



Journal

*J. Biol. Chem.
Environ. Sci., 2008,
Vol. 3(3):57-63
www.acepsag.org*

RESIDUAL BEHAVIOR OF PESTICIDES FLUFENOXURON AND DIAZINON ON AND IN EGYPTIAN APPLE

Hend A. Mahmoud^a and Sanaa A.M. El-Sawi^b

^a Central laboratory of Pesticides, Agricultural Research Center, Dokki, Giza, Egypt

^b Central Lab. of Residues Analysis of Pesticide and Heavy Metals in Foods, Agricultural Research Center, Dokki, Giza, Egypt

ABSTRACT

Residues of the pesticides flufenoxuron (10% DC) and diazinon (60%EC) on apple Anna 106 (*Malus sylvestris*) grown in Egypt and the pre-harvest interval (PHI) under the local weather and soil conditions were studied. The recovery of flufenoxuron was 89.3% while the recovery of diazinon was 99.7%. The initial deposit of flufenoxuron residues on apple was 0.89 mg/kg, which declined to 0.01 mg/kg after 25 days. While the initial deposit of diazinon was 0.9 mg/kg and was not detected (100% loss) after 20 days. The residue half life values of flufenoxuron and diazinon were 6.20 and 6.58 days, respectively. The results revealed that the pre harvest intervals (PHI) for flufenoxuron and diazinon were 25 and 6 days respectively under Egyptian conditions.

Keywords: Apple; (*Malus sylvestris*) Flufenoxuron; Diazinon, PHI; Pesticide residues; Residue decline study.

INTRODUCTION

Widespread and misuse of pesticides produces a very important problem, since their persistence in the environment is normally high. Safety intervals following the application of pesticides on crops have been established by the authorities in all countries, but their persistence may be superior to that interval. The search for means to improve the production of apples in Egypt is always the target of scientists who seek new techniques to enhance the quality and safety of this product. Recently, a number of pesticides were registered at the

Ministry of Agriculture in Egypt to control the insects and fungus, which infest fruits and causes severe damage. Among these pesticides, flufenoxuron and diazinon are widely applied on apples to control the insects and fungus in many Egyptian governorates including Dakahlia (Pdrez *et. al* 1996).

MATERIALS AND METHODS

1. Pesticides used:

Flufenoxuron: 1-[4-(2-chloro- α , α , α -trifluoro-p-tolyloxy)-2-fluorophenyl]-3-(2, 6-difluorobenzoyl)urea. It is contact acaricide and insecticide which known commercially as Cascade which used to control of immature stages of many phytophagous mites which infect apples.

Diazinon: [O,O- diethyl O-2- isopropyl-6- methylpyrimidin-4-yl phosphorothioate]. It is non-systemic insecticide and acaricide with contact, stomach and respiratory action.

2. Field experiments and sampling:

Each 60 m² of cultivated apple (*Malus sylvestris*) trees in a farm in Dakahlia governorate – Egypt were treated with flufenoxuron (Cascade 10%DC) at rate of 60 cm³/100 liter water and diazinon (60%EC) at rate of 300cm³ / 100 liter water using a knapsack sprayer respectively on 15 June 2007. Representative and randomly samples of each treated area were collected in polyethylene bags one hour after application (Initial deposit) and then after 2, 3, 6, 11, 15, 20 and 25 days for cascade and diazinon. The harvested samples were chopped well and thoroughly mixed before taking a sub-sampling portion of 100g in triplicates in polyethylene bags, labeled and kept at -18°C until residue analysis (CAC 1993).

3. Extraction and Clean-up.

3.1 Flufenoxuron

Extraction procedures for all samples were done according to Luke *et al.* (1981). Frozen samples were left until reach room temperature then three replicates of chopped apple sub-samples (100 gm) were each blended with 200 ml acetone in a blender jar for 3 min. at high speed and then filtered through a funnel with a dry pad of cotton into a graduated cylinder. Eighty ml of the sample filtrate was transferred into a separatory funnel and partitioned with a mixture of

100 ml petroleum ether and 100 ml dichloromethane. For separation, the upper organic layer was received in a 500 ml flask through a funnel with a dry pad of cotton and anhydrous sodium sulfate, and then 5 gm of sodium chloride was added to the aqueous layer, which was further extracted with two 100 ml volumes of dichloromethane. The combined dichloromethane (organic layer) was dried with anhydrous sodium sulfate and then collected in the same flask and evaporated to dryness at 40°C under reduced pressure using rotary evaporator and then the sample became ready for high pressure liquid chromatography determination.

3.2 Diazinon

Fifty g sample was extracted with 200 ml methanol and blended for three minutes then filtered through a funnel with a dry pad of cotton into a flask. A hundred ml of the extract was taken for partitioning with (100, 50, 50 ml methylene chloride and added 40 ml saturated solution of sodium chloride). The combined dichloromethane (organic layer) was filtered through pad cotton and anhydrous sodium sulfate, then collected in the same flask and evaporated to dryness at 40°C under reduced pressure using rotary evaporator (Malhof, 1975).

The residue was dissolved in 3ml n- hexane and cleaned up according to Mills, 1972 using a column with (6 gm) activated florisil (60-100 mesh) and topped with anhydrous sodium sulfate and compacted. The column was pre washed using 60ml n- hexane. The residue was transferred to the column and then eluted with 200 ml mixture of (methylene chloride 50%: hexane 48.5%: acetonitrile 1.5%) at rate of 5ml/min. The elute was evaporated to dryness by rotary evaporator at 40°C and the residues were ready for chromatographic determination.

4. Instrumentation

Samples of flufenoxuron were analyzed by high performance liquid chromatography (HPLC) Agilent 1100 series, equipped with diode array detector, mobile phase was 60:40 acetonitrile: water with flow rate 1 ml/min.

Diazinon was determined by gas chromatography, (Hewlett Packard GC 6890) equipped with a flame photometric detector (FPD) with phosphorus filter. A fused silica capillary (PAS-1701), column containing 14% cyanopropylsiloxane as stationary phase (30 m

length x 0.23 mm internal diameter x 0.25 μm film thickness). The operating conditions of GC instrument: Injector and detector temperature were 240 and 250 $^{\circ}\text{C}$, respectively. Oven temp. was 200 $^{\circ}\text{C}$. The carrier gases were nitrogen at rate 3 ml/ min, air at rate 100 ml/ min and hydrogen at rate 75. 3 ml/ min.

5. Recovery studies

Known quantities of tested pesticides dissolved in acetone and added to untreated samples of apple. Simultaneous processing frequently checked recovery of the overall method. The recovery percentages from spiked samples of apple were 89.3 and 99.7% for flufenoxuron and diazinon, respectively.

RESULTS AND DISCUSSION

The results in Table (1) shows that the initial deposit of flufenoxuron on apples of Anna 106 type was 0.89 mg/kg and gradually with time the rate of residue decline reached 98.8% after 25 days of application. This indicates that after 25 days of treatment, the amount of flufenoxuron was 0.01 mg/kg and this in the range of the maximum allowed residue set by the Codex Committee on Pesticide Residues under the Joint FAO/WHO Food Standards Program at 0.01–0.02 mg/kg for fruits (FAO/WHO, 1997). At that time the fruit is expected to be ready for sale. Therefore the pre-harvest interval (PHI) was 25 days for flufenoxuron was recommended in apples. These results are quite comparable with those reported by many investigators regardless of experiments were carried out under different climate conditions, geographical locations, time of application, application technique, concentrations, type of formulation and plant species. This findings were supported by Kamel *et al.*, (2007) who reported that the initial deposit of flufenoxuron on date was 0.68 mg/kg and declined to 0.25 (68%), 0.07 (90%) and 0.03 mg/kg (96%) after 16, 52 and 60 days, respectively (PHI = 50 days, MRL = 0.1 mg/kg).

Otherwise the initial deposits of diazinon on and in apple fruits were 0.9 ppm which decreased till reached 0.58 ppm, after 48 hours from treatment. These figures decreased gradually until reached 0.51, 0.49, 0.19, 0.05 ppm after 3, 6, 11 and 15 days, respectively, the residues was not detected after 21 days in apple fruits. The loss percentages in diazinon residues were enhanced by time elapse

recording. Therefore the pre-harvest interval (PHI) was 6 days for diazinon was recommended in apples.

The organophosphorus pesticide decay studies on malathion, fenitrothion and dichlofluanid in apple (Saenz *et al*, 1995) showed that malathion and dichlofluanid decay in a linear way in time this result is in the same trend with our results, in contrary there was no decay during the tested time for fenitrothion.

The safe period of harvesting vegetables treated with the organophosphorus insecticides was ranged between 1 and 12 days post treatment, which depending on the chemistry for tested pesticides and the kind of crops (Shady *et al* 2000 and Hegazy and Nasr 2003).

Table (1): Residues of Flufenoxuron and Diazinon in and on Apple Fruits

Time after applications (days)	Diazinon		Flufenoxuron	
	mg/kg	Loss%	mg/kg	Loss%
Initial	0.90	0.00	0.89	0.00
2	0.58	35.56	0.78	12.35
3	0.51	43.30	0.60	32.98
6	0.49	45.56	0.46	48.31
11	0.19	78.89	0.37	52.00
15	0.05	94.40	0.12	86.51
20	ND	100.00	0.10	88.76
25	ND	100.00	0.01	98.87
RL ₅₀	6.58		6.20	
MRL	0.5		0.02	
PHI	6		25	

Residues dissipation could be attributed chemical degradation (influenced by the molecular make up of the pesticide and by such factors as sunlight, moisture, and temperature). Beside plant growth, particularly for fruits which is also responsible to a great extent of decreasing pesticide residue concentration due to growth dilution effects, as the fruits become larger, the chemical residue concentrations will decrease Walgenbach *et al.*, (1991). Furthermore, Fong *et al.* (1999) reported that such noticeable reductions of the pesticide residues could be due to firstly, volatilization to the atmosphere (influenced by the insecticide's volatility or vapor

pressure, temperature and wind movement); secondly, to the environmental conditions(temperature, sunlight and moisture).

REFERENCES

- CAC, (1993). Codex Alimentarius Commission- Pesticide Residues in Food- Volum2, Second Edition. Joint FAO/WHO Food Standards Programme, Food and Agriculture Organization of United Nations World Health Organization.
- FAO/WHO. (1997). Joint FAO/WHO Food Standards Program, Codex Committee on Pesticide Residues, CX/PR 97/9, February 1997, p. 159.
- Fong, W.G.; H.A. Moye; J.N. Seiber and J.P. Toth (1999). Pesticide residues in foods: methods, techniques, and regulations. Chemical Analysis Series, Vol. 151, pp. 1-2, John Wiley & sons, Inc. New York, USA.
- Hegazy, M. E. A and I. N. Nasr (2003). Residues and half-lives of certain insecticides on and in some vegetables under field conditions. Egypt. J. Agric. Res., 81(1): 83-92.
- Kamel A. , Al-Dosary S., Ibrahim S. , Ahmed M. A.(2007). Degradation of the acaricides abamectin, flufenoxuron and amitraz on Saudi Arabian dates. Food Chemistry 100: 1590–1593.
- Luke, M.A.; J.E. Froberg; G.M. Doose and H.T. Masumoto (1981). Improved multiresidue gas chromatographic determination of organophosphorus, organonitrogen, and organohalogen pesticides in produce, using flame photometric and electrolytic conductivity detectors. J. Assoc. Off. Anal. Chem. Vol. 64 No. 5: 1187-1195.
- Mallhof, E.C. (1975). Method for gas chromatographic determination residues of tokuthion and its oxon in plant and soil samples. Pflanzenschutz Nachrichten Bayer. 28: 882- 887.
- Mills, P.A; Bong, B.A.; Kaups, L.R. and J.A. Burke (1972). Elution solvent system for florasil column clean up in organochlorine pesticide residues analysis. J. AOAC 55(1): 34-43.
- Pdrez Clavljo M.; M. Plaza Medina, J. Sanz ; Asenslo J. Galbin and Bernal (1996). Decay study of pesticide residues in apple samples. Journal of Chromatography A, 740: 146-150.

Saenz BarrioC.; J. Sanz .; M. Plaza Medina; M. Perwz Clavijo and J. Galbin Bernal (1995).

Evaluation of the decay of malathion, dichlofluanid and fenitrothion pesticides in apple samples, using gas chromatography. Food Chemistry (52): 305-309.

Shady, M.F.A.; M.E.A. Hegazy; F.A. Adam; M.A. AbdEl-Baki and S.A. Shokr (2000). Persistence of malathion and prothiofos organophosphorus insecticides on and in some vegetable crops. Egypt. J.Agric. Res. 78(2): 605-621.

Walgenbach, J. F.; R. B. Leidy and T. J. Sheets (1991). Persistence of pesticides on tomato foliage and implications for control of tomato fruitworm. J. Econ. Entomol., 84: 978-986.

تحطم المبيدات الحشرية الديازينون و الفلوفينكسيرون على التفاح المصرى

² - سناء عبد القادر الصاوى¹ همد عبد الله محمود

¹ - المعمل المركزى للمبيدات ² - المعمل المركزى لتحليل متبقيات المبيدات و العناصر الثقيلة فى الأغذية - مركز البحوث الزراعية - دقى - جيزة - مصر

تم دراسة السلوك التحطمي لمبيد الفلوفينكسيرون و الديازينون و هى من المبيدات الحشرية الفطرية و ذلك أثناء فترة ما قبل الحصاد لمحصول التفاح المصرى صنف أنا 106 المنزرع تحت الأجواء المصرية. كانت نسبة الاسترجاع لمبيد الفلوفينكسيرون 89.3% و نسبة الاسترجاع لمبيد الديازينون 99.7%. أوضحت النتائج أن متبقيات هذه المبيدات على التفاح كانت 0.89 جزء فى المليون لمبيد الفلوفينكسيرون و التى حدث لها تحطم و وصلت الى 0.01 جزء فى المليون اى 98.8% و ذلك بعد 25 يوم من المعاملة. أما مبيد الديازينون فقد كان 0.9 جزء فى المليون و وصلت قيمته الى صفر بعد 20 يوم من المعاملة. كانت قيم فترة نصف العمر للفلوفينكسيرون و الديازينون 6.2 و 6.58 يوم على التوالى. كما اظهرت النتائج ان فترة ما قبل الحصاد للفلوفينكسيرون و الديازينون 25 و 6 يوم على التوالى تحت الظروف المصرية.