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Dissipation of Penconazole in Tomatoes and Soil

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Abstract Dissipation of penconazole was estimated in tomatoes fruits cultivated in field using QuEChERS method for sample preparation and high performance liquid chromatography with diode array detector. Following one application of normal dose 25 mL 100 L^{-1} water, the average initial deposits of penconazole were observed to be 0.74 and 1.21 mg kg^{-1} for tomatoes fruits and soil, respectively. The residues dissipated below the maximum residues limit of 0.2 mg kg^{-1} after 15 days. The half-life value (T1/2) and preharvest interval of penconazole were 5.61 and 15 days, respectively. While (T1/2) of penconazole in soil was 15.51 days. Thus, a waiting period of 15 day was suggested for the safe consumption of penconazole treated Tomatoes.

Keywords Penconazole · Dissipation · Tomatoes · Soil

Tomatoes (*Solanum lycopersicum*) are one of the most widely grown vegetables in the world and also the most important item of the fruit and vegetables processing sector (Engindeniz 2006). It's cultivated over a large area in Egypt. This important dietary component is used fresh or processed and canned for later use (Abd-Alrahman et al. 2011b; EL-Nabarawy et al. 1992). Among the fungicides effective against powdery mildew of tomato Topas-100 (10 % EC) has better eradication action and longer persistence.

Penconazole [(RS)-1-[2-(2,4-dichlorophenyl)pentyl]-1H-1,2,4-triazole] is a systemic triazole fungicide used for the preventative and control of powdery mildew (Pose-Juan et al. 2010). This fungicide is normally sprayed directly onto plants and is rapidly absorbed and distributed to the interior of the leaves (Kim et al. 2002). Excessive use of pesticides for the management of insect pests and diseases in crops is being taken seriously by the public due to their ill effects on the human health. Therefore it is important to ensure that the levels of residues of the pesticides at the time of harvest in the food stuffs do not pose any hazard to the consumers and their levels are below the acceptable limits in domestic as well as in international markets. The dissipation rate of a pesticide after application is a key process for the assessment of the preharvest interval (PHI) (Castillo-Sanchez et al. 2000; Fenoll et al. 2009).

QuEChERS is a (quick, easy, cheap, effective, rugged and safe) method which has been mainly applied for the extraction of different classes of pesticides (Abd-Alrahman et al. 2011a, 2011b; Garrido Frenich et al. 2008; Lehotay et al. 2005; Paya et al. 2007). The QuEChERS method is a simple, rapid, and inexpensive procedure requiring little labor and few materials, space, and solvents. This method achieved the status of Official Method of AOAC International (Lehotay 2007). Keeping in mind the dangers of chemicals, present study was undertaken to know the persistence of penconazole in tomatoes under subtropical conditions of Egypt.

Materials and Methods

Penconazole reference standard (95.5 % purity) was obtained from central agricultural pesticides laboratory,

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agricultural research center (CAPL, Egypt). Other solvents or chemicals used in this study were of analytical or HPLC grade. A stock standard solution of 1 mg mL^{-1} was prepared and was further diluted to obtain concentrations of 1, 5, 10, 25, 50 and 100 μg mL^{-1} in acetonitrile.

Tomatoes cultivated in the open field; every trial plot was 50 m^2. Trails and control plots were randomly selected and protective lines were set up between trial plots. Block scheme was used with three replications. The treatment was replicated three times using doses prescribed by the manufacturers 25 cm^3 100 L^{-1} water. Pesticide treatments were carried out with a backpack motorized sprayer with an adjustable nozzle size of 1 mm. About 1 kg Tomatoes fruits of marketable size were collected randomly at 0, 1, 3, 7, 15 and 21 days after the application of the fungicide. A control sample was also taken at each sampling time. Immediately after collecting the samples, each individual sample were put into plastic bags and transported to the laboratory. Soil samples was collected from the surface 0–10 cm depth, dried in shade, ground to pass through 2 mm sieve, and was stored in polythene bags at room temperature.

Portions (10 g) of soil was weighed and put into a 100 mL bottle with screw cap. Penconazole residues from soil samples were extracted using ethyl acetate (25 mL) by shaking on a shaker for 3 h. The ethyl acetate layer was separated and dried over 4 g of anhydrous $MgSO_4$.

The extraction and cleanup of Tomatoes samples for residues of penconazole was carried out as per procedure reported by (Abd-Alrahman et al. 2011a, 2011b), with slight modifications. After chopping and homogenization of a 1 kg sample at high speed for 5 min, 10 g of the homogenized sample were weighed in a 50 mL centrifuge tube. Fifteen milliliters of 1.0 % acidified acetonitrile with acetic acid were added; the screw cap was closed and vigorously shaken for 1 min using a Vortex mixer at maximum speed. Afterwards, 4 g of anhydrous $MgSO_4$, 1 g of NaCl, 1 g sodium citrate dihydrate and 0.5 g disodium hydrogen citrate sesquihydrates were added, then extracted by shaking vigorously on vortex for 2 min and centrifuged for 10 min at 5,000 rpm. An aliquot of 3 mL was transferred from the supernatant to new clean 5 mL centrifuge tube and cleaned by dispersive solid-phase extraction with 75 mg of PSA and 500 mg of magnesium sulfate. Afterwards, centrifugation was carried out at 6,000 rpm for 5 min. An aliquot 2 mL from the supernatant was filtered through a 0.2 μm PTFE filter (Millipore, USA) and then analyzed by Agilent 1,100 HPLC–DAD.

High performance liquid chromatography–diode array detector analysis was performed with an Agilent 1,100 liquid chromatography equipped with a photodiode array detector and quaternary pump. The separation was performed on a C_{18} column (150 × 4.6 mm, 5 μm). The mobile phase was acetonitrile and water (70: 30 v/v), using the flow rate 0.6 mL min^{-1} detection at 220 nm. Data analysis was applied by Chemistation software (Fig. 1).

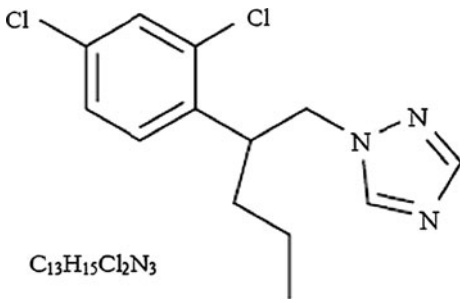

Fig. 1 Penconazole structural and chemical formula

Results and Discussion

The calibration curve of penconazole showed strong correlation between concentrations and area in the studied range (0–100 ng mL^{-1}) ($r2 \geq 0.995$). The LODs and LOQs were sufficiently low; 0.05 μg kg^{-1} and 0.1 μg kg^{-1}, respectively. These limits are, in all cases, below the maximum residue limits (MRLs) established by the codex committee on pesticide residues under the Joint FAO/WHO food standards program at 0.2 mg kg^{-1} for fruits (FAO/WHO, 2006). The method had a good repeatability expressed by the relative standard deviation (RSDs) ≤11 %. The average recoveries ranged from 92 % to 98 % in all cases, with RSD lower than 9.5 %. The QuEChERS method used to detect penconazole residues comprise an efficient extraction of each residue followed by clean-up using primary secondary amine (PSA) and

Table 1 Dissipation of penconazole in/on tomato fruits and soil

Days after application	Tomato fruits		Soil	
	Residue (mg/kg) mean ± SD	Loss %	Residue (mg/kg) mean ± SD	Loss %
Initial	0.74 ± 0.07	–	1.21 ± 0.10	–
1	0.69 ± 0.05	6.76	1.15 ± 0.08	4.96
3	0.45 ± 0.04	39.19	1.03 ± 0.08	14.88
7	0.36 ± 0.05	51.35	0.96 ± 0.10	22.31
10	0.29 ± 0.03	60.81	0.78 ± 0.06	29.75
15	0.18 ± 0.04	75.68	0.59 ± 0.08	51.24
21	0.11 ± 0.04	85.14	0.42 ± 0.10	65.29
MRL (mg/kg)	0.2		–	
t1/2 (day)	5.61		15.51	
PHI (day)	15.00		–	

Initial: 1 h post treatment

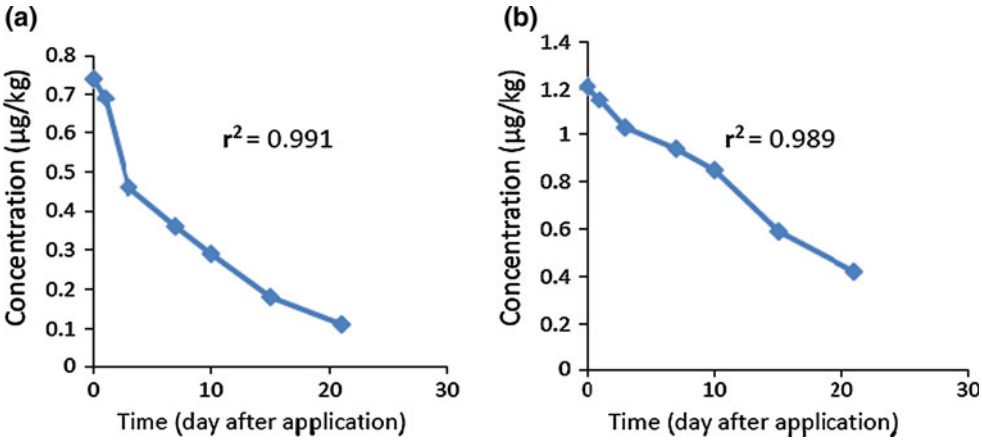

Fig. 2 Dissipation curve of penconazole **a** in Tomato fruits and **b** soil

magnesium sulfate anhydrous. This method and PSA clean up step improved the recovery of penconazole near to 100 %. The dissipation curves and mean residue levels of penconazole in tomatoes and soil during the sampling period derived from three sub samples are shown in (Table 1 and Fig. 2).

Results showed that the highest mean initial residues were 0.74 and 1.21 µg g^{-1} for tomatoes and soil, respectively. These deposits dissipated to 0.69, 0.45, 0.36, 0.29, 0.18 and 0.11 µg g^{-1} after 1, 3, 7, 10, 15 and 21 days, respectively. While in soil the residues of penconazole was degraded to 1.15, 1.03, 0.94, 0.85, 0.59 and 0.42 µg g^{-1} in 1, 3, 7, 10, 15 and 21 days, respectively. The dissipation dynamics followed the first order kinetics. The half-life value ($T_{1/2}$) was 5.61 and 15.51 days in tomatoes and soil, respectively. Earlier studies have shown that the rate of penconazole in different types of soil were found to be ranged from 41.2–57.9 days in predominantly anaerobic (flooded) and non-flooded soil, respectively (Singh and Dureja 2009). Other study reported that the half lives between 40 and 70 days are cited by Tomlin (World-Compendium 2000). However (Bromilow et al. 1999; Kim et al. 2003) showed that mineralization of propiconazole was faster in sandy loam soil than the clay loam suggesting that due to lesser sorption of the fungicide in sandy loam soil than clay loam, the fungicide was more accessible to biological degradation. The faster degradation of penconazole in our study may be due to higher microbial activity. Thorestensen and Lode have reported that propiconazole degraded faster in soil with lower organic carbon content (Thorestensen and Lode 2001). In conclusion; through QuEChERS method, we achieved a good analytical performance in terms of sensitivity (LODs, 0.05 µg kg^{-1}; LOQs, 0.1 µg kg^{-1}) and recovery rates (92 %–98 %). Thus, this method can be used for residue determination in the detection of penconazole residues with low levels. Penconazole has shown different dissipation rates: half-life(s) and PHI were 5.61 and 15 days, respectively in tomatoes fruits, while in soil half-life was 15.51 days. After PHI was determined, it was noted that the penconazole residue did not exceed the recommended MRL by the Codex Committee of 0.2 mg kg^{-1} for tomatoes.

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