



Dissipation behaviour and risk assessment of profenofos and triazophos in capsicum under sub-temperate conditions

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ABSTRACT

This study documents the residual persistence of profenofos and triazophos on capsicum fruits. The persistence was observed on 0, 1, 3, 5, 7, 10, 15 and 20 days of insecticides spray and analyzed using QuEChERS technique and estimated with Gas Chromatograph equipped with Flame Photometric Detector. The analysis revealed the presence of profenofos with less initial deposits of 1.403 mg/kg compared to 1.870 mg/kg of triazophos which further reduced to below detectable level (BDL) on 15th and 10th day with residual half-lives of 2.0 and 1.5 days, respectively. The different household processing (s) from washing to cooking gave residual relief up to 73.77%. The soil analysis revealed initial deposits of 0.913 and 0.816 mg/kg, for respective insecticides, which disappeared to BDL on 10th day. The waiting periods worked out at the limit of quantification (0.05 mg/kg) were 10 and 8 days, for profenofos and triazophos, respectively.

Key words: Bell pepper, Culinary processes, Insecticides, Persistence, Risk assessment

The presence of pesticide residues in food and their entry into the food chain has recently become a public debate pertaining to consumer's health. The rampant use of these chemicals has been resulting into a very strong campaign against the use of agro-chemicals on crops. However, tremendous benefits have been derived from the use of pesticides in agriculture, a sector upon which the Indian economy is largely dependent (Aktar *et al.* 2009). According to an estimate, every rupee invested in chemical pest control returns ₹ 3 in crops saved (Jeyanthi and Kombairaju 2005). A wide range of pesticides (13–14%) are used for the production of fruits and vegetables in India due to heavy pest infestation throughout the cropping season whereas cropped area is only 3% (Chandra *et al.* 2014). If pesticide formulations against pests are used at right dose, right time and right interval, there is no alarm about pesticide residues. However, non-approved and over use of some pesticides is the main cause of pesticide traces in the food and panic in consumers. A recent study has revealed that residues of insecticides such as profenofos and triazophos was surfacing in capsicum fruits throughout the country. India contributes one fourth of world production of capsicum with an average annual production of 0.9 million tonnes

from an area of 0.885 million ha with a productivity of 1 266 kg/ha (Sreedhara *et al.* 2013). It has occupied a pride place in Indian cuisine because of its delicacy and pleasant flavour. Capsicum is not only consumed as cooked, but taken as half cooked in many forms of fast food and as raw in salads. It is primarily chosen as a colourful enhancement in many food preparations. Hence taken into consideration the national issue, this experiment was carried out to evaluate the residual persistence of profenofos and triazophos in capsicum fruits and soil. Efforts were also made to study the effect of household processing (s) on the residues of these insecticides in capsicum fruits.

MATERIALS AND METHODS

Capsicum (*Capsicum annuum* L. var California Wonder) crop was grown as per the package of practices in a randomized block design at experimental farm of Department of Entomology of the University at Nauni, Solan (Himachal Pradesh), India during 2012-13. The insecticides, viz. profenofos and triazophos (Fig 1) were sprayed at two concentrations, i.e. single dose (500 g a.i./ha) and double dose (1 000 g a.i./ha) on the capsicum crop at fruit development stage twice at 20 days interval. Control plots were sprayed with water only. Three replicates were made for each treatment and each pesticide was applied once. Fruit samples (2 kg) were taken (2 hr) after pesticide application to determine the initial deposits of each pesticide after second spray. Afterward, the fruits were collected randomly from each treatment/replication at an interval of 1, 3, 5, 7, 10, 15 and 20 days. Similarly, the soil samples

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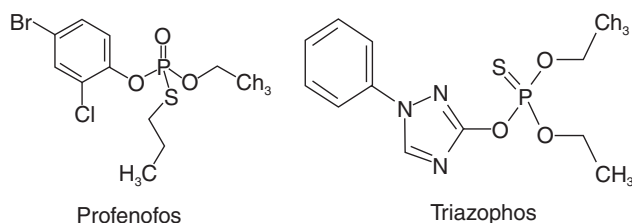


Fig 1 Chemical structure of profenofos and triazophos

(1 kg) were collected at 0 (2 hr after application), 3, 5, 10 and 15 days interval.

Samples collected at 1, 3 and 5 days after last insecticidal application washed and cooked and then analysed for insecticide residues. In the washing treatment, capsicum fruits were washed i) under a stream of running tap water by hand rubbing, dipped in ii) lukewarm water iii) 2% NaCl solution, all for 1 min, dried on a filter paper and then analysed. In cooking the fruit samples were cooked in i) an open pan and ii) in microwave, till ready to eat.

The Quick Easy Cheap Effective Rugged Safe (QuEChERS) technique was utilized with slight modifications for the residue analysis (Lehotay *et al.* 2005). The fruit sample of each replicate was chopped into small pieces and homogenized in blender at a high speed. From the homogenized sample, 15 g representative fruit sample was taken up with 20 ml acetonitrile in 50 ml centrifuge tube and homogenized at 15 000 rpm for 2 min by using low volume high speed homogenizer. The homogenizer was washed with 10 ml acetonitrile and pooled in 20 ml fraction. Anhydrous sodium chloride (10 g) was added into the tube, shaken at 50 rpm for 5 min with Rotospin mixer and then centrifuged at 2 500 rpm for 3 min. Upper layer fraction of 15 ml was transferred to another 50 ml centrifuge tube containing 10 g anhydrous sodium sulphate and was shaken for 5 min at 50 rpm. Anhydrous magnesium sulphate (900 mg), Primary Secondary Amines (150 mg) and Graphitized Carbon Black (50 mg) were taken in 15 ml centrifuge tube. The tube was capped and shaken for one minute on Spinix test tube shaker. Six millilitre fractions from 15 ml extract was added into the centrifuge tube, rotated for one min at 50 rpm in Rotospin mixer and centrifuged at 2 500 rpm for 10 min. The 4 ml fraction was transferred to the 30 ml turbo tube and evaporated in turbo evaporator to dryness in presence of nitrogen current at 45°C. The residues were dissolved in 2 ml n-hexane for gas chromatographic (GC) analysis.

Soil was analysed by another QuEChERS technique (Asensio-Ramos *et al.* 2010), with modifications. A representative 10 g sieved ground dry soil sample was taken in a 50 ml polypropylene centrifuge tube, to which 20 ml acetonitrile was added and allowed for shaking up to 1 min using a Rotospin mixer. To this 4 g of magnesium sulphate and 1 g of sodium chloride was added and centrifuged at 3 300 rpm for 3 min. After centrifugation, a 10 ml of supernatant was taken in another centrifuge tube

of 15 ml containing 1.5 g of magnesium sulphate and 0.250 g of Primary Secondary Amines, thereafter allowed for 3 min shaking. After shaking, the tube was sonicated for 3 min and then centrifuged for 10 minute at 4 400 rpm. From this tube 4 ml aliquot of the supernatant was taken in a turbo tube and evaporated to dryness in presence of nitrogen current at 45°C. The dried residue was then dissolved in 2 ml of n-hexane.

The estimation of the test insecticides was carried out by Gas Chromatograph equipped with FPD. Gas Chromatograph operating conditions were: Detector temperature 280°C, oven temperature condition for profenofos and triazophos: initial temperature 80°C held for 1 minute then increased to 250 °C @ 5°C and held for 2 minutes. Capillary glass column, Rxi®-5ms (30 mt, 0.25 mm ID, 0.25 µm film thickness), was used. Gas flow: 80.0 ml/min (hydrogen), 120.0 ml/min (zero air) and 0.9 ml/min (nitrogen). Under these conditions retention time of profenofos and triazophos was 16.252 and 18.117 min, respectively.

To ensure the results and to check the reliability of the analytical technique, as well as variation arises due to handling procedures, per cent recovery experiments were conducted with capsicum fruits and soil. The fruit and soil samples were fortified with each profenofos and triazophos at 0.05, 0.10, 0.25, 0.50 and 1.0 mg/kg. The insecticides persistence data were analyzed for correlation coefficient, regression equation residue half life (RL₅₀) and safe waiting period as per the method of Hoskins (1961).

RESULTS AND DISCUSSION

Recovery studies

The recoveries obtained were 95.33–116.00% from profenofos and 80.00–107.33% from triazophos in fruits, whereas, these were 85.33–106.66 and 84.00–98.53% in soil from the respective insecticides (Table 1). These recoveries were considered satisfactory, thus supported the method, when they were between 70 and 120%. The MRLs (Codex elementarius/PFA) of these test insecticides in capsicum were not available in the literature. Hence, the waiting periods of these insecticides in capsicum were calculated by considering Limit of Quantification as 0.05 mg/kg as MRL.

Table 1 Recovery of test insecticides from fortified capsicum fruits and soil

Fortification levels (mg/kg)	Recovery (%)			
	Fruits		Soil	
	Profenofos	Triazophos	Profenofos	Triazophos
0.05	100.00	80.00	85.33	84.00
0.10	113.33	100.00	87.33	89.66
0.25	109.33	100.00	93.33	98.53
0.50	116.00	101.33	95.33	98.00
1.00	95.33	107.33	106.66	90.33

Residue analysis of fruits

The residual persistence of tested insecticides in capsicum fruits showed that the minimum residues were traced in the profenofos as compared to triazophos treated field irrespective of doses (Table 2 and Fig 2). The initial deposits of profenofos on capsicum fruits were found to be 1.403 mg/kg at single dose and were 1.9 times lower than that obtained from double dose, i.e. 1.036 mg/kg. The residues receded to 0.953, 0.590, 0.206, 0.086 and 0.053 mg/kg after 1, 3, 5, 7 and 10 days after its treatment, respectively. Half life of profenofos was found to be 2.0 days and waiting period as 9.6 days. These results are in agreement with Sahoo *et al.* (2004) who reported 1.8 fold increase in the deposits of profenofos due to double dose over single dose on tomato fruits and less than two-fold deposits on brinjal fruits (Nigam *et al.* 2009). Profenofos dissipated to half in 2.0 and 2.6 days and receded above 90% within 7 days at respective doses. Nigam *et al.* (2009) observed reduction of 91% residues of profenofos from brinjal on 15th day of insecticide application, which supports the results of present findings. On the other hand, Renuka *et al.* (2006) observed that residues of profenofos applied at 0.05% on cardamom were dissipated to below detectable limit in 30 days after application.

The initial deposits of triazophos were observed 1.870 mg/kg at zero day, 0.943 mg/kg after one day, 0.056 mg/kg after 7 days and it decreased to below detectable limit after 10 days of its treatment. The waiting period and half-life of triazophos were worked out as 7.6 and 2.0 days, respectively. Degradation kinetics of triazophos showed 49.55% degradation after one day, 89.12% after 5 days and 96.96% after 7 days of treatment. The initial deposits of triazophos on capsicum fruits were found to be 1.870 mg/kg at single dose and 3.053 mg/kg at double dose (Table 2). The deposits of triazophos due to single dose were 1.6 times lower than that of double dose on fruits, which is in agreement with the results of XueSheng *et al.* (2005), who reported 1.8 fold increase in deposits due to double dose over single dose of triazophos in lychee fruit pulp. Triazophos dissipated to half, readily than others in 1.5

Table 2 Dissipation of profenofos and triazophos residues from capsicum fruits at single dose

Interval (Days)	Average residue (mg/kg) \pm SD	
	Profenofos (500 g a.i./ha)	Triazophos (500 g a.i./ha)
0	1.403 \pm 0.010	1.870 \pm 0.02
1	0.953 \pm 0.005 (32.07)	0.943 \pm 0.02 (49.55)
3	0.590 \pm 0.020 (57.96)	0.456 \pm 0.09 (75.57)
5	0.206 \pm 0.005 (85.27)	0.203 \pm 0.05 (89.12)
7	0.086 \pm 0.005 (93.82)	0.056 \pm 0.005 (96.96)
10	0.053 \pm 0.005 (96.20)	BDL
15	BDL	BDL
Control	ND	ND
RL ₅₀ (days)	2.0	1.5
Waiting period (days)		9.6 7.6

BDL - below detectable level (0.05 mg/kg), ND - not detected. Figures in parenthesis indicate % dissipation.

and 1.7 days and its residues persisted up to 7 and 10 days at respective single and double doses (Table 2). At double dose, the terminal residues of profenofos and triazophos recorded were 0.086, 0.053 mg/kg after 15 and 10 days, respectively after their treatment (Fig 2).

Decontamination studies

The effects of food processing on pesticide residue levels may be influenced by the physical location of the pesticide residue as well as the physicochemical properties of the pesticide such as solubility, volatility, hydrolytic rate constants, water-octanol partition coefficient and thermal degradation (Keikotlhaile *et al.* 2010). The effect of household processing on insecticide residues revealed that washing of capsicum fruits with running tap water, reduced the residues of profenofos and triazophos by 20.97-41.93 and 20.14-45.90%, respectively. However, Sheikh *et al.* (2013) observed the higher level of reduction of profenofos residues (53.6%) compared to those recorded in our study.

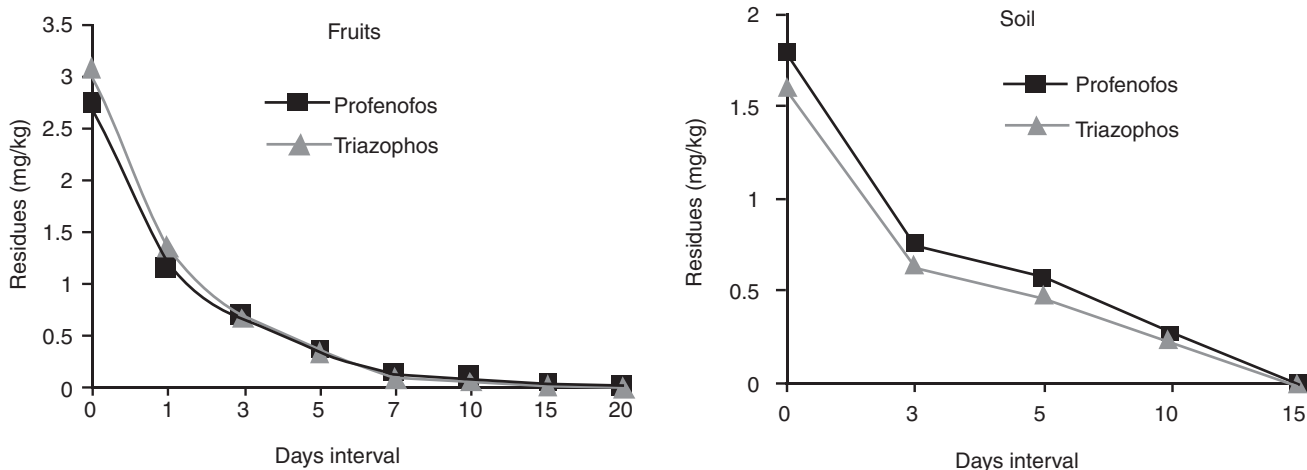


Fig 2 Dissipation of insecticide residues at double dose from capsicum fruits and soil

Table 3 Dissipation of profenofos and triazophos residues from capsicum cropped soil at single dose

Interval (Days)	Average residue (mg/kg) \pm SD	
	Profenofos (500 g a.i./ha)	Triazophos (500 g a.i./ha)
0	0.913 \pm 0.010	0.816 \pm 0.010
3	0.293 \pm 0.005 (67.88)	0.250 \pm 0.010 (69.39)
5	0.186 \pm 0.005 (80.66)	0.136 \pm 0.005 (83.67)
10	BDL	BDL
Control	ND	ND
RL ₅₀ (days)	2.1	1.9

BDL - below detectable level (0.05 mg/kg) ND - not detected. Figures in parenthesis indicates % dissipation

Washing of capsicum fruits with saline (NaCl @ 2%) water for 5 min provided 31.46-51.61 and 29.32-54.09% relief from profenofos and triazophos residues, respectively. In the present investigations, 37.76-61.29 and 32.86-40.14% relief from profenofos and triazophos residues was obtained when lukewarm water was used to wash the insecticide treated capsicum fruits. Kong *et al.* (2012) performed decontamination of rice with salt (NaCl) solutions and obtained up to 35.3% loss of residues, showing consistency with our results. Aktar *et al.* (2010) dipped cabbage in 2% brine solution followed by washing and reported 39.62-43.52% reduction of organophosphorus pesticides residues, while the reduction was increased in hot brine solution, which supports the outcome of the present findings.

An open pan cooking of capsicum fruits provided 50.34-66.12 and 48.05-68.85% relief from residues of profenofos and triazophos, which enhanced from 61.18-70.96 and 59.71-73.77% in microwave cooking, respectively. Aktar *et al.* (2008) observed washing followed by cooking as an effective residue dislodging method (25.50-81.50%) for organophosphorus pesticides on okra, depending on doses.

Residues analysis of soil

The residue data from insecticides under investigation showed that profenofos dissipated above 80% within 5 days and reached below the detectable level after 10 and 15 days at single and double doses, respectively. Like profenofos, triazophos dissipated to the extent of 83.67 and 85.00% on 5th and 10th day at the respective doses and thereafter, the residues receded to below the detectable level (Table 3 and Fig 1). The residue half-lives observed for profenofos and triazophos were 2.1 and 1.9 days, respectively, at single dose.

The results obtained by Gupta *et al.* (2011) showed that profenofos dissipated with the time. Mukherjee *et al.* (2012) reported no residues in soil samples collected after 7th day from tomato and eggplant cropped soils and thus agreed with the results of present study. The 90% disappearance of triazophos from cotton soil was observed in 21 days by Wei *et al.* (2008). These results showed

deviation from the present investigation, owing to the difference in edaphic characteristics and climatic conditions.

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