Residue and Dissipation Dynamics of Abamectin in Tomato Fruit Using QuEChERS Methodology

A. M. Abdellseid and Tarek .A. Abdel.Rahman

***Abstract*—** An effective analytical method for the residue analysis of a novel acaricides abamectin and its dissipation in tomato were studied. Abamectin residues were extracted from tomato samples and the extract was cleaned up according to QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method and determined by high-performance liquid chromatography with photo diode array detector (HPLC–DAD). At fortification levels of 0.1, 0.5, and 1.0 mg/ kg in tomato, it was shown that recoveries ranged from 89.4 % to 95.6 %. The limit of detection (LOD) and limit of quantification (LOQ) were found to be 0.02 and 0.01 mg/ kg, respectively. The dissipation half-life time of abamectin residues in tomato was 2.4 days. According to maximum residue limit (MRL) 0.5 mg /kg, the pre harvest interval (PHI) of abamectin on tomato was 8 days after the treatment. Based on the results of this study and the relevant residue regulation, abamectin residue levels will be acceptable when applied to tomato in Libya.

***Keywords*—** Abamectin, Residue, Tomato Fruit, QuEChERS and Libya.

I. Introduction

ABAMECTIN belongs to the family avermectins which are macrocyclic lactones produced by the *actinomycete Streptomyces avemitilis.* It is a mixture of two homologues containing about 80% avermectin B1a and about 20% avermectin B1b (1). Abamectin acts by stimulating the release of c-amino butyric acid thus causing paralysis .It is used to control motile stages of mites and some other insects on fruits and vegetables and has limited plant systemic activity. Flufenoxuron is a benzoylurea pesticide and acts as an insect growth regulator and chitin synthesis inhibitor. It is used to control immature stages of insects and phytophagous mites on fruits and vegetables (2). Governments and international organizations are regulating the use of pesticides and are setting the acceptable MRL When these compounds are applied according to good agricultural practices, MRL 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 (3). Tomato (Lycopersicon esculentum Mill.) belongs to the solanaceae family and is one of the most widely grown vegetables in the world [4]. 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 a pesticides are widely used in tomato because its susceptibility to insect and disease attacks [5].

This Study Aimed To:

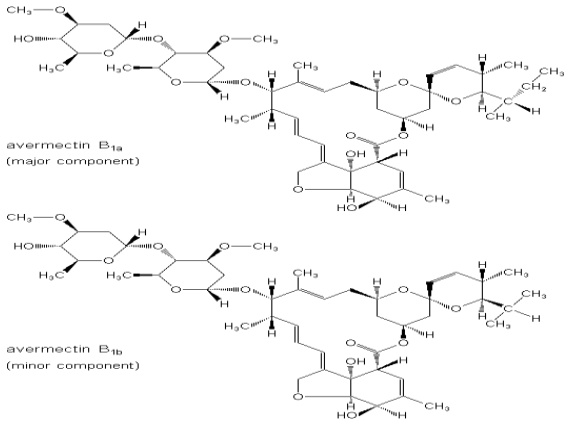
-The behavior of abamectin in and on tomato fruits grown in open field.

-Determine the dissipation rate, half-life values (RL50) and pre-harvest interval (PHI) for the abamectin.

Materials and methods

Vertimic 1.8% EC (abamectin), Abamectin analytical reference recently applied this technique for the residue standards was purchased from Dr Ehrenstorfer.

STRUCTURE



All organic solvents were of HPLC grade and supplied by Merck, USA. Primary and secondary amine (PSA, 40 lm Bondesil) was purchased from Supelco (Supelco, Bellefonte, USA). Anhydrous magnesium sulfate was of analytical grade, purchased from Merck, USA, and was activated by heating at 250_C for 4 h in the oven before use and kept in desiccators. A stock standard solution (100 lg ml-1) was prepared with methanol and stored at -20_C. The standard working solutions were prepared from stock solution by serial dilution

A. M. Abdellseid, Dept. Plant Production, Fac. Agric Benghazi Univ. LIBYA.

Tarek .A. Abdel.Rahman, Central Agricultural Pesticides Laboratory, Agricultural Research Center ARC, Dokki, Giza, Egypt..

with methanol at 0.01, 0.05, 0.1, 0.2, 0.5, 1.0 and 2.0 lg ml-1 and were stored at 4_C before use. The field experiment was conducted on tomato in private farm, El-Beida city, Libya. Treatment was carried out by knapsack sprayer equipped with one nozzle. The commercial formulation Vertimic 1.8% EC at the recommended rate of application, i.e., 40 cm 100 L-1 was used. Three randomized plots were treated by abamectin, and one untreated plot was left to serve as control. Sampling was performed by random collection from various places of the experimental plots according to the (FAO/WHO 1999) recommendations. Samples of tomato with similar ripening stage, size, and shape were located and tagged. Samples about 1.0 kg were taken 2 h after the pesticide application. Subsequent samples were taken 0, 3, 6, 10, 14, and 21 days after treatment. During the experiment, a control sample was taken in each sampling time. Immediately after collecting the samples, all the samples were packed in polyethylene bags and transported to the laboratory in an ice box. The samples were homogenized using a food processor (Thermomix Vorwerk). The homogenate of each sample was done where three representative samples of 15 g were taken. Samples were then placed into polyethylene 50-ml centrifuge tube and frozen at -20 °C until the time of analysis. The samples were comminuted using the laboratory blender and representative homogenized (15 g) of each was then placed into 50 mL polyethylene tube. Samples were extracted and cleaned up immediately after sampling using QuEChERS methodology (6) .15 mL of acetonitrile was added into each tube. The samples were well shaken using a vortex mixer at maximum speed. Afterwards, 6 g of anhydrous magnesium sulfate and 1.5 g of sodium chloride were added, then extract by shaking vigorously on vortex for 5 min and centrifuged for 10 min at 4,000 rpm. An aliquot of 4 mL was transferred from the supernatant to a new clean 15 mL centrifuge tube containing 100 mg PSA and 600 mg anhydrous magnesium sulfate. The samples were again vortexed for 3 min and then centrifuged for 10 min at 4,000 rpm. An aliquot of 2 mL was concentrated to dryness. The residue was redissolved in 2 mL of acetonitrile for analysis by HPLC. HPLC analysis was performed with an Agilent 1100 HPLC system (USA), with photodiode array detector. The chromatographic column was C8 Zorbax SB (250 9 4.6 mm, 5 lm film thickness). Flow rate of mobile phase (acetonitrile /Methanol/water = 45/ 40/15 v/v/v) was 1.5 mL/min. and injection volume was 20 L. Detection wave length for detection of abamectin was set at 245 nm. The retention time of abamectin avermectin B1a and about avermectin B1b (was about 8.5 and 11.26 min. Recovery studies were carried out by spiking 3 replicates of untreated date samples (control) with 50, 100, and 50 mg/kg of abamectin. Samples were analyzed using their prescribed procedure and mean values of the three replicates were calculated. Recovery percentages were satisfactory for the abamectin and ranged from 89.4 % to 95.6 % .The minimum detection limit of abamectin was 0.005mg/kg.

The rate of degradation (K) and half-life (t1/2) values were obtained from the following equation of (7).

Rate of degradation (K) =2.303 X slope

Half _ life (t1/2) =0.693/(K)

Data were statistically evaluated by one-way analysis of variance (ANOVA). All statistical analysis was done using the statistical package for social sciences (SPSS 16.0) program.

II. Results and discussion

The dissipation trends of abamectin in tomato fruit were shown in Table I. Abamectin dissipated rapidly after application. The concentration of abamectin 1 h after treatment was 8.006 mg/kg. The residues amount decreased to 6.203 mg/kg, in tomato fruit within the first 24 h after application. Following that period, abamectin residues in/on tomato fruit decreased to 2.106, 1.15, 0.64, 0.333 and 0.05 mg/kg, at 3, 5,7, 10,12 and 15 days after treatment, respectively. Samples taken 21 days after treatment contained no detectable amount of abamectin (below the quantification limit 0.01 mg/ kg) in tomato fruit. The dissipation rate of tomato fruit exhibited a first order kinetics. The half-life of abamectin calculated in tomato fruit treated at recommended dose was 2.4 days (Table I). The dissipation of the pesticide residues in/on crops depends on environmental condition, type of application, plant species, dosage, and interval between application, the relation between the treated surface and its weight and living state of the plant surface, in addition to harvest time (8). European Union MRL for abamectin in tomato is 0.5 mg/kg. It can thus be concluded that the preharvest interval (PHI) of abamectin on tomato was 8-days after the last treatment.

Our finding agree with (9-11), The residual levels of AVMs in paprika in a field experiment from one day to seven days after the last application decreased from 18.40 to 7.59 µg/kg. The half-life (T1/2) of AVMs in paprika was 1.47 days (9). Degradation of abamectin on date palms, grown in Saudi Arabia was studied during the post-harvest interval (PHI) under the local weather and soil conditions. The initial deposit of abamectin residues on dates was 0.09 mg/kg, which declined to 0.03 (66%) and 0.02 mg/kg (88%) after 7 and 14 days of spraying, respectively (PHI = 10 days, MRL = 0.03 mg/kg) (10). (11) Determined the pesticides residues in tomato and cucumber fruits harvest at two hours 1,3, 7, 14 and 28 days after phytosanitary treatment. The determination of residues was carried out by HPLC for Abamectin. The residue levels detected .The residue level for Abamectin in tomato was 0.12ppm, 0.09ppm for cucumber. But these levels fell to 0.14, 0.03ppm after 28 days of the application. The calculated half –life time was 6.6 days.

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TABLE I
DISSIPATION OF ABAMECTIN RESIDUES (MG KG−1 ± SD) IN/ON TOMATO FRUIT

Time (days)	Residue level (mean ± SD)	% Dissipation
Zero time	(8.006± 0.756)	00
One day	(6.203± 0.265)	22.52
3days	(2.106± 0.552)	73.69
5days	(1.15± 0.180)	85.63
7days	(0.64± 0.104)	92
10days	(0.333± 0.105)	95.84
15days	(0.05± 0. 0439)	99.37
21 days	N.D	
MRL	0.5	
T 0.5	2.4	
PHI	8	