Egypt. J. Chem. **Vol. 66,** No. SI 13 pp. 1977 - 1986 (2023)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Dissipation Behavior and Dietary Risk Assessment of Abamectin, Pyraclostrobin and Boscalid in Apple Fruit

Fayza A. Sdeek[a], Ayman S. O. Seloma [b]*, Ismail I. Ismail[b], Mahmoud M. Ramadan[c], Abdelhadi A. I. Ali[c]

[a]*Pesticides Residues &Environmental pollution Dept, Central Agricultural Pesticides Laboratory, Agricultural Research Center (ARC), Dokki, Giza, Egypt*

[b]**Pesticides Analysis Researches Department, Central Agricultural Pesticides Laboratory, Agricultural Research Center (ARC), Dokki, Giza, Egypt.*

[c] *Plant Protection Department, Faculty of Agriculture, Zagazig University, Egypt.*

Abstract

Compliance with application instructions and safety precautions significantly reduces pesticide residues that may have adverse effects. Field trials were thus carried out to determine the degradation of Agromec® 1.8% EC (abamectin 1.8% (w/v)) and Shooter® 30% SC (pyraclostrobin 20% + boscalid 10% (w/w)) in/on apple fruits. Before starting Field trials, the tested pesticide formulations were subjected to analysis before and after accelerated storage at 54 ±2 °C for 14 days; the active ingredient content, emulsion stability, and suspensibility were found to comply with the chemical and physical specifications. The pesticides were applied to the treated apple trees using a knapsack sprayer at the recommended rates. The QuEChERS method was used for sample extraction and cleaning. HPLC-UV was used to determine residue amounts up to 15 days after application. The mean recovery percentages for abamectin, pyraclostrobin, and boscalid were 82.27, 88, and 101%, respectively. Furthermore**,** the methods' coefficient variation obtained was 1.71- 2.48%. At the same time, the LOQ values for abamectin, pyraclostrobin, and boscalid were 0.1, 0.25, and 0.25 mg/kg, respectively. Abamectin, pyraclostrobin, and boscalid initial deposits on/in apple were 0.955, 2.24, and 3.66 mg/kg, respectively. The degradation rate constants were 0.803, 0.14, and 0.21, respectively, with corresponding half-life times of 0.86, 4.95, and 3.3 days and pre-harvest intervals of 4.32, 10.71, and 2.88 days for abamectin, pyraclostrobin, and boscalid. The potential health risks associated with exposure to the chemicals under investigation were calculated based on the final residue levels and acceptable daily intakes. The hazard quotient values for the pesticides tested ranged from 1.07 to 64.94%.

Keywords: Abamectin, Pyraclostrobin, Boscalid, Residue, Apple, Dissipation, Food safety.

1. Introduction

The apple is a soft, fleshy fruit that has numerous health benefits. It is one of the most valuable commercial fruit crops widely grown **[1].** Apple was consumed fresh or stored after harvest to provide apples for human consumption outside the primary season or during shipment to non-producing countries **[2].** The apple plants were exposed to a range of detrimental agricultural techniques during cultivation, such as the applying chemical fertilizers and pesticides. Excessive use of agrochemicals in apple production pollutes water, soil, and air, endangering the environment **[3].**

Additionally, toxic substances accumulated in food pose a risk to human health. The use of pesticides during apple production to avoid disease or pest infection during the growing season, particularly with pests, targets the apple fruits due to their direct effect on reducing the economic value of the yield **[4].** The pre-harvest applications protect apple fruits during critical periods between the harvesting and controlled atmosphere storage and against common apple storage diseases such as grey mold, storage scab, and bitter rot **[5].** As a result, apple fruits are harvested before the pre-harvest period indicated on the pesticide label to benefit from the presence of pesticide residues. Pesticide residues may persist in storage under controlled conditions and be higher than ADI, rendering apples unfit for human consumption **[6].**

Apples are grown in Egypt, with of these areas being newly reclaimed land **[7].** Many pests infest these monoculture plantations, necessitating the regular application of pest control methods. Therefore, the farmers employ a various control method, ranging from rational control to the use of chemical pesticides **[8].** These agricultural chemicals may be used throughout the production period if there

*Corresponding author e-mail: aymansameih@yahoo.com.; (Ayman S. O. Seloma).

Receive Date: 12 July 2023, Revise Date: 25 August 2023, Accept Date: 03 September 2023

DOI: 10.21608/EJCHEM.2023.222580.8248

is a risk of injury or recurrence **[9].** Abamectin is an avermectin group and a well-known biopesticide potent as an insecticide, acaricide and nematicide **[10].** On apple, abamectin proved to have a limited translaminar activity **[11]**. Boscalid is a pyridine carboxamide fungicide with preventive, translaminar, and systemic properties **[12]**. In 2007, boscalid was introduced in combination with the strobilurin fungicide pyraclostrobin. Pyraclostrobin is a strobilurin group. This premix product protects against Alternaria late blight, downy mildew **[13]**, and apple scab **(Venturia inaequalis).** Pyraclostrobin is a strobilurin group, while boscalid is a pyridine carboxamide fungicide. Both fungicides have a preventative mode of action by inhibiting mitochondrial respiration, but with different mechanisms **[13-14].**

Despite the vast quantities of pesticides on the crops, just about 0.1 percent of pesticides reach the target organisms, while the rest contaminate the ecosystem and human health **[15].** Besides, pesticide resistance development in target organisms **[16-17].** These repeated applications of chemical pesticides result in pollution of the environment, along with chemical pesticides residues on the edible portion of the fruits, even following the instructions indicated on the pesticide package label **[18].** As a result, testing residual pesticide levels in raw farm crops is at the top of the public health safety precautions list. Furthermore, the pre-harvest period (PHI) is required by the maximum residue limits (MRL) regulations to ensure that a pesticide dissipates below the proposed MRL at harvest time **[19].** To ensure food safety while safeguarding the environment, field dissipation research on pesticide persistence in foodstuffs and pesticide residue activities in agricultural fields is essential **[20].**

The current study established and validated an HPLC-UV method for simultaneously determining apples' three pesticides (abamectin, pyraclostrobin, and boscalid). Three pesticides' deposition and dissipation in apples were investigated. Furthermore, the dietary risk from apple pesticide residues was assessed using consumption, acceptable daily intake (ADI), and ultimate residues.

2. Experimental:

Chemical used:

The insecticide Abamectin (Agromec® 1.8% EC), produced by Advanced Agrochemicals & Veterinary Products Industrial Company (Chemvet)-Jordan, was purchased from Suez Canal Company for Agricultural Trade and Development (UNCTAD). The fungicide premix, Shooter® 30% SC (pyraclostrobin 20% + boscalid 10%), production BeijiangYulu Biotechnology Group Limited - China. supplied by Star Chem, LLC., Chemicals. The certified reference standard for the tested pesticides obtained from Dr. Ehrensdorfer (Augsburg, Germany) was> 98% purities.

Other chemicals and reagents of analytical grade were used, such as acetonitrile HPLC grade quality, anhydrous magnesium sulfate ($MgSO_4$), formic acid, trisodium citrate dihydrate and disodium citrate sesquihydrate were purchased from (Merck, Darmstadt, Germany); Before use, the anhydrous magnesium sulfate was activated by heating it at 400°C for four hours in a muffle furnace, then cooling it and storing it in desiccators.

Sodium chloride analytical grade (was obtained from El-Nasr Pharmaceutical Chemicals Co., Abu Zaabal, Cairo, Egypt). While, primary, secondary amine (PSA, 40 μmBondesil), was purchased from Agilent Technologies (Santa Clara Co., USA). A Millipore system prepared ultra-pure water.

Analytical methods

a-Confirmation of the tested pesticide formulations complies with the specifications:

Accelerated storage procedures

Agromec® 1.8% EC and Shooter® 30% SC were placed in bottles (about 50 ml). Cap the bottles and transfer them to the oven for 14 days at 54 ±2 ºC. At the end of the time, remove the bottle from the oven, remove the cap, and allow the bottles and contents to cool naturally to room temperature, replacing the cap when cool. The samples will be prepared for injection on the HPLC **[21].**

Standard Preparation

Weight 10 mg of abamectin, pyraclostrobin, and boscalid analytical standard into a 25 ml volumetric flask then dissolve it and complete to the final volume with acetonitrile.

Sample Preparation

Accurately weight sufficient formulations samples of abamectin 1.8%, pyraclostrobin 10%, and boscalid 20% to equivalent 10 mg of abamectin, pyraclostrobin, and boscalid analytical standard into a 25 ml volumetric flask mix slowly with acetonitrile and complete the volume, and then it will be determined using HPLC.

Emulsion stability

Five ml of Agromec® 1.8% EC is mixed with CIPAC standard water D (prepared according to CIPAC MT 18.1 (1995)) to give 100 ml of the aqueous emulsion. The stability of this emulsion is then assessed in terms of the amounts of free oil or cream that separates while the emulsion is allowed to stand undisturbed for 24.5 h. The ability of the system to re-emulsify at the end of the 24.5 h period is also determined **[22].**

Suspensibility

A suspension of Shooter® 30% SC in CIPAC standard water D is prepared, placed in a prescribed measuring cylinder at a constant temperature, and allowed to remain undisturbed for a specified time. The top 9/10ths are drawn off and the remaining 1/10th is then assayed gravimetrically. The methods for suspensibility have been proposed by CIPAC (Collaborative International Pesticides Analytical Council) MT methods **[23].**

Field experiment

The field trials were carried out on 7 year old apple orchard *(Malus domestica)* located at Al EzbetBahariya, Al Wasta Center, Beni Suef Governorate, Egypt. The cultivated area with apples was 0.42 hectares. The experimental area was subdivided into three parts, and two randomized sites were treated with the tested pesticide formulations, while the untreated plot was sprayed with only water as a control. The spraying was carried out on 26th April 2020 using a knapsack sprayer equipped with one nozzle with continuous apple plants receiving routine horticultural practices. During the trial, the average minimum/maximum daily air temperatures were 15/25°C, and the average relative humidity was80.5%. There was no rainfall at any time during the experimental period.

Abamectin was sprayed as Agromec® 1.8% EC at the rate of 50 cm^3/100 l, while premix of pyraclostrobin 10% + boscalid 20% (Shooter® 30% SC) was sprayed at the rate of 40 cm^3/100 l. After spraying, three replicates of representative apple fruit samples were collected randomly from each treatment. The initial apple samples were collected 2 h post-spraying. The subsequent apple samples were collected on days 1, 3, 7, 10 and 15 days before harvest to determine each compound's dissipation rates. The apple samples were collected to a recovery test before pesticide application from the control plot. A represented sample consisting of two kg of fruit was collected periodically in plastic bags and transferred preserved in icebox to the laboratory.

Sample preparation

The received apple samples were blended using a food processor. From the homogenate of each sample, triplicates of 10 g were transferred to a 50 ml centrifuge tube (with screw cap), labeled and stored at -20 °C until the field experiment endpoint period and complete samples collection.

Sample extraction and clean up

The pesticide residues were extracted and cleaned up by the QuEChERS modified method **[24-25].** Ten milliliters of acetonitrile were added to the apple sample (10 g), the screw cap was closed, and the tube was violently agitated for one minute using a vortex. Four grams of anhydrous magnesium sulfate, 1 g sodium chloride, 1 g trisodium citrate dihydrate and 0.5 g disodium citrate sesquihydrate should be added to each tube shortly after the salt. For one minute, the sample was vortexed. The extracts were centrifuged at 3000 rpm and 4 °C for 5 minutes. A 4 ml aliquot of the supernatant was transferred to a new clean 15 ml centrifuge tube containing the dispersive solid-phase extraction chemicals containing 100 mg of PSA and 600 mg of magnesium sulfate. The material was vortexed for 1 minute before being centrifuged at 3000 rpm for 5 minutes. The supernatant was then collected in 2 mL portions and evaporated to dryness at 35-40 °C under a moderate stream of nitrogen. These prepared samples were stored at -20 °C until final quantitative determination.

Instrumental determination

The HPLC analysis was performed with an Agilent 1260 HPLC system (USA). Flow rate of mobile phase (methanol/acetonitrile /water 40/45/15= v/v/v) at 0.8 ml /min, for abamectin, 0.9 ml/min (acetonitrile / water = 80/20, v/v) for pyraclostrobin and 1 ml /min (acetonitrile /water = 60/40, v/v) for boscalid. The injection volume was 20 µl. The detection wavelength for abamectin was 235 nm, while pyraclostrobin and boscalid were detected at 210 nm **[26-27].** The retention time (RT) for abamectin, pyraclostrobin, and boscalid were 3.681, 3.463, and 3.265, respectively as shown in figure 1,2 and 3. The chromatographic apparatus was controlled by Chemstation software.

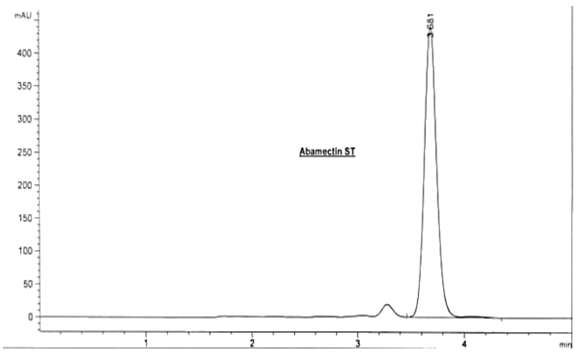

Figure 1: Standard of abamectin

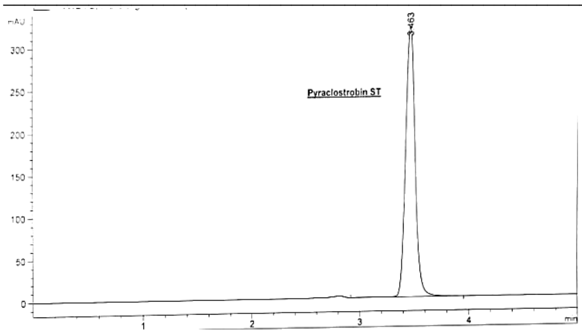

Figure 2: Standard of pyraclostrobin

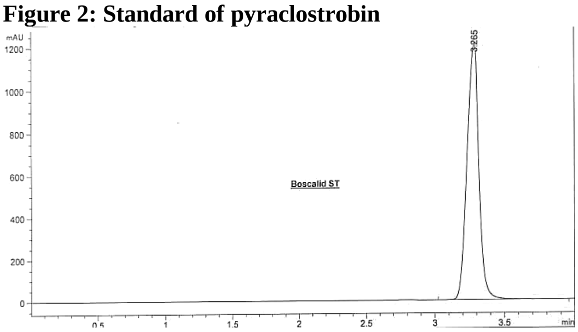

Figure 3: Standard of boscalid

Method validation

The stock solutions containing 1000 mg/l of analytic were prepared in acetonitrile and stored at - 20 °C. Standard solutions prepared in acetonitrile were used for spiking untreated homogenized apple fruit samples (10 g) with 0.1 for abamectin and 0.5 mg/kg for pyraclostrobin and boscalid. The spiked samples were subjected to extraction, clean-up, and final quantitative determination following the above procedure.

The linearity of the tested pesticides was determined using 100 mg/l to prepare a serial dilution solution using acetonitrile. The results showed good linearity with a correlation coefficient of R^2ing from 0.956 to 0.998. The test compounds' LOD (limit of detection) was 0.01mg/kg, and the method's quantification (LOQ) was 0.1, 0.25, and 0.25 mg/kg with abamectin, pyraclostrobin, and boscalid, respectively. In order to ascertain the relative response (response matrix/response solvent) in apples, the matrix effect was examined by comparing standards in a solvent with matrix-matched standards for three replicates at (MRL) mg/kg. Chromatograms of abamectin, pyraclostrobin, and boscalid standards in the matrix as shown in figures 4, 5 and 6.

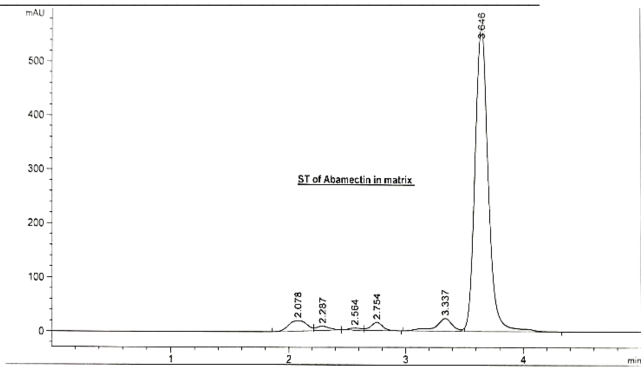

Figure 4: Standard of abamectin in matrix

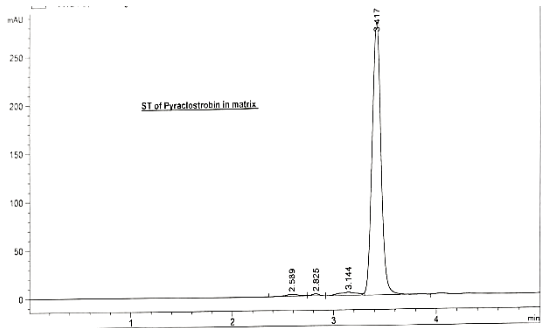

Figure 5: Standard of pyraclostrobin in matrix

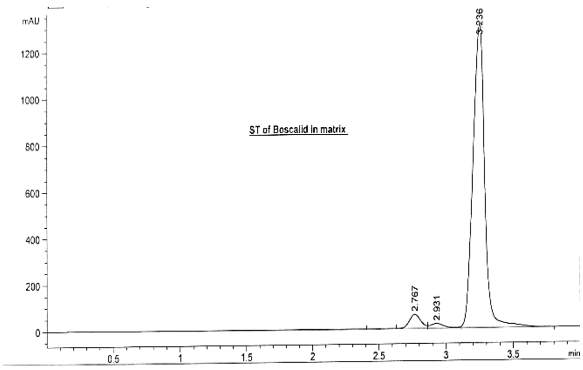

Figure 6: Standard of boscalid in matrix

Data calculation and analysis

The rate of degradation and half-life period of abamectin, pyraclostrobin and boscalid following first-order kinetics reaction were calculated according to [**28-29].** The first-order rate equation was used to obtain the degradation rate constants and half-lives: $C_t = C_0^{-kt}$, where C_t is the pesticide residual concentration at time t, C_0 is the initial concentration after application, and k is the dissipation degradation rate constant (days-1). The half-life ($t_{1/2}$) was computed using the k value for each experiment ($t_{1/2}$

= ln 2/k). The risk from these three pesticide residues in the apple was evaluated based on the data obtained from the field trial. For determining the estimated daily intake (EDI), compare it with the acceptable daily intake (ADI), given that the body weight is 80 kg per person. The following equation is used to determine the estimated daily intakes (EDI) according to **[30]:**

$$EDI = \frac{\text{Residue amount (mg / kg)} \times \text{Average consumption of fruit in Kg (Average intake)}}{80}$$

Where the residual amount is obtained from a field trial, the average intake comes from the GEMS/Food Cluster Diets database https://www.who.int/data/gho/samples/food-cluster-diets, and 80 is the standard Egyptian weight. The following equations are used to calculate the dietary risk assessment **[31-32]:**

$$HQ = EDI / ADI \times 100\ \%$$

The hazard quotient is HQ, the acceptable daily intake is ADI (mg/kg bw), and the estimated daily intake is EDI (mg/kg bw). The risk is unacceptable when HQ exceeds 100 % **[33].**

3. RESULTES AND DISSCUSSION

a-Before treatment

Effect of accelerated storage on the content of the tested pesticides at 54 ±2 ºC for 14 days.

Table 1 elucidates the effect of storage at 54 ±2 °C for 14 days on the content of the tested pesticides formulations. The data of the formulations under investigation showed no apparent differences in the content before and after storage for 14 days at 54ºC ± 2 ºC according to **[21],** suggesting that the formulations are stable at 54 ± 2 ºC for 14 days where specifications were not affected.

Table (1): Effect of accelerated storage on the content of the tested pesticides at 54 ±2 ºC for 14 days.

Storage Periods (Days)	Agromec® 1.8% EC	Shooter® 30% SC	
	abamectin content (w/v) %	pyraclostrobin content (w/w) %	boscalid content (w/w) %
Before (0) *	1.82**	9.95	19.55
After (14)	1.77	9.75	19.25

*** Samples before (0 d) and after (14 d) accelerated storage stability test were analyzed together to reduce the analytical error.**
****Each value represents an average of three replicates.**

FAO tolerance ±15% of the declared content of abamectin
FAO tolerance ±10% of the declared content of pyraclostrobin
FAO tolerance ±6% of the declared content of boscalid

Emulsion stability of Agromec® 1.8% EC before and after storage at 54 ±2 ºC

When diluted at 30 ±1°C with CIPAC standard waters D, the formulations shall comply with the FAO/WHO manual specifications of emulsifiable concentrate. Results indicated that emulsion stability comply with specification and no cream layer or any sediment before and after storage at 54 ± 2 °C for 14 days when the formulations were diluted with CIPAC standard water D **[22].**

Suspensibility of Shooter® 30% SC before and after storage at 54 ±2 ºC.

According to FAO/WHO manual specifications of suspension concentrate, a minimum of 60% of the Shooter® 30% SC shall be in suspension after 30 min in CIPAC standard water D at 30 ± 2°C. Results indicated that the suspensibility percentage before storage was 95.54% and after storage at 54 ± 2 °C for 14 days was 92.22%. From these results, suspensibility before and after storage comply with FAO/WHO specifications.

b-After treatment

Abamectin recovery was tested at 0.1 mg/kg fortification. In contrast, using three replicates to validate and evaluate the method's accuracy, pyraclostrobin and boscalid recoveries were determined at a fortification level of 0.5 mg/kg. Table 2 shows that the recoveries obtained were within the acceptable range of 82.27-101%. The methods' coefficient variation (CV%) for repeatability ranged from 1.71% to 2.48%, within the acceptable range. QuEChERS sample preparation in conjunction with the HPLC-UV is suggested for determining apples' abamectin, pyraclostrobin, and boscalid. The initial concentration of abamectin was 0.955 mg/kg, which decreased to 0.089 after three days of testing. After three days, there was a significant decrease in abamectin levels. The initial concentrations of boscalid and pyraclostrobin were 3.66 and 2.24 mg/kg, respectively, and decreased through the day of the experiment Fig (7). Abamectin, boscalid, and pyraclostrobin had half-lives ($t_{1/2}$) of 0.86, 3.3, and 4.95 days, respectively.

Table (2): Recoveries of the tested apple pesticides at various fortification levels.

Pesticide	Mean of Recovery (%)	CV (%)*
Abamectin	82.27 ±1.41	1.71
Pyraclostrobin	88 ±2.18	2.48
Boscalid	101 ±1.89	1.87

*CV = (Standard deviation/mean) ×100. Spiking untreated homogenized apple fruit samples (10 g) were amended with 0.1 for abamectin and 0.5 mg/kg for pyraclostrobin and boscalid.

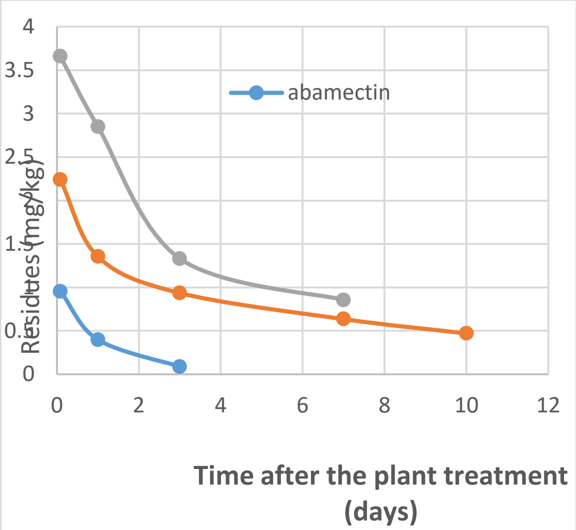

Figure 7. Dissipation pattern of abamectin, pyraclostrobin and boscalid in apple at the recommended dose.

Table 3 summarizes the half-life ($t_{1/2}$), regressive dissipation equation, and 217 correlation coefficient (R2 0.9133). The risk of pesticide residues in contaminated apple fruits was calculated in terms of daily intakes (EDI) and acceptable daily intakes (ADI). The GEMS/Food Cluster Diets database 223 provided the average daily consumption of apples per 222 capita **[34].** Apple is a fresh pome fruit, its consumption accounts for 2.73% (54.44 g/day) of total daily food consumption (1.994 kg/day). The Exposure 225 was measured in high definition.

Table (3): Regression equation, correlation coefficient, and half-life of the tested pesticides in apple fruits treated with recommended application rate.

*PHI: Preharvest interval.

Abamectin, a well-known biopesticide potent as insect-/acar-/nematicides, is a mixture of avermectins B1a and B1b **[10].** On apples, abamectin

Pesticide	ADI (mg/kg bw)	Days after spraying				
		0	1	3	7	10
Abamectin	0.001	0.955 (64.94)	0.397 (27.00)	0.089 (6.05)	—	—
Pyraclostrobin	0.03	2.24 (5.08)	1.355 (3.07)	0.936 (2.12)	0.876 (1.44)	0.471 (1.07)
Boscalid	0.04	3.66 (6.22)	2.85 (4.85)	1.33 (2.26)	0.855 (1.45)	—

proved a limited translaminar activity regardless of the leaf surface received spray solution **[11].** The younger leaves of apples exhibited higher capacity in abamectin uptake and absorption leading to increased mortality of target pests accompanied by the lengthier control efficiency duration **[35].** The initial concentration of abamectin was 0.955 mg/ kg, which decreased to 0.089 through a 3-days day of the experiment. A sharp decline in abamectin level was noted after three days after application. The initial concentration of boscalid and pyraclostrobin were recorded at 3.66 and 2.24 mg/kg, respectively, which decreased throughout the experiment day (Fig 7). The half-life ($t_{1/2}$) of abamectin, boscalid and pyraclostrobin were found to be 0.86, 3.3 and 4.95 days respectively. The half-life ($t_{1/2}$), dissipation regressive equation, and correlation coefficient ($R2 \geq 0.9133$) are summarized in Table 3. Regarding maximum residue limits (MRLs) of the tested pesticides obtained from the European Union (EU) Pesticides database showed MRL as 0.03 mg/kg for abamectin, respectively. Regarding abamectin residues in apples, half-lives range 2.6-4.4 d based on formulation active ingredient alone (12.5 % abamectin) or combined (0.25% abamectin+12.25% pyridaben) and their concentrations at the recommended rate. While higher application rates raised abamectin half-life to 7 d **[36]**. Also, **[37]** concluded that abamectin half-life in fruit was 3.6 to 4.9 d.

Table 4 depicts the risk assessment of three pesticides in apples. 226 The hazard quotient is a technique for assessing dietary risk. Based on ADI and EDI, the HQ was evaluated using 227 80 kg people. 228 Based on 229 formulations active ingredient alone (12.5% abamectin) or combined (0.25% 230 abamectin+12.25% pyridaben) and their concentrations at the recommended rate, abamectin residues in apples have half-lives ranging from 2.6 to 4.4 d. While 231 higher application rates increased the half-life of abamectin to 7 days **[36].** Also **[37]** concluded that abamectin half-life in fruit was 3.6 to 4.9 d.

Table (4): The residues in apple and dietary risk assessment of the tested pesticides.

***The numbers in parentheses refer to hazard quotient (HQ) based on the actual estimated residual amount; —**

Pesticide	Regression equation	Correlation coefficient	Half-life (days)	MRL (mg/kg)	PHI (days)
Abamectin	$C_t = 0.9639e^{-0.803t}$	0.9961	0.86	0.03	4.32
Pyraclostrobin	$C_t = 1.7504e^{-0.14t}$	0.9133	4.95	0.5	10.71
Boscalid	$C_t = 3.3196e^{-0.21t}$	0.9186	3.3	2	2.88

residual amount below LOQ so the HQ was blank.

Another factor affecting apple's abamectin residues is spray droplet size, where smaller droplets (mist sprayer) mainly increase abamectin uptake, distribution and residues on the target surface, leading to increased control efficiency despite the use of low applied doses **[38].**

Regarding maximum residue limits (MRLs) of the tested pesticides obtained from the European Union (EU) Pesticides database showed MRLs as 0.5 and 2 mg/kg for pyraclostrobin and boscalid, respectively. Based on our results, residues of pyraclostrobin seven days post-treatment were above the prescribed MRL of 0.5mg/kg prescribed by the EU pesticides database. According to the measured residual quantity, boscalid showed higher residues above the prescribed EU MRL 2 mg/kg after one day (s). From the residue results in the field trial, at harvest time, the maximum final pyraclostrobin residue in apples at intervals of 10.71 days was below 0.5 mg/kg. Also, 4.32 and 2.88 days were below 0.03 and 2 mg/kg with abamectin and boscalid residues, respectively. As for boscalid behavior on apple fruits, after two weeks of treatment showed sorption of 4.23-6.86%, with a distribution ratio ―<0.8‖ between pulp and peel concentrations. The recovery boscalid confirms that from peel because of its highest residue level **[39].**

Application boscalid 50% WDG at two dosages (349.5 and 525.0 g a.i./ha). The results illustrated strawberries' boscalid half-lives of 4.9 and 6.4 days **[28].** The Boscalid half-life in cucumber under greenhouse conditions was 1.9 days. Low half-life value due to the rapid increase in cucumber weight throughout cultivation, the dilution effect was a major contributor to the lowering of boscalid residue **[40].** Pyraclostrobin is a strobilurin fungicide with antifungal, curative, and translaminar effects and is widely employed in various crops **[41].** Pyraclostrobin is sensitive to photodegradation, leading to dissipating quickly, and application disease severity sharply increased after seven days **[42].** So, most strobilurin fungicides are commercialized and combined with other fungicides. The half-lives of pyraclostrobin in the apple were 7.9–15.1 days **[43].** The pesticides boscalid and pyraclostrobin were the most frequently detected pesticides in apples. Their concentrations in the whole fruit were lower than the European MRL. Nevertheless, peel residue amounts were ten times higher than whole fruits **[44].**

The physicochemical properties not only control the pesticide behavior on the target plant (contact, translaminar or systemic) but also define the stability of the parent compound in fluctuating environmental conditions. The accumulation of pesticides on the plant surface or penetrating for limited distances inside the plant makes the pesticide more susceptible to washing operations, whether by rain dew, or post-harvest treatments [**45].** Also, it makes it susceptible to photodegradation by sunlight and chemical decomposition e.g. oxidation and hydrolysis **[46].** All the interactions mentioned above decrease pesticide control efficacy and accelerate residue deterioration to decrease the remaining residue concentration on the edible part of the plant after the appropriate pre-harvest period for each pesticide.

The risk of the contaminated apple fruits with pesticide residues was estimated in terms of daily intakes (EDI) and acceptable daily intake (ADI). The average daily per capita consumption of apples was obtained from GEMS/Food Cluster Diets database **[34]**. Apple belongs to the pome fruit fresh group, and its consumption accounted for 2.73% (54.44 g/day) of total daily food consumption (1.994 kg/day). The exposure was measured in HQ. Table 4 shows the risk evaluation of three pesticides in the apple. The hazard quotient is a dietary risk assessment technique. The HQ was assessed using an 80 kg person's based on ADI and EDI. The findings showed that abamectin, imidacloprid, carbendazim, and difenoconazole dietary food exposure was less than 100% in apples each day after spraying when the appropriate application rates were used. The main pesticide breakdown methods include photolysis, hydrolysis, and microbial degradation **[47-48].** The dietary risks of three pesticides were evaluated based on their final residues and ADIs. The hazard quotient showed no potential risks based on the values of apple consumption with tested pesticides in agreement with **[32].** This is may be due to the low acute toxicity of the tested pesticides on mammals except for abamectin. This result suggested that it is safe to harvest 11 days after applying the recommended dose of Shooter® 30% SC (pyraclostrobin 10% + boscalid 20%) and 5 days after applying the recommended dose of Abamectin (Agromec® 1.8% EC).

4. Conclusion

After spraying abamectin (Agromec® 1.8% EC) and Shooter® 30% SC (pyraclostrobin 20% + boscalid 10%) on the apple trees. The improved QuEChERS method was used to prepare the apple fruit samples. Abamectin had an initial concentration of 0.955 mg/kg, a half-life of 20.64 h, and a PHI of 4.32 days. At the same time, the half-lives of boscalid and pyraclostrobin were 3.3 and 4.95 days, with initial deposits of 3.66 and 2.24 mg/kg and pre-harvest intervals of 10.71 and 2.88 days, respectively. The hazard quotient values for the pesticides tested ranged from 1.07 to 64.94%. Finally, this study would provide information on keeping consumers' health safe and using pesticides safely in pest management strategies.

5. Conflicts of interest

There are no conflicts to declare

6. Acknowledgment

The authors gratefully acknowledge to a Plant Protection Department, Faculty of Agriculture, Zagazig University, Egypt and Central Agricultural Pesticides Laboratory, Agricultural Research Center, Dokki, Giza, Egypt for the support this research work.

7. REFERENCE

1-Boyer, Jeanelle, and Rui Hai Liu. 2004. “Apple Phytochemicals and Their Health Benefits.” *Nutrition Journal* 3 (1): 1–15.

2-Williams, Katrina Anne. 2012. “Modeling Post-Harvest Pathogens in Apple Fruit.” PhD Thesis, University of British Columbia.

3-Mandal, Asit, Binoy Sarkar, Sanchita Mandal, Meththika Vithanage, Ashok K. Patra, and Madhab C. Manna. 2020. “Impact of Agrochemicals on Soil Health.” In *Agrochemicals Detection, Treatment and Remediation*, 161–87. Elsevier.

4-Thakur, V. S. 2006. “Apple Diseases Chemical Control in India.” In *XXVII International Horticultural Congress-IHC2006: International Symposium on Asian Plants with Unique Horticultural 769*, 177–84.

5-Büchele, Felix, Daniel A. Neuwald, Christian Scheer, Rachael M. Wood, Ralf T. Vögele, and Jens N. Wünsche. 2021. “Assessment of a Postharvest Treatment with Pyrimethanil via Thermo-Nebulization in Controlling Storage Rots of Apples.” *Agronomy* 12 (1): 34.

6-Sadlo, S., S. Walorczyk, P. Grodzicki, and B. Piechowicz. 2016. “Disappearance of Captan, Boscalid, Pyraclostrobin and Trifloxystrobin Residues in Ripe Apples during Cold Storage under Controlled Atmosphere.” *Fresenius Environmental Bulletin* 25 (6): 1959–65.

7-Boutros, H. Y. 2012. “Agricultural Production Development of Newly Reclaimed Land in Egypt.” https://scholar.google.com/scholar_lookup?title=Agricultural+production+development+of+newly+reclaimed+land+in+Egypt.&author=Boutros%2C+H.Y.&publication_year=2012.

8-Pimentel, David. 2009. “Pesticides and Pest Control.” In *Integrated Pest Management: Innovation-Development Process*, 83–87. Springer.

9-Stino, G. R. 1993. “Aspects Related to Temperate Zone Fruit Production in Egypt.” In *IV International Symposium on Growing Temperate Zone Fruits in the Tropics and in the Subtropics 409*, 203–6.

10-Sparks, Thomas C., Andrew J. Crossthwaite, Ralf Nauen, Shinichi Banba, Daniel Cordova, Fergus Earley, Ulrich Ebbinghaus-Kintscher, et al. 2020. “Insecticides, Biologics and Nematicides: Updates to IRAC’s Mode of Action Classification - a Tool for Resistance Management.” *Pesticide Biochemistry and Physiology* 167 (July): 104587. https://doi.org/10.1016/j.pestbp.2020.104587.

11-Beers, E. H., A. Andersen, and R. D. Brown. 1997. “Absorption and Translaminar Activity of Abamectin in Apple and Pear Foliage as Determined by Spider Mite (Acari: Tetranychidae) Mortality.” *Journal of Economic Entomology* 90 (2): 566–73.

12-Capriotti, M., A. Del Vecchio, A. Fagnani, E. Gentili, L. Bellettini, G. Balzaretti, M. Coatti, and M. Manaresi. 2004. “BAS 510 F (Boscalid): New Multipurpose Fungicide [Fruit, Vegetable and Ornamental Crops].” *Atti Delle Giornate Fitopatologiche (Italy)*.

13-Avenot, Herve F., and Themis J. Michailides. 2007. “Resistance to Boscalid Fungicide in Alternaria Alternata Isolates from Pistachio in California.” *Plant Disease* 91 (10): 1345–50.

14-Kanungo, Mansi, and Juhie Joshi. 2014. “Impact of Pyraclostrobin (F-500) on Crop Plants.” *Plant Science Today* 1 (3): 174–78.

15-Carriger, John F., Gary M. Rand, Piero R. Gardinali, William B. Perry, Michael S. Tompkins, and Adolfo M. Fernandez. 2006. “Pesticides of Potential Ecological Concern in Sediment from South Florida Canals: An Ecological Risk Prioritization for Aquatic Arthropods.” *Soil & Sediment Contamination* 15 (1): 21–45.

16-Ali, Md Emran, Owen Hudson, Will H. Hemphill, Timothy B. Brenneman, and Jonathan E. Oliver. 2019. “First Report of Resistance to Pyraclostrobin, Boscalid, and Thiophanate-Methyl in Colletotrichum Gloeosporioides from Blueberry in Georgia.” *Plant Health Progress* 20 (4): 261–62

17-Xue, Wenxin, Simon Snoeck, Christine Njiru, Emre Inak, Wannes Dermauw, and Thomas Van Leeuwen. 2020. “Geographical Distribution and Molecular Insights into Abamectin and Milbemectin Cross-Resistance in European Field Populations of Tetranychus Urticae.” *Pest Management Science* 76 (8): 2569–81.

18-González-Rodríguez, R. M., R. Rial-Otero, B. Cancho-Grande, C. Gonzalez-Barreiro, and J. Simal-Gándara. 2011. "A Review on the Fate of Pesticides during the Processes within the Food-Production Chain." *Critical Reviews in Food Science and Nutrition* 51 (2): 99–114. https://doi.org/10.1080/10408390903432625.

19-Karmakar, Rajib, and Gita Kulshrestha. 2009. "Persistence, Metabolism and Safety Evaluation of Thiamethoxam in Tomato Crop." *Pest Management Science: Formerly Pesticide Science* 65 (8): 931–37.

20-Waichman, Andrea Viviana, Jörg Römbke, Maria Olívia A. Ribeiro, and Nailson C. S. Nina. 2002. "Use and Fate of Pesticides in the Amazon State, Brazil." *Environmental Science and Pollution Research* 9 (6): 423. https://doi.org/10.1007/BF02987596.

21-CIPAC MT 46, Collaborative International Pesticides Analytical Council (CIPAC); Accelerated Storage Procedure. Vol., F, p. 148-151 (1995).

22-CIPAC MT 36.1.1, Emulsion Characteristics of Emulsifiable Concentrates. Vol., F, P. 108-109 (1995).

23- CIPAC MT 184, Suspensibility of formulations forming suspensions on dilution with water. Vol., K, p. 142-148 (2003).

24-Lehotay, Steven J. 2007. "Determination of Pesticide Residues in Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulfate: Collaborative Study." *Journal of AOAC International* 90 (2): 485–520.

25-Raczkowski, M., A. Hołodyńska, A. Nowacka, and B. Gnusowski. 2011. "Application of the QuEChERS method for determination of pesticide residues in tomato samples using GC-NPD/ECD." *Progress in Plant Protection* 51 (2): 727–31.

26-Lazic, S., D. Sunjka, D. Boskovic, M. Tomsik, D. Grnca, S. Vukovic, and A. Zunic. 2019. "Analysis of Fungicides Boscalid and Pyraclostrobin Residues in Lettuce." *X International Agriculture Symposium, Agrosym 2019, Jahorina, Bosnia and Herzegovina, 3-6 October 2019. Proceedings*, no. Lazic, S.: University of Novi Sad, Faculty of Agriculture, Novi Sad, Serbia: 1065–69.

27-Mohammed, Mohammed E.H., M. H.A. Soliman, M. A. Hendawy, and M. Y. Hendawi. 2021. "Influence of Adding Mineral Oil and Fertilizer on Abamectin Used in Control Spider Mite, Tetranychus Urticae Koch Infesting Cucumber." *Zagazig Journal of Agricultural Research* 48 (2): 345–55. https://doi.org/10.21608/zjar.2021.175230.

28-Chen, Li, and ShuZhen Zhang. 2010. "Dissipation and Residues of Boscalid in Strawberries and Soils." *Bulletin of Environmental Contamination and Toxicology* 84 (3): 301–4. https://doi.org/10.1007/s00128-010-9934-y.

29-Stow, Craig A., Leland J. Jackson, and S. R. Carpenter. 1999. "A Mixed-Order Model to Assess Contaminant Declines." *Environmental Monitoring and Assessment* 55 (3): 435–44. https://doi.org/10.1023/A:1005940627896.

30-Fu, Yan, Ting Yang, Jian Zhao, Liang Zhang, Ruoxia Chen, and Yinliang Wu. 2017. "Determination of Eight Pesticides in Lycium Barbarum by LC-MS/MS and Dietary Risk Assessment." *Food Chemistry* 218: 192–98.

31-Lozowicka, B., M. Jankowska, and P. Kaczyński. 2012. "Pesticide Residues in Brassica Vegetables and Exposure Assessment of Consumers." *Food Control* 25 (2): 561–75.

32-Xu, Guofeng, Jiyun Nie, Yonglong Wu, Zhen Yan, and Mengliang Ye. 2018. "The Effects of Fruit Bagging on Residue Behavior and Dietary Risk for Four Pesticides in Apple." *Scientific Reports* 8 (1): 14348. https://doi.org/10.1038/s41598-018-32358-6.

33-Szpyrka, Ewa, Anna Kurdziel, Aneta Matyaszek, Magdalena Podbielska, Julian Rupar, and Magdalena S\lowik-Borowiec. 2015. "Evaluation of Pesticide Residues in Fruits and Vegetables from the Region of South-Eastern Poland." *Food Control* 48: 137–42.

34-WHO. 2013. "GEMS/Food Cluster Diets Database." 2013. https://www.who.int/data/maternal-newborn-child-adolescent-ageing/advisory-groups/gama/gama-advisory-group-members.

35-Beers, E. H., A. Andersen, and R. D. Brown. 1996. "Effect of Leaf Age on Length of Residual Activity of Abamectin in Pome Fruit Foliage." *Journal of Economic Entomology* 89 (2): 488–92. https://doi.org/10.1093/jee/89.2.488.

36-Sun Rui, Shi Na, Liu HuiJun, and Chen Yan. 2021. "Study on abamectin residue analysis and digestion dynamics in apples.” *Journal of Food Safety and Quality* 12 (3): 1247–53.

37-Song, GuoChun, TianXing Yu, RuiJuan Li, and JianLei Yu. 2011. “Residue dynamics and safety evaluation of abamectin in apple.” *Journal of Fruit Science* 28 (5): 880–82.

38-Yu, Qin, RenJun Fan, ZhongFang Liu, YunTao Feng, PengJiu Zhang, GuiMing Guo, and RunXiang Zhang. 2016. “Effects of Droplet Density, Spraying Volume and Spraying Equipment on Efficacy of Abamectin Microemulsion against Panonychus Ulmi in Apple Tree.” *Journal of Fruit Science* 33 (1): 81–87.

39-Zou Nan, Yuan ChunHao, Chen RongHua, Yang Juan, Li YiFan, Li XueSheng, and Pan CanPing. 2017. “Study on Mobility, Distribution and Rapid Ion Mobility Spectrometry Detection of Seven Pesticide Residues in Cucumber, Apple, and Cherry Tomato.” *Journal of Agricultural and Food Chemistry* 65 (1): 182–89. https://doi.org/10.1021/acs.jafc.6b03084.

40-Lee, Jong-Hwa, Hee-Won Park, Young-Soo Keum, Chan-Hyeok Kwon, Young-Deuk Lee, and Jeong-Han Kim. 2008. “Dissipation Pattern of Boscalid in Cucumber under Greenhouse Condition.” *The Korean Journal of Pesticide Science* 12 (1): 67–73.

41-Cabrera, A., L. Cox, K. Spokas, M. C. Hermosín, J. Cornejo, and W. C. Koskinen. 2014. “Influence of Biochar Amendments on the Sorption–Desorption of Aminocyclopyrachlor, Bentazone and Pyraclostrobin Pesticides to an Agricultural Soil.” *Science of The Total Environment* 470–471 (February): 438–43. https://doi.org/10.1016/j.scitotenv.2013.09.080.

42-Guan, L., P. Zhang, X. K. Wang, Y. P. Ren, B. B. Guo, and F. Liu. 2015. “Photodegradation of Pyraclostrobin in Water Environment and Microencapsulation Effect on Its Photostability.” *J. Agro-Environ. Sci* 34: 1493–97.

43-Fan, XueQi, ShengMing Zhao, XiaoXin Chen, and JiYe Hu. 2018. “Simultaneous Determination of Pyraclostrobin, Prochloraz, and Its Metabolite in Apple and Soil via RRLC-MS/MS.” *Food Analytical Methods* 11 (5): 1312–20. https://doi.org/10.1007/s12161-017-1065-1.

44-Giacinti, G., C. Raynaud, S. Capblancq, and V. Simon. 2016. “Matrix-Matching as an Improvement Strategy for the Detection of Pesticide Residues.” *Journal of Food Science* 81 (5): T1342–50. https://doi.org/10.1111/1750-3841.13296.

45-Gao, Jie, Yu Wang, Bin Gao, Lei Wu, and Hao Chen. 2012. “Environmental Fate and Transport of Pesticides.” In *Pesticides—Evaluation of Environmental Pollution. CRC Press Taylor and Francis Group, Boca Raton*, 29–41.

46-Bansal, O. P. 2012. “Degradation of Pesticides.” In *Pesticides Evaluation of Environmental Pollution (S. Hamir, Rathore and LML Nollet, Ed.). CRC Press, New York, United States of America*, 47–77.

47-Higson, Frank K. 1992. “Microbial Degradation of Nitroaromatic Compounds.” In *Advances in Applied Microbiology*, edited by Saul L. Neidleman and Allen I. Laskin, 37:1–19. Academic Press. https://doi.org/10.1016/S0065-2164(08)70250-8.

48-Kromer, Thomas, Holger Ophoff, Andreas Stork, and Fritz Führ. 2004. “Photodegradation and Volatility of Pesticides.” *Environmental Science and Pollution Research* 11 (2): 107–20. https://doi.org/10.1007/BF02979710.