Degradation dynamics of quinalphos on cabbage under subtropical conditions of Ludhiana, Punjab, India

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ABSTRACT: A study was undertaken to determine the disappearance trends of quinalphos residues on cabbage under subtropical conditions at Ludhiana. Single application of quinalphos was made @ 500 and 1000 g a.i. ha\(^{-1}\) on cabbage and samples were collected at intervals of 0 (1 h), 1, 3, 5, 7, 10 and 15 days after application. Average initial deposits of quinalphos on cabbage were found to be 0.41 and 0.75 mg kg\(^{-1}\) at single dose and double dosages, respectively. Residues of quinalphos dissipated below determination limit of 0.01 mg kg\(^{-1}\) in 7 and 10 days, respectively at single and double dose. The half-life of quinalphos on cabbage was observed to be 3.02 and 2.70 days for single and double dose, respectively. The study suggested a waiting period of 7 days for safe consumption of cabbage.

Keywords: quinalphos; residues; cabbage; persistence; waiting period

Introduction

Cabbage (Brassica oleracea var. capitata L.) is an important cole crop of India. This is widely cultivated throughout the sub-tropical parts of north India, with annual production of 3.39 million tonnes [1]. In Punjab, the area under cabbage is 3.34 thousand hectares with a production of 73.23 thousand tonnes [2]. Cabbage is heavily attacked by many insect pests, resulting in severe loss of quality and production. The major insect pests responsible for crop losses are stem borer (Hellula undalis), diamond-back moth (Plutella xylostella), leaf eating caterpillars and aphids [3, 4]. A number of organochlorine, organophosphate, carbamate and pyrethroid insecticides have been

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recommended against various insect pests of cabbage. Quinalphos, O,O-diethyl-O-quinoxalin-2-yl-phosphorothioate (Figure 1) is a selective insecticide, intensively used by the farmers in many parts of India as a crop protection measure. It is solid at low temperature having melting point 31.5 °C and is very toxic to mammals (LD₅₀ 71 mg kg⁻¹) [5]. It is recommended (@ 500 g a.i. ha⁻¹) for the management of diamond-back moth and tobacco caterpillar on cabbage [6]. Accumulation of quinalphos residues in cabbage pose human health hazards as quinalphos is very toxic chemical [7]. Studies revealed that in India about 50-70% of vegetables are contaminated with insecticides residues [8], mainly due to harvesting the crops before the safe waiting period. Waiting period between the time of application and harvesting of vegetables reduced the risk of harmful effects of insecticides on consumer [9]. Therefore, the present investigation was carried out to study the dissipation of quinalphos on cabbage and soil, with the objective to estimate safe waiting period.

![Figure 1. Structure of quinalphos.](image)

**Material and Methods**

**Chemicals and reagents**

The certified reference standard of quinalphos (purity 99.2%) was obtained from Dr Ehrenstorfer, India. All the solvents used in this study were of analytical grade. Before use these were redistilled in all glass apparatus and their suitability was ensured by running reagent blanks along with actual analysis. Stock solution of quinalphos was prepared at 1000 μg mL⁻¹ in hexane. Working standards ranging from 0.10 to 2.0 μg mL⁻¹ were prepared by appropriate dilutions and stored at 4 °C.

**Field experiment and collection of samples**

The field experiment was conducted at Entomological Research Farm, Punjab Agricultural University, Ludhiana during 2009. Cabbage (var. Drum head) was raised according to recommended agronomic practices [5]. There were three replications for each treatment i.e. untreated control (T₁), Quinalphos 25 EC @ 500 g a.i. ha⁻¹ (T₂) and Quinalphos 25 EC @ 1000 g a.i. ha⁻¹ (T₃). Single application of quinalphos 25 EC was made @ 500 and 1000 g a.i. ha⁻¹ on cabbage crop at 50 percent head formation using knapsack sprayer equipped with triple action nozzle. Water used to dissolve the formulation was @ 500 mL ha⁻¹. Untreated control plots were sprayed with water only.
The experiments were laid out in randomized block design (RBD). Analysis of cabbage samples were carried out on 0, 1, 3, 5, 7, 10 and 15 days after the application of insecticide. Soil samples were collected after 15 days of the application. The characteristics of field soil were sand 78.0%, slit 10.2%, clay 11.8%, organic carbon 0.30%, EC 0.30 dsm\(^{-1}\) and pH 8.0.

**Extraction and clean-up of residues**

The cabbage samples were harvested from each plot, pooled together, packed in plastic bags and transported to laboratory for processing. A total of 2 kg sample were collected for each treatment. Samples were cut into small pieces, mixed in a waring blender and a representative 50 g chopped and macerated cabbage sample was dipped overnight into 100 mL acetone in an erlenmayer flask. The extract was filtered into 1 L separatory funnel along with rinsings of acetone. The filtrate in the separatory funnel was diluted with 600 mL brine solution and partitioned the contents into with dichloromethane (2 × 75 mL) and hexane (2 × 75 mL). Dichloromethane and hexane fractions were combined, dried over anhydrous sodium sulfate and treated with 500 mg activated charcoal powder for about 2-3 hours at room temperature. The clear extract so obtained was filtered through Whatman filter paper No.1, concentrated to near dryness and again added about 20 mL hexane and concentrated using rotary vacuum evaporator at 30 °C. Repeated the process to completely evaporate dichloromethane and the final volume was reconstituted to about 5 mL using hexane. A representative 50 g soil sample were taken for analysis and processed as per the method described above without any charcoal cleanup.

**Estimation of residues**

Gas chromatographic (GC) analysis was carried out on gas chromatograph (Shimadzu GC 2010) equipped with a FTD and capillary column (Rtx-5, 30.0 m × 0.25 mm ID, 0.25-μm film thickness). The column temperature was initially held at 190 °C for 2 min., raised to 220 °C at a rate of 10 °C min\(^{-1}\) and held for 10 min. Other conditions were: injector temperature 290 °C, detector temperature 300 °C, gas flow: nitrogen- 30 mL min\(^{-1}\); hydrogen -3.0 mL min\(^{-1}\) and zero air -145 mL min\(^{-1}\). Under these operating conditions the retention time of quinalphos was found to be 9.98 min. The 2 μL extracts were injected onto the GC column in a pulsed splitless mode.

**Confirmation of residues**

The residues of quinalphos on cabbage were confirmed by gas chromatograph mass spectrometer (GC-MS) in selective ion monitoring (SIM) mode. The gas chromatograph (Shimadzu-QP 2010) with autoinjector, equipped with mass spectrometer and capillary column Rtx-5 Sil MS (30 m × 0.25 mm i.d. × 0.25 μm film thickness) was
used to verify the results. The system software used was GCMS solution version 2.5. The
GC-MS operating conditions were: injector temperature 285 °C, oven initial temperature
was 80 °C and held for 3.0 min, raised to 180 °C at a rate of 20 °C min⁻¹ and held for 2
min, then ramped 5 °C min⁻¹ to 260 °C, ion source temperature 200 °C, interface
temperature was 290 °C. Helium was used as a carrier gas with a flow rate of 0.94 mL
min⁻¹. The fragmentation of quinalphos produced selective m/z ions 118, 146, 156, 157
and 269. The treated samples also showed the presence of these ions, it confirms the
presence of quinalphos.

**Calculation of residues**

The residue content was calculated by using the formula:

\[
\text{Residues in ppm (μg/g)} = \frac{A_1 \times C \times V_1}{A_2 \times W \times V_2}
\]

Where,
- \(A_1\) = Peak area of the sample, in chromatogram
- \(A_2\) = Peak area of the standard, in chromatogram
- \(V_1\) = Total volume of the sample (mL)
- \(C\) = Concentration of analytical standards in ng
- \(W\) = Weight of sample (g)
- \(V_2\) = Injected volume of the sample (μL)

**Recovery studies**

Recovery assays were performed by spiking blank samples prior to extraction at
three different concentration levels viz. 0.05, 0.10 and 0.15 mg kg⁻¹, with three
replicates for each level. Recoveries were calculated by the formula that the actual
measured concentrations were compared against the expected concentrations in the
blank samples. Mean recoveries of quinalphos were found to be consistent and more than
80% (Table 1).

**Results and Discussion**

The results of dissipation of quinalphos in cabbage and soil are presented in Table 2 (Figure 2). Average initial deposit of quinalphos on cabbage were found to be 0.41 and
0.75 mg kg⁻¹, in recommended dose and double the recommended dose, respectively.
About 40-43 % dissipation of quinalphos was observed after 24 hours of spraying. After
5 days, the residues further reduced to 0.10 and 0.20 mg kg⁻¹, respectively, in single
dose and double dose. The residues of quinalphos dissipated below its determination limit
of 0.01 mg kg⁻¹ in 7 and 10 days at recommended and double the recommended
dosages, respectively. Soil samples collected 15 days after the spraying did not reveal the presence of quinalphos residue (Table 2). The half-life of quinalphos on cabbage were observed to be 3.02 and 2.70 days, respectively, in single and double dose. The residues were confirmed on GC-MS with m/z ratio 146. The identified ions were 118, 146, 156, 157 and 269 (Figure 3).

**Table 1. Recovery of quinalphos on cabbage and soil**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Level of fortification (mg kg(^{-1}))</th>
<th>% Recovery*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cabbage</td>
<td>0.15</td>
<td>90.44 ± 1.39</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>88.67 ± 2.08</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>88.33 ± 2.31</td>
</tr>
<tr>
<td>Soil</td>
<td>0.15</td>
<td>85.31 ± 1.42</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>87.26 ± 2.65</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>88.73 ± 3.09</td>
</tr>
</tbody>
</table>

* Mean ± SD of the three replication

**Table 2. Residues of quinalphos (mg kg\(^{-1}\)) on cabbage and soil at different time intervals after application of quinalphos 25 EC @ 2000 mL and 4000 mL ha\(^{-1}\)**

<table>
<thead>
<tr>
<th>Days after application</th>
<th>Quinalphos @ 500 g a.i. ha(^{-1})</th>
<th>Quinalphos @ 1000 g a.i. ha(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Replicates</td>
<td>Mean±S.D.</td>
</tr>
<tr>
<td>Before application</td>
<td>BDL</td>
<td></td>
</tr>
<tr>
<td>0 (1 hr after spray)</td>
<td>BDL 0.40</td>
<td>0.41 ± 0.01</td>
</tr>
<tr>
<td>1</td>
<td>0.23 ± 0.02</td>
<td>43.90</td>
</tr>
<tr>
<td>3</td>
<td>0.21 ± 0.01</td>
<td>48.78</td>
</tr>
<tr>
<td>5</td>
<td>0.10 ± 0.01</td>
<td>75.61</td>
</tr>
<tr>
<td>7</td>
<td>BDL</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>BDL</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>BDL</td>
<td></td>
</tr>
<tr>
<td>Soil samples after 15 days</td>
<td>BDL</td>
<td></td>
</tr>
</tbody>
</table>

**T\(_{1/2}\) (days)**  3.02  2.70

BDL= Below determination limit of 0.01 mg kg\(^{-1}\)

In a persistence study of quinalphos on cabbage [4] the initial deposits of quinalphos was found to be 1.59 and 3.62 mg kg\(^{-1}\), respectively, when quinalphos was applied @ 0.05 and 0.10 % concentration and calculated waiting period and half-life were
2.5 and 4.2 days and 1.3 and 1.3 days for lower and higher dosages, respectively. In another study [1] it was observed that following four applications of quinalphos @ 500 and 1000 g.a.i. ha⁻¹, the residues of quinalphos dissipated below determination limit of 0.01 mg kg⁻¹ in 10 days, in both the treatments. The results were in conformity with findings of present work. On cauliflower curds the initial deposits of quinalphos was observed to be 2.28 and 3.94 mg kg⁻¹ in single and double dose, respectively [10]. The variations in initial deposits reported by other researchers may be due to variation in insecticide formulation, growing season, variety of crop, method of analysis and weather conditions.

![Semi-logarithm graph showing dissipation kinetics of quinalphos on cabbage.](image)

**Fig.2** Semi-logarithm graph showing dissipation kinetics of quinalphos on cabbage. Regression equation $y = -0.36x + 2.13$ (single dose) and $y = -0.33x + 2.38$ (double dose).
Conclusion

Quinalphos is intensively used by the farmers in northern India as plant protection in cabbage. The half life values of quinalphos were 3.02 and 2.70 days, in recommended and double the recommended dosages, respectively, which showed the persistence nature of the quinalphos. The safe waiting period 7.0 days is suggested for recommended dose of quinalphos on cabbage. Therefore, quinalphos could be used as a protective measure in cabbage without any risk of toxic residues to consumers if the safe waiting period is maintained after recommended application.

References and Notes

11, 194.


