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DISSIPATION OF HEXYTHIAZOX AND ABAMECTIN RESIDUES ON STRAWBERRY GROWN IN OPEN FIELD

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ABSTRACT

Supervised field trial was conducted to study the dissipation rates of two widely used acaricides hexythiazox (Makoyt 10%WP) and abamectin (Veractin 25 % EC) on strawberry under Egyptian climatic condition. Samples were collected randomly at successive intervals after pesticides spraying at recommended rate of applications. The samples were extracted and cleaned up using QuEChERS method and quantified by HPLC- equipped with Diode-Array Detector (DAD). The LOD&LOQ of hexythiazox and abamectin were 0.01mg/kg and 0.03mg/kg, respectively.The recovery of the tested pesticides was 90%and 81 %.The results showed that, the initial deposits were 3.64 and 1.31mg/kg and the calculated half-life's (t½) were 2 and 1.5 days in strawberry for hexythiazox and abamectin, respectively. However, Pre harvest intervals (PHI) on strawberry were 4 and 7 days for hexythiazox and abamectin, respectively

Keywords: strawberry, hexythiazox, abamectin, PHI, HPLC

INTRODUCTION

Pesticide use in commercial agriculture practices has led to an increase in farm productivity. Despite the significant benefits of using pesticides in agriculture, several improper applications can result in high and undesirable levels residues in the produce that reaches to consumers. These include inappropriate selection of pesticides used on foodstuffs besides over use of pesticides and harvesting the crops before the residues have washed off after application (Chen *et al*.2011). Exposure to pesticides can occur via a number of pathways such as indirect (e.g., through food, drinking water, residential and occupational exposure) and direct routes (oral, inhalation and dermal). However, the major concerns are of consumption of food crops laden with pesticide residues (Boobis *et. al*., 1992). Pesticides have been linked to a wide spectrum of human health hazards, ranging from acute impacts, such as headaches and nausea, to chronic impacts, such as cancer, reproductive harm and endocrine system disruption (Blasco *et. al*., 2004). In addition to incorrect applications of pesticides may cause harm to the environment, increased resistance of target pest organisms and deleterious effects on non-target organisms. Strawberry is one of the most widely grown fruits world wide. In Egypt, strawberry considered to be the third most prominent fruits. Spider mite, two spotted spider mites, is one of the most sever pests attacking strawberry. It causes significant economic damage in terms of yield and quality deterioration of the fruits (Ellen *et. al*., 1997; and Banerjee *et. al*., 2008).

Hexythiazox is a non systmic broad spectrum acaricide with contact and stomac action. It has good transilaminar activity. It is applied at any growth stage from budding to fruitting. Hexythiazox effeciency extends from ovicidal and larvae to adult control) . Abamectin belongs to the family of avermectins which is 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 (Pesticide Manual, 1994). Abamectin acts by stimulating the release of c-aminobutyric acid thus causing paralysis (Turner & Shaeffer, 1989). It is used to control motile stages of mites and some other insects on fruits and vegetables with limited systemic properties.

Dissipation of hexythiazox in birinjia, bean pods and peach was studied by Majumder *et. al*., (2015), Abd–Alrahman (2012) and Guo *et al*. (2012). Also, the dissipation behavior of abamectin in date, green grocy,cabbages ,tobacco vegetables and cabbage and tomatoes were examined (KAMAL 2007; Chuan (2012) *et. al.,* Xie*et al*. (2008), Qui *et. al*.; 2013; Gao-gnowen 2005.and Nasr *et. al*., (2009).

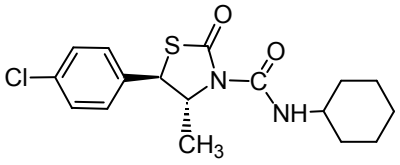
As those pesticdes are frequently used in strawberry so the dissipation study and determination of PHI arehighly required The objective of the present work is to investigate the dissipation rates and PHI of hexythiazox and abamectin in strawberry under open field conditions.

MATERIALS AND METHODS

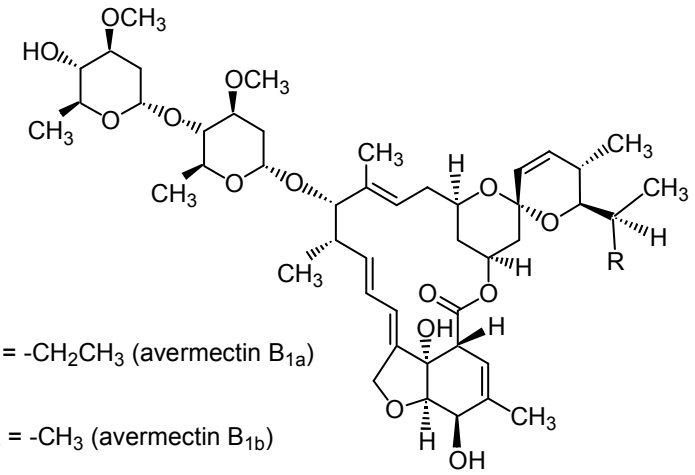
Field Experiment:

Strawberry was planted at Nawa, Qalubia governorate in Egypt on September 2014. The experimental area was divided to plots of 1/100Feddan per each. The plots were sprayed with (Makomyt10%WP) hexythiazox or (Veramictin1.8% EC) abamectin using knapsack hand sprayer fitted with one nozzle. The rates of application were 20 cm³/100L water and 40cm³/100L water for hexythiazox (Makomyt) and abamectin (Vermectin), respectively.

The Tested Pesticides:



Structure of hexythiazox



(i) R = -CH_2CH_3 (avermectin B_{1a})

(ii) R = -CH_3 (avermectin B_{1b})

Structure of abamectin

The Laboratory Experiment:

Sample Collection:

Samples (1 kg for each) were taken randomly from each plot according to FAO /WHO recommendations (1986). Samples were taken in triplicates after one hour of spraying then were collected at 1, 3, 6, 9, 12 and 15 days. Samples were transported immediately in ice box to the Lab. Sub sampling was obtained in laboratory and the samples were kept in freezer at -20 C till residue analysis.

Residues Analysis Technique:

The samples were prepared with QuEChERS Anastassiades *et. al*., (2003). Method. It consisted of (1); homogenized around 500 g samples; (2) weight 10 g previously chopped fresh sample into a 50 ml Teflon centrifuge tube; (3) add 4g magnesium sulphate anhydrous (Mgso4), 1g sodium citratrate dehydrate and vortex immediately for 1min; (5) centrifuge the extract for 3-min at 5000 rpm; (6) transfer a 6ml aliquot of the upper layer into 15ml Teflon centrifuge tube containing 150mg Primary Secondary Amin (PSA) and 950 mg $MgSO_4$; (7) centrifuge the extract for 3 min at 5000 rpm; (8) filter through 0.45um filter; (9) transfer 1.5 ml of the extract into an auto sampler vial containing 15ul of a 5% formic acid solution (for the stabilization of extracts) for HPLC analysis

Recovery Experiment:

The reliability of the analytical methods was tested by fortifying untreated samples with known quantities of the investigated pesticides at the level of 0.1 mg/kg. The abovementioned procedures of extraction, clean up and quantitation were followed. The rates of recovery of hexythiazox and abamectin were 90% and 81%, respectively.

Instrumental Conditions:

Samples were analyzed by HPLC (Agilent 1100 series, equipped with diodaray detector with the wave length of 220nm and 245nm for hexythiazox

and abamectin, respectively.).The used column was C 18 ODS Hypersil (150mm x 4mm x5um). The Mobile phase was (70% acetonitril: 30% water) and (60% acetonitrile: 40%water) for hexythiazox and abamectin, respectively while the flow rate was 0.8 ml/min and 1ml/min.

Residues half- life Estimation (t½):

The half-life time (t½) for each investigated pesticides were calculated using the following equation of Moye *et. al*., (1987)

$(t½)=LN2/K= 0.6932/K$

$K´=1/T_x \ LN(a/b_x)$

K´=rate of decomposition T_x = time in days

A = initial residue b_x= residue at time

RESULTS AND DISCUSSION

Initial Deposits of The Tested Pesticides:

The initial deposits of hexythiazox and abamectin were 3.64 and 1.31mg/kg, respectively. The amount of active ingredients (a.i) of hexythiazox and abamectine sprayed on strawberry was 2 g a.i and 0.72 g per 100L water, respectivley with the ratio of 2.7. The ratio between the detected intial depostis on strawberry at zero time was 2.7 which proved the good sparying practice and reliable analytical performance.

Dissipation Rate of Hexythiazox:

Results of hexythiazox residues on strawberry fruits are presented in Table (1) and (Fig. 1). The initial deposit of hexythiazoxwas 3.64 then gradually decreased to be 1.77mg/kg one day after application, this revealing 51.3 % of loss. Residues reached 0.045, 0.18 and 0.04 mg/kg with rate of loss 87.63, 95.05, 96.97 and 98.9% at 1, 3, 7, 10 and 15 days, respectively. The residues of hexythiazoxwere not detected in strawberry fruits after 21 days from application. By plotting the logarithm of residue concentration (log of mg/kg) against time (days after application), the dissipation curve was constructed Fig. (1). The dissipation reaction followed the first order kinetic with regression coefficient R^2=0.9322. The calculated (t ½) of hexythiazox was 2-days. The obtained results showed that strawberry fruits could be safely consumed after 4 days of application as the Maximum Residue Limit (MRL) of hexythiazox in strawberry fruit is 0.2 mg/kg. This result is agreed with Majumder *et. al.,* (2015) they found that the half- life values of hexythiazonx in brinjal were in the range of 1.42 to 2.32 and pre harvest periods found to be in the range of 3-5 days irrespective of dose and location. Also, Guodong *et. al*., (2012) concluded that the half- life of hexythiazox was 6.8-days in peach and Abd–Alrahman (2012) found that PHI value was 4 days for hexathiazox in bean-pods.

Table (1): Dissipation of Hexythiazox Residues in Strawberry Fruits.

Days after application	Residues (mg/kg) (RSD%)	
	Means (RSD %**)	% Dissipation
Initial*	3.64 (6.89)	0.00
1	1.77 (6.49)	51.3
3	0.45 (7.69)	87.63
7	0.18 (5.56)	95.05
10	0.11 (4.16)	96.97
15	0.04 (25.00)	98.9
21	ND	-
t ½	2 days	
MRL(mg/kg)	0.5 days	
K´	0.016	
R^2	0.932	
PHI	4-days	

*** Samples were taken one hour application. ** RSD: Relative Standard Deviation**

Dissipation rate of abamectine

Results in Table (2) and Fig.(2) showed the concentration of initial deposits of abamectine in strawberry fruits was 1.31mg/kg then gradually decreased to 0.52 mg/kg one day after application (83% loss). The residues decreased at 1, 3, 7, 10, 15 days to 0.21, 0.085, 0.045 and 0.0013 recording the dissipation rate 93.3, 90.1, 95, 96 and 98.9, respectively. However, No residues were detected in strawberry fruits after 21 days of application. The dissipation rate of abamectin followed the first order kinetic reaction Fig. (2). The regression coefficient R^2 was 0.605. The calculated t ½ were 4 days, the data showed that strawberry fruits could be harvested after 7 days of application as the MRL of abamectine in strawberry fruits is 0.1mg/kg. . The result in the present study is agreed with Qiu*et al*.(2013) who reported that half–life of emamectin benzoate in tobacco was 2.13 days and linear correlation coefficient (R^2) was 0.884. Also, Xie *et. al.,* (2008) found the half-life of abamectin in cuali flowers and cabbage were 1.63 and1.46 days, respectively. Additionally, the results are harmonized with li bao- tong and Peichun-mei, (2009) that reported the half –life in brassica was 1.56. Alla, et al. (2007) found initial deposits and PHI were 0.09 mg/kg and 10 days on Saudi Arabia dates for abamectine.

Examination of the aforementioned results revealed that hexythiazox is more degradable than abamectine hence $t_{1/2}$ values are 2 and 4-days, respectively. Correspondingly, the hexythiazox is more applicable to be safely used close to the harvest as the PHI is 4-days. However, abamectine application before harvest requires more precautions as the PHI is 7 days based on the MRL set by European commission regulation (EU) 2012 and (EU) 2010 respectively.

Table (2): Dissipation of Abamectin Residues in Strawberry Fruits.

Days after application	Residues (mg/kg)(RSD%**)	
	Means (RSD %**)	% Dissipation
Initial*	1.31 (4.64)	0.00
1	0.52 (5.77)	61.3
3	0.21 (7.78)	83.4
7	0.085 (8.32)	93.1
10	0.045 (8.89)	99.9
15	0.0013 (23.08)	-
21	---------	--------
t ½	1.5	
MRL(mg/kg)	0.1	
K´	0. 0228	
R^2	0.605	
PHI	7 day	

*** Samples were taken one hour application. ** RSD: Relative Standard Deviation**

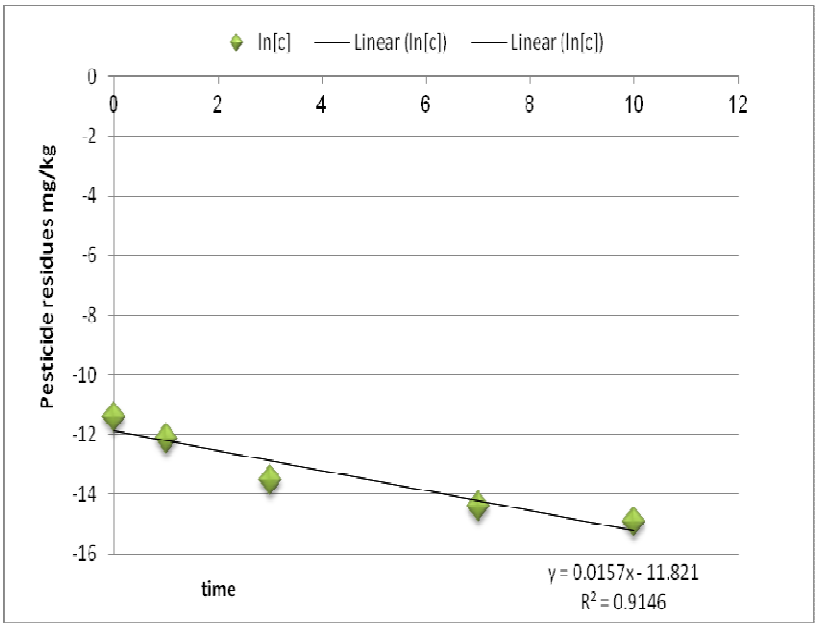


Fig. (1): Dissipation of hexythiazox residues in strawberry fruits

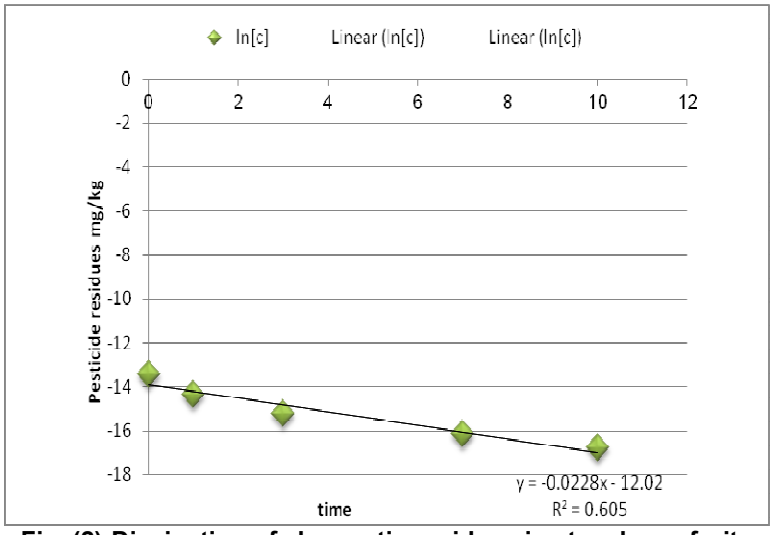


Fig. (2):Dissipation of abamectin residues in strawberry fruits

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دراسه انهيار الهكسثيازوكس والابامكتين على ثمار الفراوله فى الحقل المفتوح

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[١] **المعمل المركزى للمبيدات – مركز البحوث الزراعية**

[٢] **قسم الوقاية والمبيدات - كلية الزراعة – جامعة عين شمس**

الهدف من البحث تقدير متبقيات مبيد الهكسثيازوكس والابامكتين على ثمار الفراوله تحت الظروف المناخ المصريه . تم اجراء التجربة فى مركز نوى محافظة القليوبيه و تم اخذ عينات من ثمار الفراوله بطريقة عشوائية بعد ساعة، ١، ٣، ٧، 10 و١٥و 21يوم من المعاملة. تم تحليل مستخلص الثمار باستخدام جهاز السائل الكروماتوجرافى عالى الاداء والكروماتوجرافى الغازى على التوالى باستخدام بطريقه كاتشرزتم حساب نسبه الاسترجاع لكل من الهكسثيازوكس والابامكتين وكانت ٩٠٪ و ٨١٪ على التوالى . اظهرت النتائج ان كمية المتبقى بعد ساعة من الرش لكل من الهكسثيازوكس والابامكتين كانت ٣,٦ و١١,٣ ملجم/كجم فى ثمار الفراوله. على التوالى. كانت قيم نصف العمر لكل من الهكسثيازوكس والابامكتين ٢ يوم و١,٥ يوم فى ثمار الفراوله على التوالى. كانت قيم فترة ما قبل الحصاد لمبيد الهكسثيازوكس والابامكتين ٤ يوم و ٧يوم على ثمار الفراوله على التوالى.