

PERSISTENCE OF DINICONAZOLE AND ETOXAZOLE IN BROAD BEAN PODS, PEELS, SEEDS AND ITS PLANTED SOIL

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ABSTRACT

Field experiments were conducted to investigate the persistence of diniconazole and etoxazole in broad bean pods, peels, seeds and soil. Samples were taken after zero, 1, 3, 5, 7, 9, 14 and 21 days after pesticides application. The diniconazole residue in plant samples was extracted by methanol, partition with dichloromethane, cleaned up using coagulation solution, while the soil samples were extracted with ethyl acetate. Estimation of diniconazole residues were performed by (GLC- ECD). Etoxazole was extracted from plants samples with acetone, and from soil samples using acetone: water (8: 2 v/v). The extract was partitioned with dichloromethane and cleaned-up through a florisil column. Determination of etoxazole residues were performed by HPLC-DAD. The recoveries of etoxazole and diniconazole were in the range between 81–99 %. The results indicated that the half-life values of diniconazole in pods, peels, seeds and soil were 2.46, 2.29, 5.25 and 5.56 days, respectively. While these values of etoxazole in pods, peels and soil were 2.27, 1.62 and 4.91 days, respectively. No residues of etoxazole could be detected in seeds. Diniconazole residue was below the MRL in seeds. The pre-harvest interval (PHI) of pods was in diniconazole application 9 days. And in case of etoxazole these were 11 days.

Keywords: persistence; diniconazole; etoxazole; broad bean; PHI; GLC

INTRODUCTION

Legumes in general are considered staple foods for many communities in different areas of the world. Broad bean *Vicia faba* L. is considered one of the most important economic crops in Egypt. It is grown on a large scale for human consumption and animal feed since its seeds are recognized as a good source of dietary protein and carbohydrates. The broad bean was subject to attack by many pests and a wide variety of plant protection products are applied to control diseases and attacks by insects and mites. This may lead to the presence of pesticide residues in pods offered commercially for public consumption (Ahmed *et al.* 2002; Eskenazi *et al.* 2008; Ismail *et al.* 2013).

Diniconazole is an azole fungicide exhibiting a broad spectrum of diseases such as powdery mildew, scab, brown rust, septoria and rhynchosporium through the inhibition of ergosterol biosynthesis. This fungicide is steroid demethylation inhibitors, acting mainly on the vegetative stages of fungi by blocking the mycelial growth either inside or on the surface

of the host plant (Khalfallah *et al.* 1998; Amer *et al.* 2007). The residual behaviour and dissipation half-life of diniconazole in cucumber, pepper, grapes, wheat, pear, strawberry, banana and soil were investigated (Cabras *et al.* 1990; Mahmoud 2004; Mahmoud and Eissa, 2007; Wei1 *et al.* 2007; Khay *et al.* 2008; Xia 2009; Hui-qin 2010; Mahmoud *et al.* 2010)

Etoxazole is considered fungicide, insecticide and acaricide. Main pests targeted are tetranychid spider mites such as *Panonychus spp.* and *Tetranychus spp.* Etoxazole is acting against eggs, larvae and nymphs of spider mites, but lacks any efficacy against male and female adults (Suzuki *et al.* 2002), works by inhibiting moulting (Shibuya 1999). Level and fate of etoxazole in vegetable crops and soil were reported (Malhat and Hassan 2011; Dedola *et al.* 2014). Pesticides reach the soil by direct or indirect way, then those chemicals are exposed to the degradation by either chemical/or microbial pathways involved with the soil system (Gruzdyev *et al.* 1983). The influence of soil properties along with environmental factors thus plays an important role in the persistence, transformation and efficacy of pesticides (Walker 1991; Yaduraju *et al.* 1994; Hirahara *et al.* 1997; Shokr *et al.* 2000; Malhat 2012). The pesticide residues on vegetable crops after application should be followed and the waiting periods between application and harvesting (PHI) should also be recommended to be sure that residues are below tolerance levels before marketing. Therefore, this research aims to estimate the residues of diniconazole and etoxazole in broad bean at different days of pre-harvest intervals to ensure its safe consumption.

MATERIALS AND METHODS

1. Reagents, Chemicals and Insecticides

All reagents and solvents used were analytical-reagent grade (Algomhuria Company for Trading Chemicals and Medical Appliances - Egypt). Analytical standard of diniconazole [(E)-1-(2, 4-dichlorophenyl)-4, 4-dimethyl-2-(1, 2, 4-triazol-1-yl)-1-penten-3-ol] (99%), etoxazole (RS)-5-tert-butyl-2-[2-(2, 6-difluorophenyl)-4, 5-dihydro-1, 3-oxazol-4-yl] phenetole (purity $\geq 98\%$), the formulated products of diniconazole, (Sumi-eight 5% EC) and of etoxazole (Baroque 10 % SC) were supplied by Sumitomo Chemical Co., Japan.

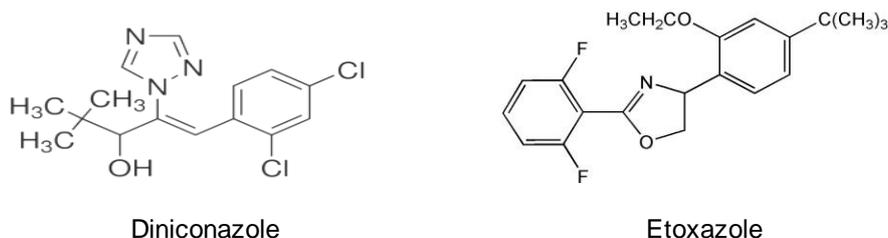


Figure 1: Chemical structure of diniconazole and etoxazole

2. Field trials

The field tests were carried out at the farm of Zarzora Research Station, Etay El-Baroud, at Beheira Governorate. Broad bean [(*Vicia faba* L.) cv. Nobarria 1] was planted on 13th November 2011. The experiments were designed in the following ways: plot size, 7 x 6 m; plot to plot distance, 1.5 m; plant to plant distance, 0.3 m and row to row distance, 0.7 m. Treatment plots were arranged in a randomized complete block design with four replications. Irrigation and fertilization were made according to the crop schedule.

Diniconazole and etoxazole were applied to bean plants as aqueous solutions of (Sumi-eight and Baroque trade names) with a knapsack sprayer (20 L) at the recommended rates (35 cm³/100 L) and (25 cm³/100 L), respectively. The spray was used at a recommended formulation volume of 200 L/feddan.

3. Sampling

After spray of the two pesticides, samples (500 g) of pods, peels, seeds (of broad bean) and soil were collected randomly from treated and untreated plots at zero time (one hour after treatment) as the initial deposits on 3rd April 2012, then 1, 3, 5, 7, 9, 11, 14 and 21 days after treatment. All samples were placed in bags and transported in ice boxes to laboratory chopped using a food cutter, all undesired parts involved in samples were avoided, and then the seeds were removed out of pods. Subsampling (50 g) was performed at the laboratory, and the subsamples were kept in deep freezing until analysis.

4. Extraction and clean up:

Diniconazole

The extraction and cleaning up of diniconazole residue from the broad bean plants were carried out according to Mallhof (1975). Representative subsamples of 50 g of sample was transferred into a blender stainless steel jar and homogenized with 200 ml of methanol for 2 min the macerate was filtered through a cotton pad into a graduated cylinder. A known volume (100 ml) of the extract was partitioned successively with 100, 50, 50 ml of methylene chloride in a 500 ml separating funnel after adding 30 ml of NaCl saturated solution. The combined methylene chloride phase was dried by filtration through a cotton pad and activated sodium sulphate anhydrous (Na₂SO₄) activated overnight at 110°C. The filtrate was evaporated to dryness with a rotary evaporator at 35°C. Then the residue was dissolved in 5ml methanol and cleaned up according to the method of Johnson (1963) using coagulation solution which was prepared as followed (ammonium chloride 0.5 g and 1 ml of orthophosphoric acid 85 % in 400 ml of distilled water). The solution was shaken well and cooled in a refrigerator. The dry extracts were dissolved in 5ml of distilled methanol and thoroughly mixed with 10 ml of coagulation solution and then filtered under vacuum through a 5 cm layer of Hyflo-super cell prepared in a 2.5 cm i.d. glass column on a plug of glass wool. The transfer was repeated three times using 5ml of methanol and 10 ml of coagulation solution each time. The filtrate was then collected in a 125 ml separating funnel and extracted with 30, 20, 10 ml methylene chloride, which was received on a layer of activated sodium sulphate anhydrous and

collected in a 100 ml flask, and then taken to evaporation using a rotary evaporator at 35°C. Residue of diniconazole was extracted from soil samples as follows: 50 g representative soil sample was transferred into a 500 ml stopper conical flask and extracted by shaking mechanically with 150 ml of ethyl acetate for 30 min. The extract was carefully decanted and filtered through a clean pad of cotton into 100 ml graduated cylinder. The filtrate was concentrated by using a rotary vacuum evaporator at 35°C.

Etoxazole

Extraction and cleaning up of etoxazole residue from the broad bean plant were carried out according to Malhat and Hassan (2011). Representative subsamples of 50 g of pods, peels, and seeds were blended with 150 ml of acetone for 2 min, and then filtrated through pad cotton into a graduated cylinder. The filtrate was evaporated to remove the acetone with a rotary evaporator (35°C). The concentrated solution was transferred into 500 ml separating funnel and partitioned with 100, 80, 50 ml methylene chloride after adding 30 ml of NaCl saturated solution. The combined methylene chloride phase was dried by filtration through a cotton pad and activated sodium sulphate anhydrous (Na₂SO₄) and concentrated to dryness with a rotary evaporator at 35°C. 50 g of the soil sample was transferred into a 500 ml stopper conical flask and extracted by shaking mechanically with 200 ml of acetone: water (80:20 v/v) for 1 h. The extract was carefully decanted and filtered through a clean pad of cotton. 100 ml of the filtrate was concentrated by using a rotary vacuum evaporator at 35°C to remove acetone and then extracted twice by 100 ml dichloromethane. The combined dichloromethane was dried through the anhydrous sodium sulphate and then evaporated near dryness at 35°C using a rotary vacuum evaporator. The extract was cleaned up using a chromatographic column (1.5 cm i.d. × 40 cm) prepared by adding a plug of glass wool, 6 g activated florisil (60-100 mesh) and 2 g of anhydrous sodium sulfate. The column was pre washed with about 40 ml of n-hexane and then the extract was eluted with 170 ml of n-hexane: acetone (97:3 v/v). The collected elute was concentrated to dryness with a rotary evaporator at 35°C.

5. Chromatographic analysis

Diniconazole

Agilent 6890 series gas chromatography (GC) system equipped with an Agilent 7673 auto-sampler, an electron- capture detector. A 30 m × 0.32 mm capillary column coated with a 0.25 µm thick film of 5 % phenyl methyl polysiloxane (HP-5) from Hewlett and Packard was used in combination with the following oven temperature program:

Initial temperature 230°C for 2 min, 6°C/min up to 280°C and held for 1 min. Nitrogen Carrier gas 4 ml/min., splitless injection of a 1µl volume was carried out, the detector and injector temperatures were 300°C and 280°C, respectively, under these conditions the retention time was 10.6 min.

Etoxazole

Estimation of etoxazole residues was performed by Agilent 1100 HPLC equipped with diode array detector. A hypercell ODS analytical column (150 mm × 4.6 mm i.d, 5 µl) was used. The mobile phase was (methanol/acetonitrile/water) (45/40/15, v/v/v) with a flow rate of 0.8 ml/min.,

and the injection volume was 20 µl. Detection wavelength set at 240 nm. At this condition the retention time of etoxazole was 9.1 min.

6. Residues calculation

The residues were calculated by applying the following equation of Mallhof (1975).

$$P_s \cdot B \cdot V / P_{st} \cdot G \cdot C * F$$

Where:

F=100/R (recovery factor)

P_{st} = standard peak area.

R =average of recovery.

V=final volume of sample solution (ml).

P_s = sample peak area.

B= amount of standard injected (ng).

G = sample weight

C= amount of sample solution injected (µl).

7. Recovery efficacy studies

Recovery studies were carried out to define the efficacy and the limit of quantization of the method used. The untreated samples of pods, peels, seeds and soil were fortified with pesticides used diniconazole and etoxazole active ingredient solution level 1, 0.5 and 0.1 mg kg⁻¹ for all plant matrices, then the procedures of extraction, cleaning up and determination that mentioned was performed on these spiked samples. Averages of recovery from spiked samples were illustrated in Table (1), the recovery values were calculated according to the following formula:

$$\text{Recovery \%} = (\mu\text{g pesticide residue/g sample found} / \mu\text{g pesticide residue/g sample added}) \times 100$$

8. Half-life calculation

Half-life times ($t_{1/2}$) of diniconazole and etoxazole were calculated mathematically according to Moye *et al.* (1987). The dissipation kinetics of pesticide residues were determined by plotting residue against elapsed time of application, and equation of best curve fit with maximum coefficients of determination (R^2) was determined. For dissipation of targeted pesticides in the samples, exponential relationship was found to be applicable corresponding to the general first-order kinetics equation:

$$C_t = C_0 e^{-kt}$$

Where C_t represents the concentration of the pesticide residue at the time of t , C_0 represents the initial deposits after application and k is the constant rate of pesticide disappearance per day. From this equation, the dissipation half-life periods ($t_{1/2} = \ln(2)/k$) of the pesticides.

9. Statistical analysis

Data were subjected to analysis of variance (ANOVA) followed by least significant difference (CoStat Statistical Software, 1990).

RESULTS AND DISCUSSION

Recovery of diniconazole and etoxazole

As clear from the Table 1, the recoveries ranged from 80.5–114 % and 80.91-92.37 for diniconazole and etoxazole, respectively.

Table (1) Recoveries and relative standard deviations of diniconazole and etoxazole from broad bean and soil at three levels

Pesticide	Fortification level (mg kg ⁻¹)	Pods	Peels	Seeds	Soil
		Recovery ^A (%)±RSD	Recovery ^A (%)±RSD	Recovery ^A (%)±RSD	Recovery ^A (%)±RSD
Diniconazole	0.1	81.25±2.7	80.91±3.72	89.40±4.53	109.02±1.94
	0.5	101.53±3.47	81.63±1.55	88.88±3.36	95.21±1.26
	1	114.00±4.16	82.80±2.77	80.50±1.11	95.56±1.87
Etoxazole	0.1	86.85±3.88	84.58±4.88	81.97±2.37	88.04±2.31
	0.5	92.37±1.47	84.41±1.28	83.15±1.46	89.75±1.54
	1	84.37±2.57	80.91±0.97	92.26±0.76	85.70±2.1

A: each value an average of three replicates

LOD: 0.002 mg kg⁻¹ for diniconazole and 100pg for etoxazole.

Residue of diniconazole and etoxazole in/on broad bean botanical parts

Residues and loss rates of diniconazole in and on broad bean pods were illustrated in Table (2). The initial deposit which remained on pods one hour after treatment was 0.262 mg kg⁻¹, this amount dropped to 0.174 mg kg⁻¹ one day after application indicating a loss rate of 33.58 %. Residue of diniconazole in and on pods of broad beans gradually decreased to 0.108, 0.071, 0.033, 0.007, and 0.004 mg kg⁻¹ indicated loss rates of 58.77, 72.90, 87.40, 97.32 and 98.47 %, at 3, 5, 7, 9 and 14 days after treatment, respectively. The residues at 21 days were below the estimated detection limit of diniconazole 0.002 mg kg⁻¹. The half-life time values were 2.46, 2.29 and 5.25 days from application in pods, peels and seeds, respectively.

Moreover, the residues of diniconazole residues in and on peels were 0.44 mg kg⁻¹, decrease to 0.259 mg kg⁻¹ indicating loss rate of 41.14 % at one day after treatment. Residue levels decreased to 0.175, 0.092, 0.055, 0.022 and 0.004 mg kg⁻¹ indicating loss rates of 60.23, 79.09, 87.50, 95 and 99.09 % at 3, 5, 7, 9 and 14 days after application, respectively. Furthermore diniconazole residues detected in seeds were 0.01, 0.016, 0.012, 0.008, 0.005, 0.004 and 0.001 mg kg⁻¹ at 0, 1, 3, 5, 7, 9 and 14 days after treatment, respectively. Diniconazole was not detected in the pods, peels and seeds after 21 days of the application. Data indicated that broad bean pods could be consumed safely after 9 days of application according to European Union (2013), where the recommended maximum residue limit (MRL) for diniconazole in broad bean (0.01 mg kg⁻¹). Statistical analysis showed that, there were significant differences of the mean residues among the parts of plants (peels, pods and seeds), the amount of residues on peels was more than that in/on pods and seeds. The highest half-life value was recorded in seeds (5.25 days), followed by pods (2.46 days) and peels (2.29 days). The dissipation of the pesticide residues in/on crops depends on environmental condition, type of application, plant species, dosage, and interval between applications, the relation between the treated surface and its weight and living state of the plant surface, in addition to harvest time (Cabras *et al.* 1990; Khay *et al.* 2008).

In previous study of Ahmed *et al.* (2002), who determined chlorpyrifos methyl and malathion in broad bean (pods, fresh seeds and peel). The half-

life values of chlorpyrifos methyl on a peel and pods were 25 and 23 hours, respectively. The pre-harvest interval should not be less than three weeks for whole fresh pods, while the half-life values of malathion on peels and pods were 5 days and 1 day, respectively. The pre-harvest interval of 13 and 6 days should be enforced for the consumption of peel and whole pods. No safety interval was needed for fresh or dry seed. Also Mahmoud (2004) found the initial deposits of diniconazole residue 0.32 and 0.12 mg kg⁻¹ in broad bean leaves and peels, respectively, decreased gradually to reach 0.03 and 0.02 mg kg⁻¹ at twenty days from application. The half-life values of diniconazole were 1.4, 4.2 and 1.2 days in leaves, peels and seeds, respectively.

Table (2) Residues and loss rate percentage of diniconazole fungicide in and on broad bean pods, peels, and seeds of broad bean plants

Time after application (Day)	Pods		Peels		Seeds	
	Residues ^A (mg kg ⁻¹)±SD	Loss (%)	Residues ^A (mg kg ⁻¹)±SD	Loss (%)	Residues ^A (mg kg ⁻¹)±SD	Loss (%)
Z	0.262±0.005	00.00	0.440±0.071	00.00	0.010±0.003	--
1	0.174±0.012	33.58	0.259±0.038	41.14	0.016±0.001	00.00
3	0.108±0.014	58.77	0.175±0.026	60.23	0.012±0.004	25.00
5	0.071±0.022	72.90	0.092±0.030	79.09	0.008±0.001	55.00
7	0.033±0.007	87.40	0.055±0.011	87.50	0.005±0.001	68.75
9	0.007±0.001	97.32	0.022±0.010	95.00	0.004±0.001	75.00
14	0.004±0.001	98.47	0.004±0.001	99.09	0.001±0.00	93.75
21	ND	100.00	ND	100.00	ND	100.00
\bar{X}	0.082 ^b		0.131 ^a		0.007 ^c	
HL (Day)	2.46		2.29		5.25	

A: Each value represents an average of three replicates

Z: One hours after the pesticide application (zero time) **ND:** Not detected

HL: Half-life time ($t_{1/2}$) **\bar{X} :** The mean residues of pods or peels or seeds

L.S.D_{0.05} among pods, peels and seeds= 0.0373

Residues and loss rates of etoxazole in and on broad bean pods were illustrated in Table (3). The initial deposit which remained on pods one hour after treatment was 0.355 mg kg⁻¹, this amount dropped to 0.191 mg kg⁻¹ one day after application indicating a loss rate of 46.19 %. Residue of etoxazole in and on pods of broad beans gradually decreased to 0.146, 0.076, 0.036, 0.026, 0.012 and 0.008 mg kg⁻¹ indicated loss rates of 58.87, 78.59, 89.85, 92.67, 96.62 and 97.74 % at 3, 5, 7, 9 and 14 days after treatment, respectively. In addition to data also showed that the value of etoxazole residue in and on peels was 1.69 mg kg⁻¹, and this decreased to 0.571 mg kg⁻¹ indicating loss rate of 66.2 % at one day after treatment. Residue levels decreased to 0.353, 0.225, 0.129, 0.067, 0.036 and 0.019 mg kg⁻¹ indicating loss rates of 79.11, 86.68, 92.36, 96.04, 97.87 and 98.87 % at 3, 5, 7, 9, 11 and 14 days after application, respectively. Residues were below the estimated detection limit of etoxazole after 21 days of the application. The half-life time values were 2.27 and 1.62 days after treatment for pods and

peels, respectively. Maximum residue limits (MRL) for etoxazole on broad bean according to Codex Alimentarius (2013) was 0.02 mg kg^{-1} . Data indicated that broad bean pods could be consumed safely after 11 days. While after one hour of the treatment, etoxazole was not detected in the seeds. It was found that a significant variation of the mean residues between peels and pods. While Malhat and Hassan (2011) indicated that the dissipation of etoxazole in green bean, in green bean pods and leaves the half-life values were 3.13 and 2.73 days, respectively, and its PHI was 4 days after the application. In the recent studies of Dedola *et al.* (2014), who reported that, etoxazole residues in tomatoes were lower than the limit of quantitation (LOQ) of the analytical method just after the treatment.

Residues and loss rates of diniconazole and etoxazole in soil under plants were presented in Table (4). The initial deposit which remained in the soil under broad bean plants, one hour after treatment was 0.045 mg kg^{-1} , this amount dropped to 0.038 mg kg^{-1} one day after application indicating a loss rate of 15.55 %. Residue of diniconazole in soil under broad bean plants gradually decreased to 0.028, 0.02, 0.016, 0.015, 0.006 and 0.004 mg kg^{-1} indicated loss rates of 37.77, 55.55, 64.44, 66.66, 86.66, and 91.11 %, respectively at 3, 5, 7, 9, 14, 21 and 28 days after treatment. The half-life time value was 5.56 days after treatment. The initial deposit of etoxazole remained in the soil under broad bean plants, one hour after treatment was 0.014 mg kg^{-1} , this amount dropped to 0.012 mg kg^{-1} one day after application indicating a loss rate of 14.28 %. Residue of etoxazole in soil under broad bean plants gradually decreased to 0.009, 0.006, 0.004, and 0.002 mg kg^{-1} indicated loss rates of 35.71, 57.14, 71.42, and 85.71 %, respectively, after 3, 5, 7, and 9 days of treatment, the half-life time value was 4.91 days after treatment. On the other hand, the results revealed that the degradation half-lives in soil were slower compared with half-lives on plant parts of broad bean, these are in agreement with Shokr *et al.* (2000), who reported that the residual behaviour of pirimiphos-methyl and prothiofos organophosphorus insecticides on the green pods of broad bean plants and the contamination of soil under these plants. The residue half-life values determined on green pods, peels and soil were 15.6, 15.6 and 144 hours for pirimiphos-methyl and 24.3, 16.8 and 120 hours for prothiofos, respectively. These results also agree with the data of Xia (2009) who investigated the dissipation half-life of diniconazole in wheat and soil, which was 6.77 and 11.97 days, respectively. And Malhat (2012) determined the residue levels of fenitrothion in/on green bean pods, leaves and soil under the treated plant. The results showed that the half-life ($t_{1/2}$) values of fenitrothion in green bean pods, leaves and soil were 1.79, 2.00 and 6.08 days, respectively.

Table (3) Residues and loss rates of etoxazole in and on broad bean pods, and peels of broad bean plants

Time after application (Day)	Pods		Peels		Seeds	
	Residues ^A (mg kg ⁻¹)±SD	Loss (%)	Residues ^A (mg kg ⁻¹)±SD	Loss (%)	Residues ^A (mg kg ⁻¹)±SD	Loss (%)
Z	0.355±0.035	00.00	1.69±0.125	00.00	ND	--
1	0.191±0.003	46.19	0.571±0.055	66.21	ND	--
3	0.146±0.012	58.87	0.353±0.029	79.11	ND	--
5	0.076±0.008	78.59	0.225±0.051	86.68	ND	--
7	0.036±0.003	89.85	0.129±0.004	92.36	ND	--
9	0.026±0.004	92.67	0.067±0.017	96.04	ND	--
11	0.012±0.003	96.62	0.036±0.003	97.87	ND	--
14	0.008±0.001	97.74	0.019±0.003	98.87	ND	--
21	ND	100.00	ND	100.00	ND	--
\bar{X}	0.345 ^a		0.094 ^d		--	
HL (Day)	2.27		1.62		--	

A: Each value represents an average of three replicates

Z: One hour after the pesticide application (zero time) ND: Not detected

HL: Half-life time ($t_{1/2}$) \bar{X} : The mean residues of pods or peels or seeds

L.S.D_{0.05} among pods, peels and seeds = 0.1238

Table (4) Residues and loss rate percentage of diniconazole and etoxazole in and on soil under broad bean plants

Time after application (Day)	Diniconazole		Etoxazole	
	Residues ^A (mg kg ⁻¹)±SD	Loss (%)	Residues ^A (mg kg ⁻¹)±SD	Loss (%)
Z	0.045±0.001	00.00	0.014±0.001	00.00
1	0.038±0.001	15.55	0.012±0.001	14.28
3	0.028±0.002	37.77	0.009±0.002	35.71
5	0.02±0.0002	55.55	0.006±0.001	57.14
7	0.016±0.001	64.44	0.004±0.0001	71.42
9	0.015±0.0001	66.66	0.002±0.004	85.71
14	0.006±0.0002	86.66	ND	100.00
21	0.004±0.001	91.11	ND	--
28	0.002±0.00	94.83	ND	--
\bar{X}	0.022 ^a		0.006 ^b	
HL (Day)	5.56		4.91	

A: Each value represents an average of three replicates ND: Not detected

Z: One hour after the pesticide application (zero time)HL: Half-life time ($t_{1/2}$)

L.S.D_{0.05} between diniconazole and etoxazole = 0.0028

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ثبات مبيد الدينيكونازول و الايتوكسازول فى قرون و قشور و بذور الفول البلدى و التربة المنزرعة به
على محمد شمس الدين^١ , محمد محمد عزب^١ , تهانى رشدى عبد الظاهر^١ ,
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أجريت دراسات حقلية لتقدير ثبات مبيد الدينيكونازول و الايتوكسازول فى القرون و القشور و البذور لنبات الفول البلدى و التربة المنزرعة به. و قد أخذت العينات على فترات زمنية مختلفة بعد ساعة واحدة من المعاملة , ١ , ٣ , ٥ , ٧ , ٩ , ١٤ , ٢١ يوم من المعاملة بالمبيدات تحت الدراسة.

حيث تم تقدير مبيد الايتوكسازول باستخدام التحليل الكروماتوجرافى السائل على الأداء بينما أستخدم الكروماتوجرافى الغازى المزود بالكشاف القابض للالكترونات فى تقدير مبيد الدينيكونازول. و كان معدل أسترجاع الايتوكسازول و الدينيكونازول يتراوح بين (٨١-٩٩%). و قد أوضحت النتائج أن فترة نصف العمر لمبيد الدينيكونازول فى القرون, القشور, البذور و التربة تساوى ٢,٤٦ و ٢,٢٩ و ٥,٢٥ و ٥,٥٦ يوم على التوالى. بينما كانت فترة نصف العمر لمبيد الايتوكسازول فى القرون و القشور و التربة ٢,٢٧ و ١,٦٢ و ٤,٩١ يوم على التوالى.

كما أوضحت النتائج أن فترة ما قبل الحصاد (فترة الامان) لمبيد الدينيكونازول فى قرون الفول البلدى ٩ يوم. بينما كانت لمبيد الايتوكسازول فى القرون ١١ يوم على القرون و لم يلاحظ وجود اى متبقى لمبيد الايتوكسازول فى البذور.