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# Estimation of Residues of Profenofos in/on Tomato, *Lycopersicon esculentum* Mill

S. K. Sahoo, S. K. Kapoor, B. Singh

Department of Entomology, Punjab Agricultural University, Ludhiana 141 004, India

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Tomato (*Lycopersicon esculentum* Mill) is one of the most important vegetable crop of tropical and subtropical regions of the world. The tomato yield in India is considerably lower because of several factors, the most important being the damage caused by insect pests. The tomato fruit borer, *Helicoverpa armigera* (Hubner) which is the most serious pest of tomato has been found to exhibit resistance to all the groups of synthetic insecticides (Kapoor *et al*., 2000). However, profenofos @ 500 g a.i. $ha^{-1}$ have been found to be quite effective in management of this pest (Sagar *et al*., 2001). Profenofos is a non-systemic insecticide and acaricide with contact and stomach action. Pesticides applied to food crops leave residues which may be hazardous to the consumers. The dissipation of an insecticide varies with the nature of the insecticide, dosage applied, number of applications, interval between applications, crop variety, agroclimatic conditions, etc. Since no published information seems to be available on the residues of profenofos on tomato under Indian climatic conditions, the present studies were, undertaken to determine the residues of profenofos on tomato at different time intervals and suggest suitable waiting periods.

## MATERIALS AND METHODS

Tomato crop (var. Punjab Chhuhara) was raised at the Entomological Research Farm, Punjab Agricultural University, Ludhiana, during *Rabi* season 2001-2002 following recommended agronomic practices (Anonymous 2001a). The technical material of profenofos (92.1%purity) and its formulation (Carina 50EC) were supplied by M/s Pesticide India, Udaipur, India. All the solvents used were of laboratory grade and redistilled. The suitability of solvents and other chemicals was ensured by running reagent blanks before actual analysis. Profenofos (Carina 50EC) was sprayed @ 500 and 1000 g a.i. $ha^{-1}$ first at 50 % flowering stage and subsequently at 15 days intervals. There were three replications for each treatment. Representative samples of tomato were collected from each treatment at varying intervals after second and third spray. About one kg samples of marketable size tomato fruits were taken at 0, 1, 3, 5, 7, 10 and 15 days after the second and third spray. These samples were extracted, cleaned up and analyzed following method of Luke *et al* (1975) with slight modification as described below:-

*Correspondence to:* S. K. Sahoo, c/o S. K. Kapoor

A representative sample of chopped fruits (50g) was blended with 100 ml of water in a blender for 2 minutes. Acetone (100ml) was added to the blender and shaken gently for 5minutes. The extract was filtered through glass wool plugged in a funnel. The residual pulp was re-extracted with 50 ml of acetone and filtered. Finally, a washing was given to the blender and the funnel containing the residual pulp with acetone and the extracts were combined.

The combined extracts thus obtained were transferred to a separatory funnel of 1 litre capacity, diluted with 500 ml of 2 per cent aqueous solution of sodium chloride and partitioned thrice into 100, 50 and 50 ml of dichloromethane. The combined dichloromethane extracts thus obtained were concentrated to 2–3 ml *in vacuo* using a rotary evaporator at a temperature below 35°C.

The extracts were cleaned up by column chromatography using silica gel (60-120 mesh) as an adsorbent. Before use, the silica gel was activated at 110°C for 2 hours. A glass column (1.5cm dia x 60 cm long) was packed with activated silica gel (10–12 g + 1g charcoal) in between the two small layers of anhydrous sodium sulphate supported on a plug of glass wool. The column was pre washed with hexane following which the concentrated extract was poured over it. The extract was eluted with a freshly prepared solvent mixture of chloroform-acetone (1:1, v/v). The eluate was concentrated to near dryness in a rotary evaporator *under vacuum* and then transferred to 5 ml acetone for further analysis.

The estimation of profenofos residues was carried out on a gas liquid chromatograph (GLC) equipped with nitrogen–phosphorus detector (NPD) and a pyrex glass column (1m x 2mm i.d.) packed with 3 per cent DC 200 on 100–120 mesh gas chrom Q. The operating conditions of GLC were as follows: Detector temperature:280°C, Oven (column) temperature:205°C, Injector temperature:260°C, Carrier gas ($N_2$) flow rate:3.5 kg $cm^{-2}$, Air flow:1.2 kg $cm^{-2}$ and Hydrogen flow: 0.5 kg $cm^{-2}$. Under these operating conditions, profenofos gave a peak with retention time of 4.2 minutes. The average recoveries from tomato samples spiked with concentration ranging from 0.25 to 1.0 mg $kg^{-1}$ were found to be more than 80%. Therefore the results are presented as such without applying correction factor. The minimum limit of detection for profenofos was found to be 0.08 mg $kg^{-1}$. The half- life ($RL_{50}$) as well as time required to reach below the tolerance level ($T_{tol}$) was calculated by using Hoskins formula (1961).

## RESULTS AND DISCUSSION

The overall results of the analysis of tomato fruits following 2nd and 3rd spraying of the crop with profenofos @ 500 and 1000 g a.i. $ha^{-1}$ are presented in Table 1. Immediately after the second spray, the mean initial deposits of profenofos were 1.37 and 2.52 mg $kg^{-1}$ on the fruits of tomato at minimum effective and double the effective dosages respectively. The results are in agreement with the findings of Abdalla *et al* (1993) who reported an initial deposit of 2.85 mg $kg^{-1}$ following

application of profenofos @ 0.75 lit $ac^{-1}$ . These levels were reduced to 0.78 and 1.37 mg $kg^{-1}$ and 0.30 and 0.47 mg $kg^{-1}$ after one and five days respectively. Following the third spray, the mean initial deposits of 1.40 and 2.62 mg $kg^{-1}$ dissipated to levels of 0.77 and 1.36 mg $kg^{-1}$ and 0.18 and 0.23 mg $kg^{-1}$ after one and seven days, respectively. The maximum residue limit (MRL) of 0.5 mg $kg^{-1}$ has been prescribed for profenofos in/on tomato (Anonymous, 2001b). Following application @ 500 a.i.$ha^{-1}$, the residues of profenofos in/on tomato were found to be below the MRL after 3 days of application. However, it took 5 days to reach below the MRL when the crop was sprayed @ 1000 g a.i.$ha^{-1}$. These results can be further substantiated with the help of dissipation parameters calculated in the present investigations. It was found that profenofos residues reached below the MRL on 3.10 and 5.01 days (Ttol) at single and double dose respectively following second spray while it was found to be 2.96 and 4.60 days following third spray. The residues reached below the detectable limit of 0.08 mg $kg^{-1}$ after 15 days of application. Ahmed and Moursy (1991), also reported that profenofos residues persisted in tomato, garlic and strawberries up to three weeks after its 2nd application.

**Table 1.** Mean residues (mg $kg^{-1}$) of profenofos in/on tomato.

| Days after Spray | Residues level (mg $kg^{-1}$) | | | |
|---|---|---|---|---|
| | Second Spray | | Third Spray | |
| | 500 g a.i.$ha^{-1}$ | 1000 g a.i.$ha^{-1}$ | 500 g a.i.$ha^{-1}$ | 1000 g a.i.$ha^{-1}$ |
| 0 (1hr) | 1.37 | 2.52 | 1.40 | 2.62 |
| 1 | 0.78 (43.1)* | 1.37 (45.6) | 0.77 (45.0) | 1.36 (48.1) |
| 3 | 0.42 (69.3) | 0.71 (71.8) | 0.40 (71.4) | 0.65 (75.2) |
| 5 | 0.30 (78.1) | 0.47 (81.4) | 0.27 (80.7) | 0.39 (85.1) |
| 7 | 0.18 (86.9) | 0.30 (88.1) | 0.18 (87.1) | 0.23 (91.2) |
| 10 | 0.10 (92.7) | 0.14 (94.4) | 0.08 (94.3) | 0.12 (95.4) |
| 15 | BDL | BDL | BDL | BDL |
| $T_{tol}$ (days) | 3.10 | 5.01 | 2.96 | 4.60 |
| $RL_{50}$ (days) | 2.79 | 2.55 | 2.59 | 2.33 |

BDL = Below Detectable Limit (< 0.08 mg $kg^{-1}$)
*Figures in parenthesis indicates % dissipation

The half-life ($RL_{50}$) values varied from 2.59 to 2.79 and 2.33 to 2.55 days at lower and higher dosages respectively. The present results are similar to Abdalla *et al* (1993) who also reported a half life of 3.2 days following application of profenofos @ 0.75 lit $ac^{-1}$.

Enzyme inhibition thin layer chromatography (EI –TLC), described by Mendoza (1972) was used with slight modifications for the confirmation of profenofos residues in tomato at different intervals. The limit of detectibility of profenofos by this method was found to be 0.20 mg $kg^{-1}$. Following applications of profenofos @ 500 and 1000 g a.i.$ha^{-1}$, the residues of the toxicant could be detected upto 5 and 7 days in tomato samples collected from both the treatments, respectively. However the residues were found to be present at trace levels at the $7^{th}$ and $10^{th}$ days after applications at the lower and higher dosages. The residues couldn't be detected after 10 and 15 days of application at both the dosages, respectively. A similar trend was observed when the samples were analyzed after $3^{rd}$ spray of profenofos.

The mean initial deposit of 1.40 mg $kg^{-1}$ of profenofos on tomato samples @ 500g a.i. $ha^{-1}$, were reduced to 0.81 mg $kg^{-1}$ as a result of washing, thus accounting for a loss of 42 per cent. In case of tomato fruits taken after one day of application, washing reduced profenofos residues by 36.4 per cent. Tomato fruits collected one hour after spray @ 1000g a.i. $ha^{-1}$ when washed contained profenofos residues at a level of 1.36 mg $kg^{-1}$ as compared to unwashed fruits which were having 2.62 mg $kg^{-1}$(Table 2).

**Table 2.** Effect of washing on the reduction of profenofos residues on tomato following $3^{rd}$ spray.

| Days after spray | Mean residue level ( mg $kg^{-1}$ ) | | Per cent reduction |
|---|---|---|---|
| | Before washing | After washing | |
| | 500 g a.i. $ha^{-1}$ | | |
| 0 | 1.40 | 0.81 | 42.0 |
| 1 | 0.77 | 0.49 | 36.4 |
| | 1000 g a.i. $ha^{-1}$ | | |
| 0 | 2.62 | 1.36 | 48.0 |
| 1 | 1.36 | 0.82 | 39.7 |

Thus washing of tomato fruits with water removed 48 per cent of profenofos residues. However only 39.7 per cent residues could be removed from samples collected after one day following application of 1000g a.i of profenofos per hectare. Jain *et al* (1979) reported removal of 52 per cent fenvalerate residues from treated tomato by washing with water whereas Ismail *et al* (1993) reported only 22.9 per cent removal of profenofos from treated tomato by washing.

These studies, therefore suggest that the use of profenofos at the minimum effective dosages does not seem to pose any hazards to the consumers if a waiting period of 3 day is observed. Moreover, the consumer can further reduce the risk by washing the treated tomato fruits thoroughly with plain water before consumption.

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