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Behavior of Some Pesticide residues in and on Tomato and Kidney Beans Fruits Grown in Open Field

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Abstract: The residual behavior of Thiamethoxam (Actara 25% W.G) Oxycarboxin (Plantfax 20% E.C), Chlorothalonil (Chlorothate 75% W.P) and Bifenazate (Acramite 48% S.C), in Kidney bean and Tomato fruits under the environmental condition of Egypt was studied. The tested pesticides were sprayed at recommended dose of 80g / fed., 100 cm^3/100 L of water, 250 g/100 L of water and, 35cm^3/100 of water for actara, plantfax, Chlorothate and Acramite respectively on Kidney bean and Tomato plants. The treated kidney bean and tomato were randomly sampled in triplicates after one hour, 1, 3,7,10 and 15 days period after pesticides application. Samples were extracted, clean up and analyzed using HPLC and GC/ ECD. The half - life values were calculated to be 4.14, 1.09, 0.84 and 2.63 days for Actara, Plantfax, Chlorothate and Acramite respectively. The pre - harvest interval (PHI) was determined to be 1, 3,7,10 and 15 days for kidney bean with actara and plantfax and tomato with chlorothate and acramite under prevailed local field conditions respectively. Results showed that waiting for the recommended pre - harvest intervals, indicated on the prospectuses of both pesticides, lowered the residue levels to within acceptable limits.

Key words: Actara · Plantfax · Chlorothate · Acramite · Pesticide residues · Kidney bean · Tomato

INTRODUCTION

The use of pesticides in agriculture is necessary to combat a variety of pests that could destroy crops and to improve the quality of the food produced. Agricultural use of pesticides plays a beneficial role in providing a plentiful, low- cost supply of high quality fruits and vegetables. On the other hand, as a consequence of this use, the presence of residues in food that was critical elements of overall population health is unavoidable and pesticide residues in food is of great importance in the evaluation of food quality [1]. Governments and international organizations are regulating the use of pesticides and are setting the acceptable MRL_S. When these compounds are applied according to good agricultural practices, MRL_S are not exceeded, but there in correct application may leave harmful residues, which involve possible health risk and environmental pollution. Teratogenic, carcinogenic and toxic properties of these compounds have been reported by Bernard and Gordon [2]. Tomato (*Lycopersicon esculentum* Mill.) belongs to the solanaceae family and is one of the most widely grown vegetables in the world [3]. Tomato is one of the basic component of the Mediterranean and Asian diet and is used almost daily in several countries, raw, home - cooked or processed as a canned product, Juice or paste and pesticides are widely used in tomato because its susceptibility to insect and disease attacks [4, 5]. Kidney bean *Phaseolus vulgaris* L. was originally a crop of the new world, but is now grown extensively in all major continental areas [6]. The diversity of conditions under which beans are grown, coupled with highly- specific local preferences for particular seed types or colors have complicated attempts at bean improvement. As a result, the greatest progress has been in breeding for the resolution of disease, insect and nutritional constraints, with only limited. If any improvement in yield potential. For earlier reviews that treat this important grain legume from a number of different perspectives [7, 8]. Tomatoes and kidney bean plant were liable to be infested with different insect pests. The control of these pests is considered an integral part of any strategy insecticides, however, still used in a large scale throughout the world, especially in the developing countries, as a major mean for pest management [9]. Residual pesticides on food materials decreased by various culinary applications or

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with time, depending on the type and properties of the pesticides. Several investigators have found by the pre harvest intervals [10-13].

This Study Aimed To:

- The behavior of (actara and plantphax) on kidney bean and chlorothate and acramite) in and on tomato fruits grown in open field.
- Determine the dissipation rate, half-life values (RL_{50}) and pre-harvest interval (PHI) for the Tested pesticide.

MATERIALS AND METHODS

Field Applications: Kidney bean and tomato were planted at Kaha, Qalubia, Governorate Egypt on 20th 28thJanuary 2011 in plots of 1/100 feddan (one feddan = 4200 m^2) each respectively. The treatment was performed 2nd April. Untreated plots were left as control check. A knapsack hand sprayer fitted with one nozzle boom was used.

Sample Collection: Three replicates samples of Treated and untreated samples of kidney bean and Tomato were randomly packed up one hour after treatments and then 1, 3, 7, 10 and 15days after pesticides spraying for residue analysis. Samples were transported to the laboratory immediately after collected (kept in an ice box). Sub-sampling was carried out in the laboratory and three replicates sub-samples were taken from fruits, which weighed (50 g). Samples were kept in polyethylene pages in a deep freezer at -20°C till residue analysis.

Pesticides Used: Four (4) crop protection products were included in the analysis and were categorized:

- Thiamethoxam (Actara 25% WG) is an insecticides use against *Aphis* (Fig. 1). It was used at the rate of 80g/fed. It is an insecticide with contact, stomach and systemic activity, [14].
- Oxycarboxin (plantfax 20% EC) is fungicides against Rust (Uromces appendiculatus) in kidney bean (Fig. 2).
- Chlorothalonil (chlorothate 75 % WP) is fungicides against Late bight (*Phytophthora infestans*) in tomato. It was used at the rate of 250g/100 L of water (Fig. 3).
- Bifenazate (Acramite 48 % SC) has been used in agriculture as acaricides against *red spider*. It was used at the rate of 35cm^3/ 100L of water (Fig. 4).

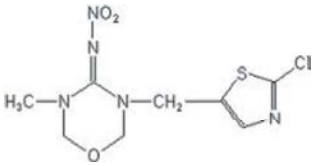

Fig. 1: Thiamethoxam (3-(2- chloro-1,3- thiazol-5-yl methyl) -1,3,5- oxadiazinan -4-ylidene(nitro)amine

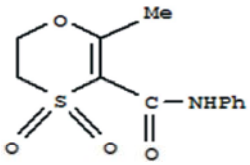

Fig. 2: Oxycarboxin (1,4-Oxathiin-3-carboxamide,5,6-dihydro-2-methyl-N-phenyl-, 4,4-dioxide)

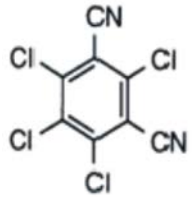

Fig. 3: Chlorothalonil (Tetrachloro isopthalonitrile)

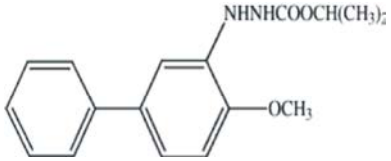

Fig. 4: Bifenazate (isopropyl 3-(-4- methoxy biphenyl-3-yl) carcazate

Residue Analysis Technique

Thiamethoxam (Actara 25% WG): The extraction technique mentioned by Mollhoff [15] was adopted to use methanol instead of acetone as a solvent for extraction Kidney bean (50-100 g) were placed in the blende cup. A constant volume of distilled methanol (150 ml) was used for extraction of the sample which was blended for three minute at high speed and filtered through dry cotton into graduated cylinder. A known volume of the extracts was taken and shaken successfully with 50, 30 and 20 ml of methylene chloride in separator funnel. The combine methylene chloride phases were dried by filtration through anhydrous sodium sulfate. Then the residue was dissolved in 5ml methanol and cleaned up using the coagulating solution [16]. The coagulating solution was prepared as followed (0.5 g of ammonium chloride was dissolved in 400 ml of distilled water and 1 ml of orthophosphoric acid 85% was added and shacked well).

The extracts were dissolved in 5 ml of methanol and thoroughly mixed with 10 ml of freshly prepared coagulation solution. The content was filtered under vacuum through a 5 mm layer of hyflo-super cell, prepared in a 2.5 cm i.d. glass column on a plug of glass wool. Then taken to dryness on a rotary evaporator at 40°C. The residue was dissolved in known volume of ethyl acetate for GLC analysis.

Oxycarboxin (Plantfax 20% EC) and Chlorothalonil (Chlorothate 75 % WP): The extraction and cleaning up of plantfax residue from kidney bean and Chlorothate from tomato fruits were carried out according to Mills *et al.* [17]. Exactly 50g of chopped samples were weighed into a 250 ml flask and 200 ml of ethyl acetate was added and 50 gram anhydrous sodium sulfate. The mixture was blended for three minute at high speed and filtered through dry cotton into graduated cylinder. A known volume of the extracts was taken to clean up by use florisel column using the (50 % methelene chloride + 1.5% acetointrile + 48.5% hexane). This elute was evaporated to dryness on rotary evaporator at 30°C and the residue dissolved in 1ml methanol.

Bifenazate (Acramite 48 % SC): Pesticide screening, 10 - 20 grams of homogenized sample of tomato is extracted with 15 ml acetonitrile. The mixture was blended and then placed in freezer, followed by the addition of four grams of magnesium sulfate and one gram of sodium chloride which was blended for three minute at high speed and centrifuged for 3 minutes at 4000 rpm / minute at 4°C then filtered through dry cotton into graduated cylinder. A known volume of the extracts was taken and is transferred to a 2 ml mini-centrifuge vial containing 25 mg of PSA and 150 mg of magnesium sulfate and centrifugation for five minute. The extract is syringe-filtered using a 0.25 µm filter into 2 ml autosampler vials for analysis by high performance liquid chromatograph [18].

Calculation of the Residues: The residues were calculated by applying the following equation:

Ps BV/ Pst G C x F

F = 100/R (recovery factor)
Pst = Standard peak area.
R = Average of recovery.
V = Final volume of sample solution (ml).
Ps = Sample peak area.
B = Amount of standard injected (ng).
G = Sample weight
C = Amount of sample solution injected (µl).

Instrumental Conditions: Samples of (Thiamethoxam and chlorothalonil) were analyzed by using an Agilent 6890 HP gas chromatograph equipped with an ECD, Programmed for external standardization using peak area. The column was PAS-5, 25mx0.32mmi.d.x0.25 um film thickness and injection port temperature was 280°C. The column temperature was as fallow:

Initial temperature 200°C
Initial time 2min.
Rise: 5°C/min.
Hold for 10 min
The flow of carrier gas was applied as 3 ml / min.

The residue of actara and chlorothate were quantitatively determined by comparison with standard solution of both pesticides injected under identical GLC condition.

Plantfax and acramite were analyzed by Agilent HPLC (1100) was equipped with a diodarry detector (Table 1).

Recovery Efficiency Studies: The reliability of the analytical methods was tested by fortifying the untreated samples with known quantities of the investigated pesticides, actara and plantphax, chlorothate and acramite at 0.1 ppm levels, followed by the same procedures of extraction, clean up and quantitation. The average rates of recovery of, actara and plantphax were 90 and 80% on kidney bean. While the average rates of recovery of chlorothite and acramite pesticides were 70 and 87.8% respectively, on tomato fruits.

RESULTS AND DISCUSSION

Residue of Thiamethoxam: Results in Table 2 showed that the concentration of initial deposits of Thiamethoxam in kidney bean were 0.29 ppm, then gradually decreased to 0.21 ppm one day of application revealing 27.58 % loss. This value decline to 0.15, 0.08, 0.02 and 0.01 ppm recording the rate loss 48.27, 72.41, 93.10 and 96.55% at 3, 7, 10 and 15 days after treatment respectively the calculated half-life values (RL_{50}) of Thiamethoxam were 4.14 days. The data show that kidney bean could be safely consumed after 7 days of application according to the recommended maximum residue limit (MRL) for Thiamethoxam in kidney bean (0.2 ppm).These results are in agreement with those obtained by Precheur *et al.* [19] and Alaa *et al.* [20].

Table 1: The conditions

Parameters	Oxycarboxin (Plantfax)	Bifenzate (Acramite)
Column	ODS C 18 Hypersil column (150 mm x 4.6 mm x 5 um).	C18 Nuclosil column (250mm x 4.6 mm x 5 um).
Mobile phase	Acetontril 70% + water 30%	Acetontril 65% + water 35%
Flow rate	0.8ml/min.	1ml/min
Wave length	205nm	230nm

Table 2: Behavior of actara and plantfax in kidney bean

	Actara			Plantfax		
Time after treatment (days)	Residues (ppm)	% Loss	% Persistence	Residues (ppm)	% Loss	% Persistence
* initial	0.29	0.00	100.00	3.78	0.00	100.00
1	0.21	27.58	72.42	2.06	45.50	54.50
3	0.15	48.27	51.73	0.47	87.56	12.44
7	0.08	72.41	27.59	0.05	98.67	1.33
10	0.02	93.10	6.90	0.02	99.47	0.53
15	0.01	96.55	3.45	0.01	99.73	0.27
RL_{50} (days)		4.14			1.09	

* Samples were taken one hour after application
MRL: 0.2 ppm [21] for actara
: 0.1 ppm [22] for plantfax
LOD: 0.01

Table 3: Behavior of acramite and chlorothate in Tomato

	Acramite			Chlorothate		
Time after treatment (days)	Residues (ppm)	% Loss	% Persistence	Residues (ppm)	% Loss	% Persistence
* initial	4.06	0.00	100	3.71	0.00	100
1	3.64	10.34	89.56	1.49	59.83	40.16
3	1.74	57.14	42.86	1.30	64.96	35.04
7	0.85	79.06	20.94	0.91	75.47	24.53
10	0.41	89.90	10.10	0.79	78.71	21.29
15	0.06	98.52	1.48	0.09	97.57	2.43
RL_{50} (days)		2.63			0.84	

* Samples were taken one hour after application
MRL: 0.5 ppm [25] for acramite
LOD: 0.01for acramite
MRL: 2 ppm [21] for chlorothate
LOD: 0.02

Residue of Oxycarboxin: The results in Table 2 also indicated the residues of Oxycarboxin in kidney bean. The initial deposits found after one hour was 3.78 ppm. The residue levels were decreased to 2.06, 0.47, 0.05, 0.02 and 0.01ppm showing the percentage loss, 45.50, 87.56, 98.67, 99.47 and 99.73 % after 1, 3, 7, 10 and 15 days respectively. The estimated half-life value (RL50) for Oxycarboxin on kidney bean 1.09 day. The maximum residue limits (MRL) for Oxycarboxin on kidney bean was 0.1 ppm. Data indicated that kidney bean could be consumed safely after 15 days.

Residues of Bifenazate: Data in Table 3 also showed the residues of Bifenazate in tomato. The initial deposit of Bifenazate was 4.06 ppm one hour after application then decreased to 3.64, 1.74, 0.85, 0.41 and 0.06 ppm indicated the rate loss were 10.34, 57.14, 79.06, 89.90 and 98.52% after 1, 3, 7, 10 and 15 days, respectively, these results are in agreement with Scholz and Reinhard [23] who found that imidachloprid on tomato leaf surface is rapidly degraded under field conditions. The half life value of Bifenazate was 2.63 days. The data indicated that tomato could be consumed a safely after 3 days after application, where (MRL) of Bifenazate residue in tomato was 0.5 ppm The present results indicated that: Bifenazate was found to be more persistent on tomato compared with the other two tested pesticides; data also reported that the lowest residue level 0.06 ppm in tomato was detected after 15 days of Bifenazate application. While the lowest residue of other pesticides was 0.01 ppm at the same time. These results are in agreement with Gambacorta *et al.* [24].

Residues of Chlorothate: The results presented in Table 3 indicated the residues of Chlorothate in tomato. The initial deposits found after one hour was 3.71 ppm. The residue levels were decreased to 1.49, 1.30, 0.91, 0.79 and 0.09 ppm showing the percentage loss 59.83, 64.96, 75.47, 78.71 and 97.57 % after 1, 3, 7, 10 and 15 days respectively. The estimated half-life value (RL50) for Chlorothate on tomato 0.84 day. Maximum residue limits (MRL) for Chlorothate on tomato was 2 ppm. Data indicated that tomato could be consumed safely after 15 days.

CONCLUSIONS

The MRLS (maximum residue limits) of actara, plantfax, acramite and chlorothate in kidney bean and tomato are 0.2, 0.1, 0.5 and 2 ppm, respectively as stated by the EU [21, 22] and Codex [25]. The results presented herein clearly show that the detected residues of actara, plantfax, acramite and chlorothate after spraying directly were 0.29, 3.78, 4.06 and 3.71, which are above the maximum residue limits from the present investigation it could be concluded that kidney bean and tomato fruits could be used safely for human consumption after 15 days.

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