleaned-up and analyzed following the same procedure to find out the stability of the pesticides at freezing condition during storage.

3. Results And Discussion

The residual level of five pesticides namely chlorpyrifos, cypermethrin, imidacloprid, acephate and lambda-cyhalothrin were analyzed in eight vegetable samples *i.e.*, tomato, cabbage, cauliflower, bottle gourd, sweet gourd, sponge gourd, green chili and cucumber by GC-ECD using external standard calibration method. The percentage recoveries of chlorpyrifos at 0.5 & 0.2, 0.5 & 1, 0.5 & 1, 0.5 & 1, 0.5 & 0.2, 0.2 & 1, 0.5 & 1, 0.2 & 1 μg mL^{-1} fortification levels in tomato, cauliflower, cabbage, bottle gourd, sweet gourd, sponge gourd, green chili, cucumber, respectively were 84 & 74%, 93 & 99%, 96 & 73%, 93 & 85%, 89 & 77%, 80 & 85%, 74 & 88%, 83 & 95% with relative standard deviation (RSD) values of 2.30 & 4.05, 1.10 & 2.60, 4.24 & 2.05, 2.78 & 3.50, 2.50 & 1.20, 1.25 & 2.70, 1.35 & 2.27, 3.61 & 0.52%, successively (Table 1) which is within acceptable range [Codex 2010].The calibration curves showed excellent linear coefficients (r2) of 0.995 & 0.997 for higher and lower concentration calibration curves and the linearity ranges were 1.0– 3.2 & 0.10– 0.30 µg mL^{-1}, accordingly. The LOD and LOQ of chlorpyrifos in these vegetables were 0.019 & 0.057 µg mL^{-1} (Table 1).

Table 1
Linearity range, correlation coefficients (r^2), LOD and LOQ

Pesticide	Calibration curve	Linearity range (µg mL^{-1})	Correlation coefficient(r^2)	LOD (µg mL^{-1})	LOQ (µg mL^{-1})
Chlorpyrifos	higher	1.0- 3.2	0.995	0.019	0.057
	lower	0.10–0.30	0.997		
Cypermethrin	Higher	1.5–3.5	0.995	0.019	0.057
	Lower	0.05–0.20	0.994		
Imidacloprid	higher	1.0–2.0	0.998	0.009	0.027
	lower	0.03–0.08	0.994		
Acephate	higher	0.80-3.0	0.996	0.019	0.057
	lower	0.10–0.35	0.997		
Lambda-cyhalothrin	higher	0.08–0.30	0.998	0.009	0.027
	lower	0.04–0.08	0.996		

The chlorpyrifos residues were 3.12 ± 0.8, 4.30 ± 0.8, 2.94 ± 0.18, 2.75 ± 1.01, 4.23 ± 1.03, 4.11 ± 0.33, 5.14 ± 1.33, 4.21 ± 1.01 µg g^{-1} in tomato, cabbage, cauliflower, bottle gourd, sweet gourd, sponge gourd, green chili and cucumber, respectively on 1 day samples (Table S1). Chlorpyrifos dissipated with time and went to 1.31 ± 0.4, 0.51 ± 2.1, 0.31 ± 0.31, 0.61 ± 0.77, 1.23 ± 0.22, 1.95 ± 0.02, 1.42 ± 2.11, 1.35 ± 0.09 and 0, 0.11 ± 1.1, 0.05 ± 0.74, 0, 0, 0.81 ± 0.08, 0, 0.82 ± 0.19 in tomato, cabbage, cauliflower, bottle gourd, sweet gourd, sponge gourd, green chili and cucumber on fifth day and eight day, respectively. The percentage of dissipation of the pesticide in these vegetable samples were 91%, 93%, 99%, 100%, 86%, 80%, 100%, 81% on eight day. The maximum residue limit (MRL) of tomato, cabbage, cauliflower, sweet gourd, chili, cucumber are 0.5, 0.05, 0.05, 0.1, 0.2, 0.05 µg/g, respectively. In our study the chlorpyrifos residue dissipated to below the MRL within 5 days after application on/in tomato, bottle gourd, sweet gourd, green chili and on/in cabbage, cauliflower, sponge gourd, cucumber within 8 days.

The degradation of a component is described by the first order function (C_t= C_0x e^{kt}). The half-lives of the pesticides were obtained by the equation $t_{½}$= ln2/k, where C_t is the concentration (µg L^1) at time t (days) after application, C_0 is the initial concentration (µg L^1) and k is the first order rate constant (day^1) [Munia et al. 2018, Zhang et al. 2012]. The dissipation of chlorpyrifos followed a pseudo first-order kinetics pattern. The half lives of chlorpyrifos for tomato, cabbage, cauliflower, bottle gourd, sweet gourd, sponge gourd, green chili and cucumber were 0.99, 1.2, 1.1, 1.3, 1.4, 1.3, 0.80 and 0.90 days, respectively (Fig. 1).

Ravi and Verma (1997) reported that initial chlorpyriphos was degraded below MRL (0.2 mg kg^{-1}) within 20 days from its initial residues of were 5.41 mg kg^{-1}. Subhash (2014) reported that chlorpyrifos dissipated below MRL in okra value after 15 days. Our results are also in consistent that the persistence of chlorpyrifos and is lengthier than other pesticides and dissipates slowly. It was reported that dissipation rate of chlorpyrifos is slower than other modern pesticides.

Nitro 505 EC is a mix formulation of chlorpyrifos (50%) and cypermethrin (5%) and was sprayed on the eight kind of vegetables at a dose of 1 mL per Liter of water/ha. The percentage recoveries of cypermethrin at 0.05 & 0.2, 0.5 & 2, 0.5 & 2, 0.5 & 2, 0.05 & 0.2, 0.2 & 1, 0.5 & 2, 0.2 & 1 μg mL^{-1} fortification levels in tomato, cauliflower, cabbage, bottle gourd, sweet gourd, sponge gourd, green chili, cucumber, respectively were 96 & 88%, 98 & 102%, 84 & 93%, 85 & 88%, 92 & 90%, 93 & 76%, 82 & 85%, 77 and 98% with relative standard deviation (RSD) values of 1.25 & 2.61, 1.97 & 2.20, 2.97 & 0.54, 3.52 & 2.84, 1.30 & 0.56, 1.07 & 3.20, 3.04 & 2.36, 1.29 & 1.53%, respectively (Table 1) which is within acceptable range (Codex 2010). The calibration curves showed excellent linear coefficients (r2) of 0.995 and 0.994 for higher and lower concentration calibration curves and the linearity ranges were 1.5– 3.5 and 0.05–0.20 μg mL^{-1}, respectively. The LOD and LOQ of cypermethrin in these vegetables were 0.019 and 0.057 μg mL^{-1}.

The cypermethrin residues were 1.22 ± 0.08, 1.27 ± 0.15, 1.01 ± 0.08, 0.85 ± 0.03, 1.32 ± 0.02, 1.87 ± 0.06, 1.94 ± 0.02, 1.02 ± 0.20 μg g^{-1} in tomato, cabbage, cauliflower, bottle gourd, sweet gourd, sponge gourd, green chili and cucumber, respectively on 1 day samples. Cypermethrin dissipated with time and went to 0.13 ± 0.05, 1.05 ± 0.06, 0.63 ± 0.04, 0.49 ± 0.07, 0.13 ± 0.55, 1.04 ± 0.09, 0.41 ± 0.08, 0.17 ± 0.08 and 0.07 ± 0.05, 0.08 ± 0.10, 0.09 ± 0.15, 0.10 ± 0.12, 0, 0.07 ± 0.35, 0, 0, respectively in tomato, cabbage, cauliflower, bottle gourd, sweet gourd, sponge gourd, green chili and cucumber on third and fifth day. The percentage of dissipation of the pesticide in these vegetable samples were 94%, 95%, 91%, 88%, 100%, 100%, 100%, 100% on fifth day.

However, chlorpyrifos residues were 2.11 ± 0.08, 1.20 ± 0.08, 1.35 ± 0.35, 1.91 ± 0.22, 2.43 ± 0.09, 3.44 ± 0.07, 2.28 ± 0.10, 2.10 ± 0.02 μg g^{-1} in tomato, cabbage, cauliflower, bottle gourd, sweet gourd, sponge gourd, green chili and cucumber, respectively on 1 day samples and were 0.62 ± 0.46, 0.13 ± 0.36, 0.38 ± 0.08, 0.13 ± 0.65, 0.15 ± 0.11, 0.92 ± 0.05, 0, 0.08 ± 0.10 on fifth day sample which indicated that the percentage of dissipation were 76%, 89%, 71%, 93%, 93%, 78%, 100%, 99%.

The MRL value of cypermethrin and chlorpyrifos in tomato, cabbage, cauliflower, cucumber, green chili, sweet gourd, bottle gourd are 0.2, 1.0, 1.0, 1.0, 0.5, 1.0, 1.0 and 1.0, 0.05, 0.05, 0.05, 0.5, 0.5 mg kg^{-1}, respectively [Codex 2010]. The initial amounts of chlorpyrifos and cypermethrin in all vegetables on the first day were much higher than the MRL values of both pesticides. Cypermethrin in tomato, cauliflower, sweet gourd, sponce gourd, green chili and cucumber went below MRL value on 1st day after application of pesticide but within 3rd day of application in cabbage and sponce gourd. 100% dissipation of cypermethrin occurs within 5 days after application of pesticides. The dissipation of chlorpyrifos and cypermethrin followed pseudo first-order kinetic patterns (Fig. 2–3). The half-lives of cypermethrin for tomato, cabbage, bottle gourd, cauliflower, were 0.6, 0.5, 0.4, 0.5 days, respectively.

From the dissipation curves, the average half-lives of chlorpyrifos and cypermethrin in nitro were found to be 0.92 and 0.58 days, respectively. The average half –life value in chlorpyrifos is higher than that of cypermethrin. Similar results were reported by Awasthi (1994) whereas he determined persistence and degradation of different pyrethroids on green chilli fruits [Awasthi 1994]. The half-life of permethrin was 0.42–0.68 days as that of cypermethrin in the current study was 0.46–0.81 days.

Double 50 EC is a mix formulation of imidacloprid (40%) and cypermethrin (10%) and was sprayed on the eight kind of vegetables at a dose of 800 mL per Liter of water/ha. The percentage recoveries of cypermethrin at 0.05 and 0.2, 0.5 and 2, 0.5 and 2, 0.5 and 2, 0.05 and 0.2, 0.2 and 1, 0.5 and 2, 0.2 and 1 µg mL^{-1} fortification levels in tomato, cauliflower, cabbage, bottle gourd, sweet gourd, sponge gourd, green chili, cucumber, respectively were 96 and 88%, 98 and 102%, 84 and 93%, 85 and 88%, 92 and 90%, 93 and 76%, 82 and 85%, 77 and 98% with relative standard deviation (RSD) values of 1.25 & 2.61, 1.97 & 2.20, 2.97 & 0.54, 3.52 & 2.84, 1.30 & 0.56, 1.07 & 3.20, 3.04 & 2.36, 1.29 & 1.53%, respectively (Table 1) which is within acceptable range [Codex 2010]. The calibration curves showed excellent linear coefficients (r2) of 0.995 and 0.994 for higher and lower concentration calibration curves and the linearity ranges were 1.5– 3.5 and 0.05– 0.20 µg mL^{-1}, respectively. The LOD and LOQ of cypermethrin in these vegetables were 0.019 and 0.057 µg mL^{-1}.

The percentage recoveries of imidacloprid at 0.5 and 1.0 µg mL^{-1} fortification levels in tomato, at 0.5 & 2.0 µg mL^{-1} in cauliflower, cabbage, bottle gourd, at 0.05 & 2.0 µg mL^{-1} in sweet gourd, 0.2 & 1.0 µg mL^{-1} in sponge gourd, cucumber, at 0.5 & 2.0 µg mL^{-1} in fortification levels green chili, respectively were 71 & 80%, 96 & 104%, 95 & 102%, 87 & 90%, 83 & 82%, 88 & 93%, 87 & 79%, 76 & 80% with relative standard deviation (RSD) values of 0.7 & 0.8, 2.2 & 1.4, 1.5 & 1.9, 2.8 & 1.1, 4.2 & 1.2, 2.8 & 1.6, 1.3 & 1.2, 3.2 & 3.7 respectively which is within acceptable range [Codex 2010]. The calibration curves showed excellent linear coefficients (r2) of 0.995 and 0.998 for higher and lower concentration calibration curves and the linearity ranges were 1.5– 3.5 and 0.05– 0.20 µg mL^{-1}, respectively. The LOD and LOQ of imidacloprid in these vegetables were 0.009 µg mL^{-1} and 0.027 µg mL^{-1} respectively.

The cypermethrin residues were 0.65 ± 0.09, 1.61 ± 0.08, 1.05 ± 0.08, 1.17 ± 0.15, 1.25 ± 0.06, 1.60 ± 0.05, 0.52 ± 0.03, 1.87 ± 0.04 µg g^{-1} in tomato, cabbage, cauliflower, bottle gourd, sweet gourd, sponge gourd, green chili and cucumber, respectively on 1 day samples. Cypermethrin dissipated with time and went to 0.17 ± 0.09, 0.45 ± 0.10, 0.13 ± 0.05, 1.03 ± 0.10, 1.00 ± 0.06, 1.02 ± 0.06, 0.09 ± 0.06, 1.01 ± 0.04 & 0.04 ± 0.10, 0.06 ± 0.03, 0.06 ± 0.09, 0.06 ± 0.04, 0.35 ± 0.05, 0.30 ± 0.10, 0, 0.10 ± 0.06 respectively in tomato, cabbage, cauliflower, bottle gourd, sweet gourd, sponge gourd, green chili and cucumber on third and fifth day. The percentage of dissipation of the pesticide in these vegetable samples were 93%, 96%, 94%, 96%, 80%, 82%, 100%, 95% on fifth day.

However, imidacloprid residues were 1.13 ± 0.15, 1.44 ± 0.08, 1.62 ± 0.06, 1.65 ± 0.10, 1.58 ± 0.09, 1.98 ± 0.03, 1.02 ± 0.10, 2.05 ± 0.02 µg g^{-1} in tomato, cabbage, cauliflower, bottle gourd, sweet gourd, sponge gourd, green chili and cucumber, respectively on 1 day samples and were 0.06 ± 0.15, 0.05 ± 0.15, 0.04 ± 0.10, 0.03 ± 0.15, 0.65 ± 0.08, 1.01 ± 0.08, 0.03 ± 0.07, 0.33 ± 0.04 on fifth day which indicated that the percentage of dissipation were 94%, 97%, 96%, 98%, 58%, 56%, 97%, 83%.

In the current study, half-lives for tomato, cabbage, cauliflower, bottle gourd, sweet gourd, sponce gourd, green chili and cucumber were found to be 0.38, 0.85, 0.80, 0.41, 0.40, 0.52, 0.35 and 0.7 day and 0.30, 0.72, 0.52, 0.39, 0.53, 0.60, 0.34 and 0.41 day for imidacloprid and cymermethrin, respectively (Fig. 4–5). The average half–life value in imidacloprid is higher than that of cypermethrin. Similar results were reported by Awasthi (1994) whereas he determined persistence and degradation of different pyrethroids on green chilli fruits.

The active component of Asataf 75 SP is acephate and was sprayed at a dose of 1 g per Liter of water/ha. The percentage recoveries of acephate in cauliflower, cabbage, bottle gourd, sweet gourd, sponge gourd (0.05 & 2.00 µg mL^{-1} fortification levels) and in green chili, cucumber, tomato (0.05 & 1.00 µg mL^{-1} fortification levels), were 105 & 95%, 83 & 96%, 80 & 75%, 88 & 78%, 80 & 76%, 86 & 95%, 77 & 80%, 99 & 94%, respectively with relative standard deviation (RSD) values of 1.9 & 2.8, 1.4 & 0.5, 1.8 & 1.3, 1.1 & 2.9, 1.4 & 1.1, 3.2 & 3.6, 3.2 & 1.2, 1.6 & 2.5%, respectively which is within acceptable range [Codex 2010]. The calibration curves showed excellent linear coefficients (r2) of 0.996 and 0.997 for higher and lower concentration calibration curves and the linearity ranges were 0.10– 0.35 and 0.80– 3.0 µg mL^{-1}, respectively. The LOD and LOQ of acephate in these vegetables were 0.019 and 0.057 µg mL^{-1}.

The acephate residues were 1.85 ± 0.03, 2.75 ± 0.04, 2.61 ± 0.06, 2.03 ± 0.03, 2.1 ± 0.08, 2.44 ± 0.03, 1.69 ± 0.01, 1.71 ± 0.05 µg g^{-1} in tomato, cabbage, cauliflower, bottle gourd, sweet gourd, sponge gourd, green chili and cucumber, respectively on 1 day samples and went to 0.6 ± 0.01, 2.12 ± 0.05, 2.01 ± 0.05, 1.27 ± 0.02, 1.28 ± 0.05, 2.0 ± 0.07, 0.88 ± 0.05 and 0.96 ± 0.07 µg g^{-1} on 3rd day which is 64%, 26%, 23%, 37%, 40%, 28%, 47%, and 43% dissipation from the initial value (Fig. 6).

The MRL value of acephate in tomato, cucumber and green chili is 1 µg g^{-1} and cabbage, cauliflower and sweet gourd is 2 µg g^{-1} .The present study revealed that residual acephate in all vegetable samples were less than MRL value on 3rd day except cabbage and cauliflower which went down to MRL on 5th day. Acephate might have more persistency in vegetables like cabbage and cauliflower (brassica vegetables). This can be explained that they grow in upper direction and their surface are large and non-homogeneous, and pesticide has much space to accommodate. As a results pesticide reaches to the target point properly.

The active ingredient of Reeva 2.5 EC is lambda-cyhalothrin. The percentage recoveries of lambda-cyhalothrin at 0.03 and 0.20 µg mL^{-1} fortification levels in tomato, green chili, cucumber and at 0.03 and 0.50 µg mL^{-1} fortification levels in cauliflower, cabbage, bottle gourd, sweet gourd, sponge gourd, respectively were 78 & 90%, 82% & 80%, 79 & 84%, 95 & 98%, 85 & 80%, 85 & 74%, 86 & 88%, 79 & 80%, with relative standard deviation (RSD) values of 1.5 & 1.3, 3.1 & 2.5, 1.3 & 1.8%, 0.4 & 1.3, 2.6 & 0.6, 3.5 & 3.4, 1.2 & 2.8, 1.1 & 0.5, respectively (Table 1) which is within acceptable range [Codex 2010]. The calibration curves showed excellent linear coefficients (r2) of 0.998 and 0.996 for higher and lower concentration calibration curves and the linearity ranges were 0.08–0.30 and 0.04–0.08 μg g^{-1}, respectively. The LOD and LOQ of lambda-cyhalothrinin in these vegetables were 0.009 and 0.027 μg mL^{-1}.

Residual lambda-cyhalothrin in tomato, cabbage, cauliflower, bottle gourd, sweet gourd, sponge gourd, green chili and cucumber were 0.19 ± 0.09, 0.26 ± 0.01, 0.22 ± 0.10, 0.24 ± 0.02, 0.21 ± 0.03, 0.23 ± 0.02, 0.12 ± 0.05 and 0.16 ± 0.02 μg g^{1} on first day and dissipated to zero on 5th day which indicates that the percentage of dissipation is 100%. The MRL values of lambda-cyhalothrin for tomato, cabbage, cauliflower, green chili and cucumber are 0.05 μg g^{-1} and for sweet gourd and bottle gourd are 0.10 μg g^{-1} [FAO 2002]. The concentrations of lambda-cyhalothrin went down to MRL on 3rd day after application on/in this vegetables.

To analyze the storage stability of the pesticides at freezing condition, control vegetable samples were fortifiedwith higher concentrations of the five pesticides with two replicates each and the samples were then stored in a freezer. The vegetable samples fortified with chlorpyrifos, cypermethrin and imidacloprid, were freezed on 12th January, 2016 and kept at freezer for about 35 days. Control vegetable samples spiked with lambda-cyhalothrin and acephate were freezed for about 39 days, from 18th February to 27th March, 2016. Then these spiked samples were extracted, cleaned-up and analyzed following the same procedure to find out the stability of the pesticide residues at freezing condition.

The average recoveries of the pesticides were found in the range of 84–93% with RSD value ranging from 1.1 to 4.2 which indicated that pesticide residues were quite stable at -20°C storage condition because the recovery results were consistent with the range listed in the Codex guidelines (Codex 2010). The storage stability results showed that the pesticides were quiet persistent at freezing condition and not degraded during the period of this test.

4. Conclusions

All pesticides are suitable to use in different vegetables under agro climatic condition of Bangladesh. However, farmers should apply pesticide as recommended dose and harvest after 2–3 days depending on pesticides. The present study recommends to keep vegetable at ambient temperature rather keeping in refrigerator after buying from marker for consumer safety.

Declarations

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Ethical Approval:

Not application as human or animal have not been involved.

Consent to participate:

All co-authors agreed to submit after reading carefully.

Consent to publish:

All co-authors agreed to publish.

Contribution:

Mohammad Shoeb and Zerin Sultana carried out laboratory work. MS and NN collected samples and supervised work. ZS made the first draft. MS and NN finalized.

Funding:

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Competing interests

Authors have declared no conflicts of interest.

Availability of data:

All data original.

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Figures

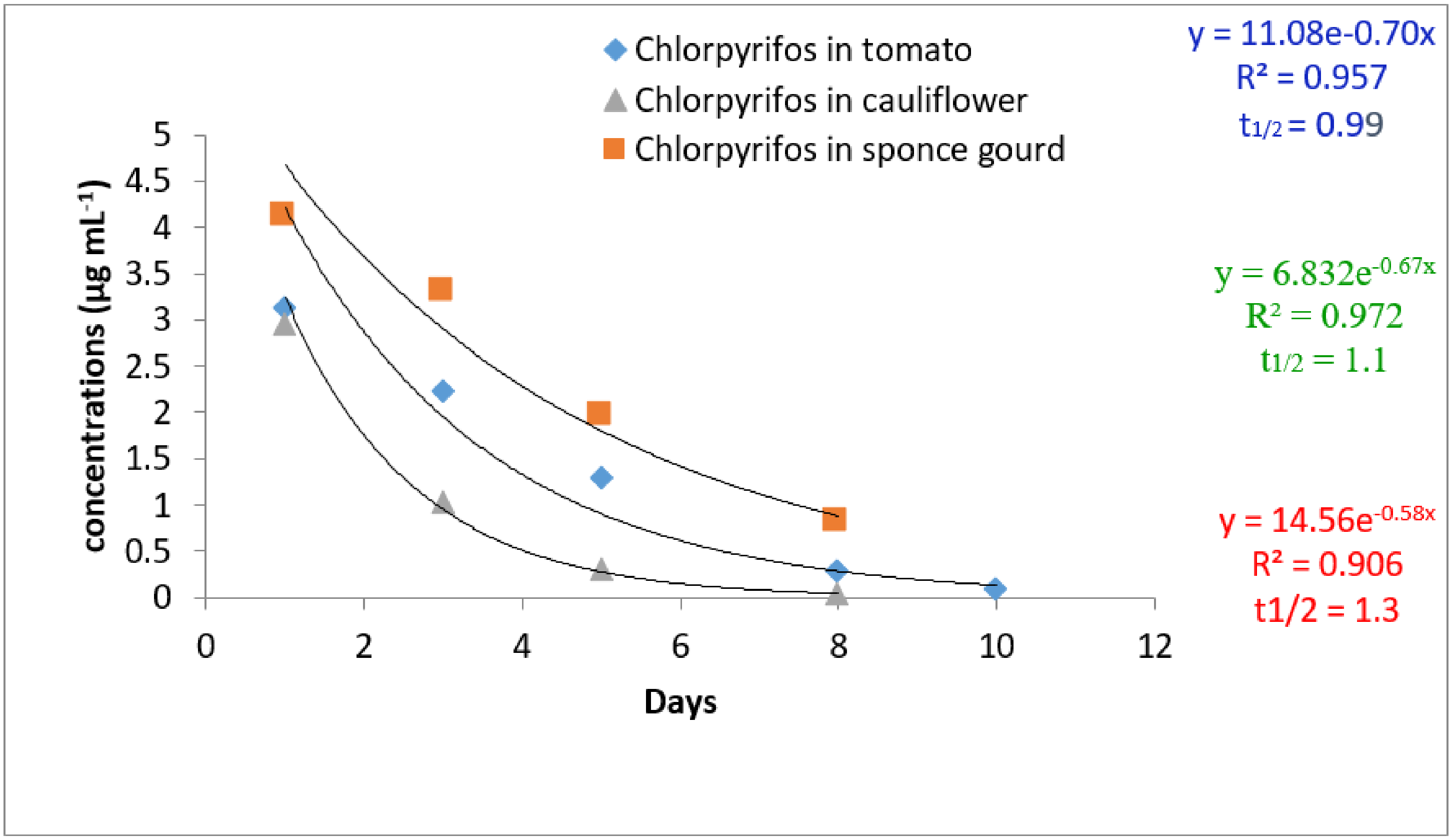

Figure 1

Dissipation curve of chlorpyrifos in tomato, cauliflower and sponce gourd

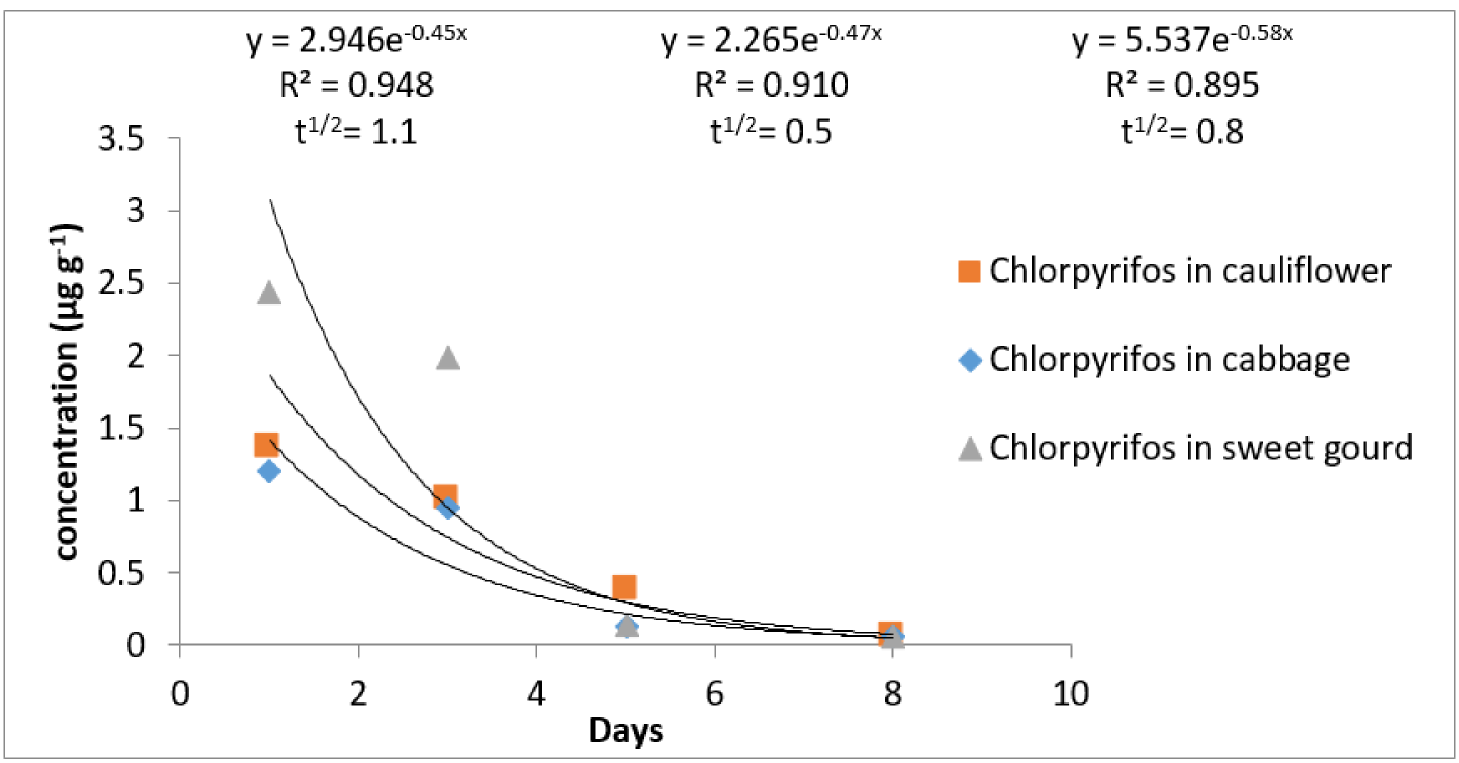

Figure 2

Dissipation curve of chlorpyrifos in cauliflower, cabbage and sweet gourd as the constituent of Nitro 505 EC

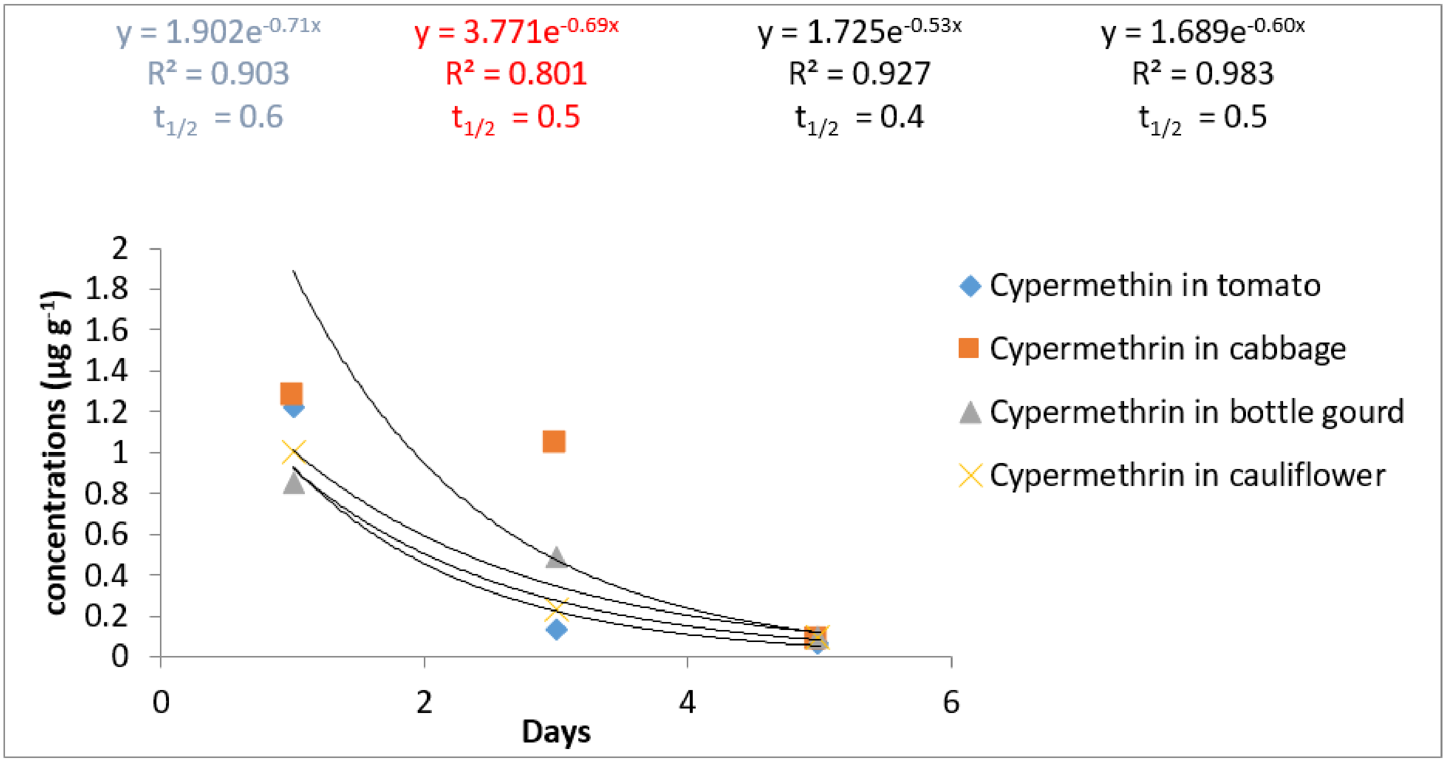

Figure 3

Dissipation curve of cypermethrin in tomato, cabbage, bottle gourd and cauliflower as a constituent of Nitro 505 EC

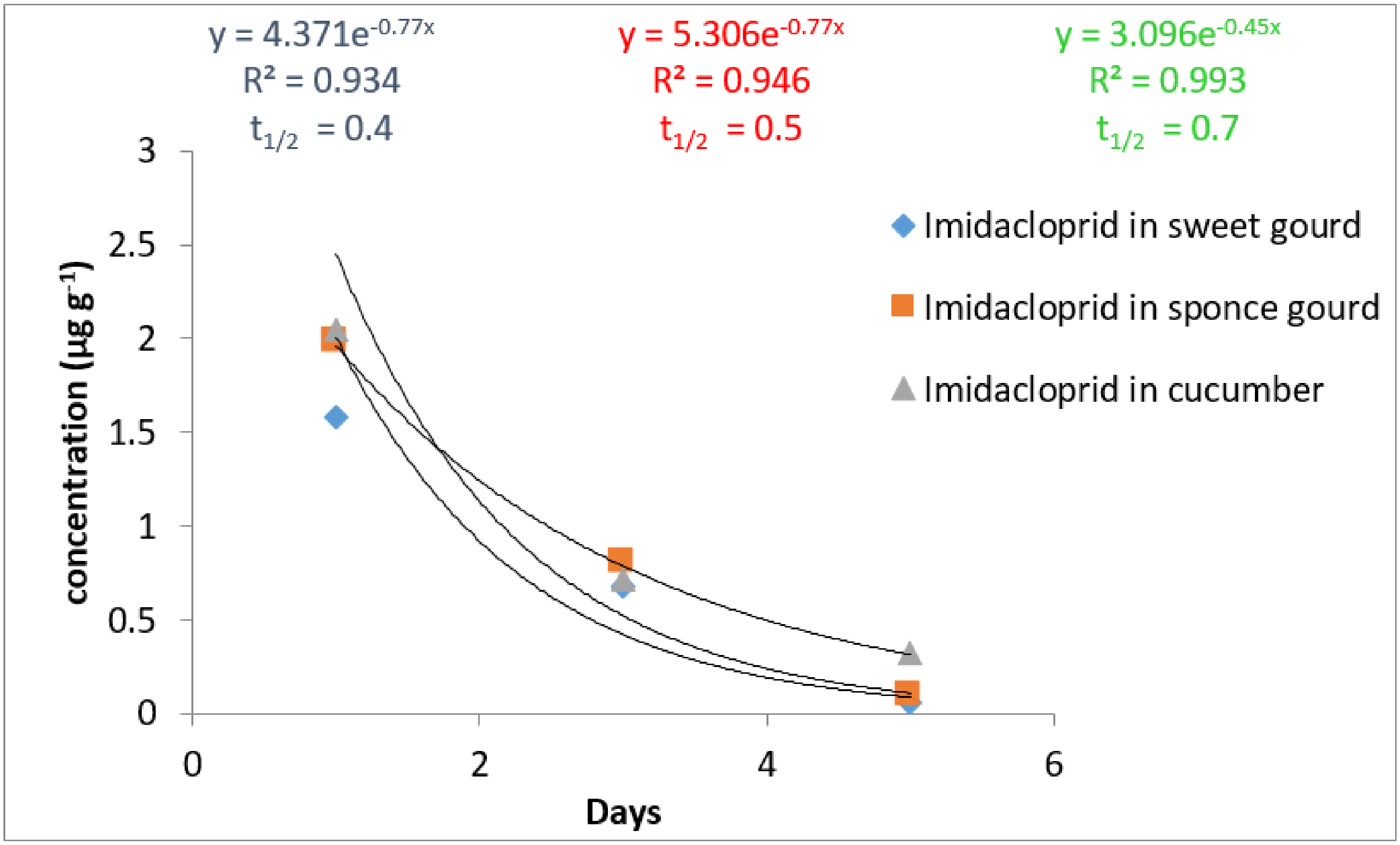

Figure 4

Dissipation curve of imidacloprid in sweet gourd, sponce gourd and cucumber as a constituent of Double 50 EC

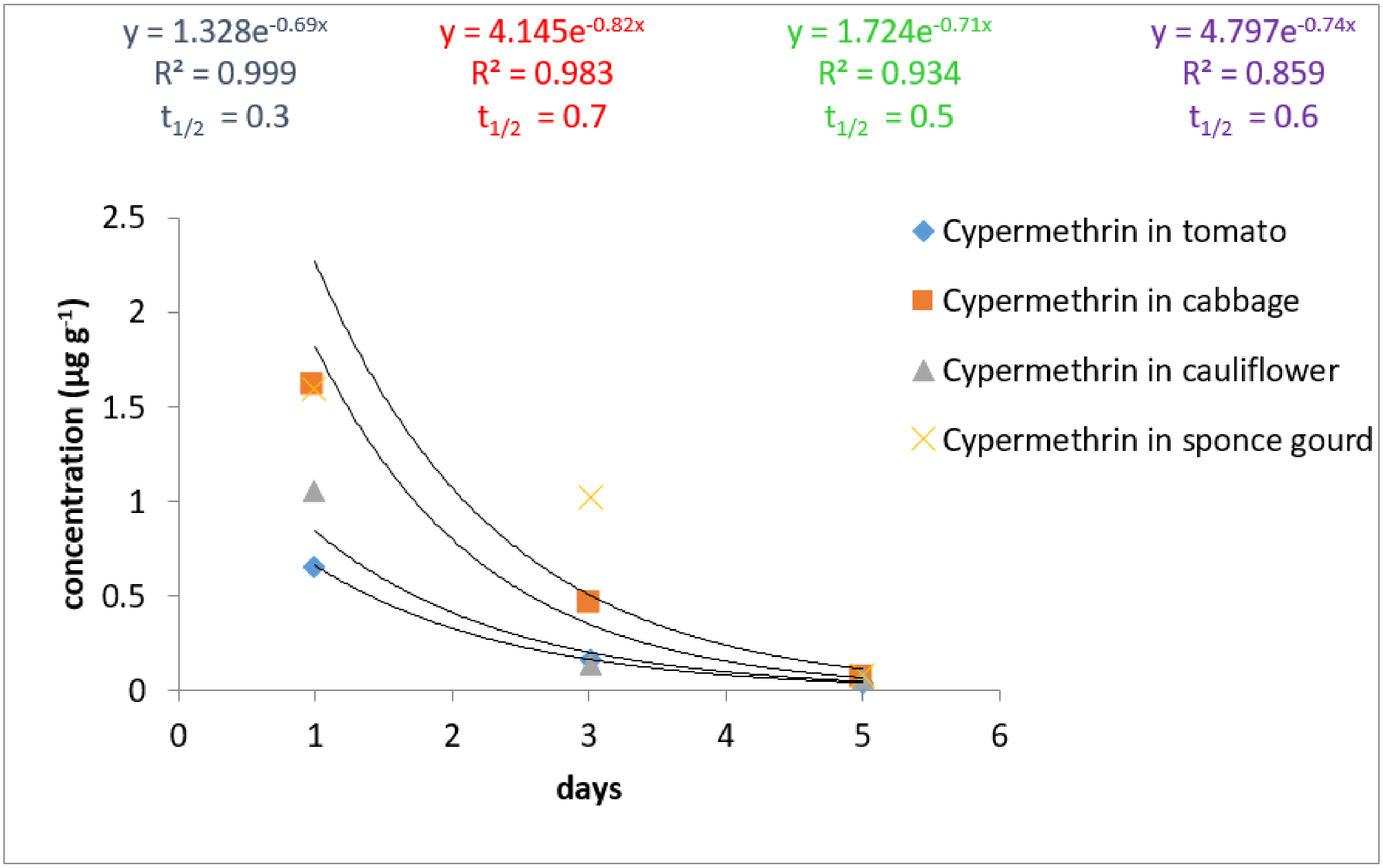

Figure 5

Dissipation curve of cypermethrin in tomato, cabbage, cauliflower and sponce gourd as a contituent of Double 50 EC

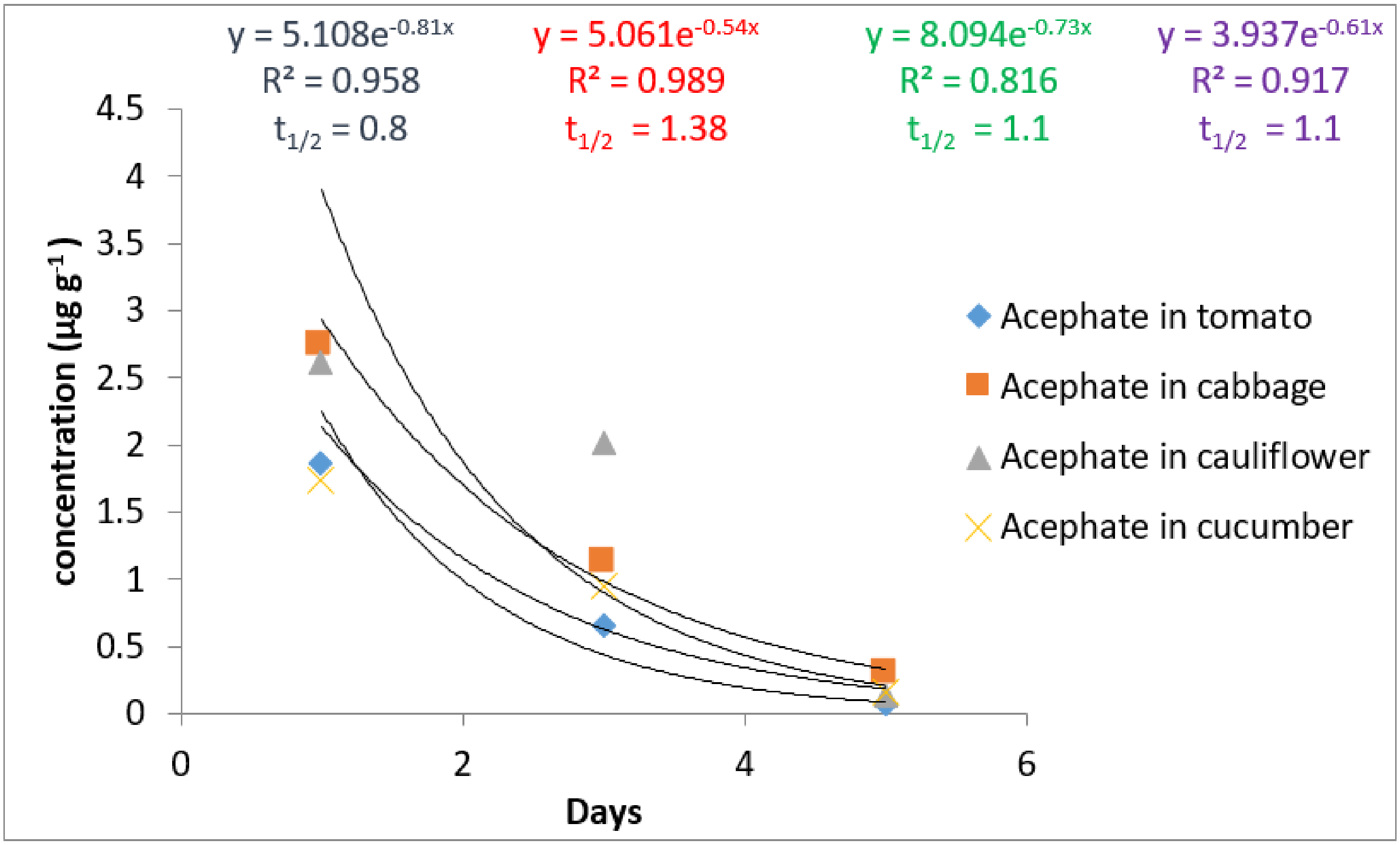

Figure 6

Dissipation curve of acephate in tomato, cabbage, cauliflower and bottle gourd in Asataf 75 SP

Supplementary Files

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