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Dissipation of Quinalphos in Kinnow Mandarin Fruits under Subtropical Conditions of Punjab, India

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Abstract Quinalphos residues were studied separately in the pulp and rind of kinnow mandarin fruits by following a standardized methodology and estimated on gas liquid chromatograph (GC) by employing nitrogen phosphorus detector. Following application of quanilphos (Ekalux 25EC) at 10.0 and 20.0 mL per tree (per 5 L of water) on kinnow mandarin fruits at both these dosages were found to be 0.05 and 0.16 mg/kg, respectively. These initial deposits were found to be less than its maximum residue limit (MRL) of 0.25 mg/kg. The corresponding values in the rind were found to be 0.65 and 1.64 mg/kg, respectively. These residue levels in the rind dissipated below the MRL in 5 and 15 days, respectively. The half-life value for quanilphos in the rind at single and double dosages were found to be 3.2 and 4.0 days, respectively. Low dissipation rate of quanilphos in the rind may be attributed to the fibrous nature of the peel where the insecticide can be adsorbed, high moisture content and oil based nature of the rind. The results clearly show that quanilphos does not penetrate into the pulp of the kinnow mandarin and the fruit is safe for consumption even after one day of the application at both these dosages.

Keywords Quanilphos · Kinnow mandarin fruits · MRL · Residues

Quinalphos (0,0-diethyl 0-quinoxlin-2-yl phosphorothioate) has been found to be quite effective for the citrus psylla, *Diaphorina citri* Kuwayana (Anonymous 2002; Batra et al. 1990; Chakravarty et al. 1998). However, considerable concern is being expressed by various agencies over the magnitude of pest control chemicals left in food stuffs following their use while raising the crop. Therefore, it is important to ensure that the levels of harvest time residues of quinalphos in kinnow mandarin fruits do not pose any hazard to consumers and are admissible in domestic as well as international trade. Although some scanty information on this aspect is available in literature (Cabrus et al. 1997; Torress et al. 1997), the present field trials were conducted to study the persistence of quinalphos in the pulp and rind of kinnow mandarin fruits separately under subtropical conditions of Punjab, India.

Materials and Methods

Field experiments were conducted during 2003–2004 on 20 year old kinnow mandarin plants at Regional Research Station, Abohar, Punjab. The crop were raised according to the recommended agronomic practices (Anonymous 2002). Three replicates were selected for each treatment i.e. control, recommended dose and double the recommended dose. Each fruiting tree required 5 L of spray volume. Control trees were treated with water only. Two applications of quinalphos (Ekalux 25EC) were made at weekly interval both for recommended dose of 2.0 mL/L and double the recommended dose of 4.0 mL/L of water. About 10–12 fruits were collected randomly covering all directions from treated trees before and after 0, 1, 3, 5, 7, 10 and 15 days of the second application of the insecticide. The fruit samples collected from each treated tree were packed into separate polythene bags and transported to the laboratory. Each polythene bag containing treated fruits

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was unpacked and the fruits were peeled and separated into pulp and rind. Individual pulp units were pooled together, mixed thoroughly and quarterised and sub-sample of about 300 g drawn, out of which 50 g was processed immediately and the rest was stored in deep freezer at −20°C. A similar treatment was given to the rind units from each treated tree.

A representative 50 g pulp was blended in a mixture using about 100 mL acetone. The extract was filtered through glass wool plugged in a filtering funnel into 1 L separatory funnel. The residual material was rinsed with acetone and transferred to the same separatory funnel. The contents of 1 L separatory funnel were diluted with 600 mL brine solution and partitioned into 100, 50 and 50 mL dichloromethane and was dried over anhydrous sodium sulfate. Treated the extract with 500 mg activated charcoal powder for about 2 h. Filtered the clean extract through Whatman filter paper No.1 and concentrated to about 5 mL at less than 30°C using rotary vacuum evaporator.

The residues of quinalphos were estimated on GC-NPD. A pyrex glass column 1 m × 2 mm i.d. packed with 3% OV-101 on Chromosorb W HP, 80–100 mesh was used for estimation of residues of quinalphos. The operating parameters of the instrument were: injection port temp 250°C, column 240°C and detector 270°C, nitrogen flow at 40 mL/min, hydrogen flow 30 mL/min and zero air flow 100 mL/min. Under these operating conditions the retention time of quinalphos was found to be 2.62 min.

The control samples of both the rind and pulp of kinnow mandarian fruits were spiked at 0.1 and 0.2 mg/kg, respectively, and processed by following the methodology as described above. The results revealed that per cent mean ± SD recoveries for pulp samples at both these levels were 94.8 ± 7.6 and 107.7 ± 3.8, respectively. The corresponding values for the rind samples were 101.3 ± 6.7 and 92.6 ± 5.6, respectively (Table 1). The results have been reported as such without applying any correction factors. The minimum limits of determination for quinalphos in both the pulp and the rind of kinnow mandarin fruits was found to be 0.01 mg/kg.

Table 1 Recovery of quinalphos from the pulp and the rind of kinnow mandarin fruits

Substrate	Level of fortification (mg/kg)	Recovery
Pulp	0.10	94.8 ± 7.6
	0.20	101.7 ± 3.8
Rind	0.10	101.3 ± 6.7
	0.20	92.6 ± 5.6

Each value is mean ± SD of three replicates

Results and Discussion

Residues of quinalphos were detected separately both in the rind and the pulp of kinnow mandarin fruits after its second application at 2.0 (0.05% a.i.) and 4.0 (0.10% a.i.) mL/L, respectively. The average initial deposits of quinalphos at single and double the dosages were observed to be 0.65 and 1.64 mg/kg, respectively, in the rind (Table 2). However, the corresponding average initial deposit of quinalphos in the pulp was found to be 0.05 and 0.16 mg/kg, respectively, at both the dosages which were found to be less than its maximum residue limit (MRL) of 0.25 mg kg^{-1} (Table 3). However, quinalphos residues in the pulp were below determination limit of 0.01 mg/kg after third day of application of the insecticide. These results clearly indicate that quinalphos does not penetrate into the pulp of the fruit. Cabrass et al. (1997), reported persistence of seven organophosphorus insecticides, viz; chlorpyriphos methyl, dimethoate, fenthion, methidithion, parathion, parathion methyl and quinalphos. The residues of these insecticides were found only in fruits peel with exception of dimethoate. Geetha and Regupathy (1999) in a field trial on cashew fruits revealed that residue levels of quinalphos 20AF applied four times at monthly interval at 0.5, 0.2 or 1.10% were below detectable limits of 0.05 and 0.10 mg/kg in both the fruits and the nuts, respectively, at harvest time. Pesticide in orange juice sold in Connecticut and originating from Florida and Brazil were detected in 6 out of 17 samples analyzed and contained residues of ethion, azinphos methyl, chlorpyriphos or phorate, however, all the residues were below EPA limits (Hankin and Pylypiw 1991).

It was interesting to note the residues of quinalphos dissipated in the rind slowly initially up to three days to the extent of about 32 and 18% at single and double dosages, respectively. However on day five the residues declined suddenly corresponding to the extent of 67 and 74%, respectively. Thereafter, the residues of quinalphos degraded very slowly and at the end of 15 days the residues declined to the extent of 75 to 87%, respectively. Half-life value (Table 2) for quinalphos in rind at single and double dosages were found to be 3.2 and 4.0 days, respectively. The residues of quinalphos in the rind were found below its MRL of 0.25 mg/kg at recommended and double the recommended dosages on day 5 and 15, respectively. Cabras et al. (1995) studied the degradation of quinalphos use to control *Dacus oleae* (*Bactrocera oleao*) and found that degradation showed pseudo first order kinetics with correlation coefficients ranging between −0.936 and −0.998. During 8 months storage of Olive oil, quinalphos did not show any remarkable difference in its concentration. In a dissipation study, done on grapes, the initial deposits of quinalphos at recommended and double the recommended

Table 2 Residues of quinalphos (mg/kg) in the rind of kinnow mandarin fruits

Days after treatment	Single dose (2 mL/L water)			Double dose (4 mL/L water)		
	Replicates	Mean ± SD	Dissipation (%)	Replicates	Mean ± SD	Dissipation (%)
Before application	BDL	BDL	–	BDL	BDL	–
	BDL			BDL		
	BDL			BDL		
0	0.70	0.65 ± 0.05	–	1.86	1.64 ± 0.24	–
	0.66			1.38		
	0.59			1.67		
1	0.60	0.63 ± 0.08	3.10	1.82	1.53 ± 0.27	6.80
	0.72			1.28		
	0.57			1.50		
3	0.49	0.44 ± 0.08	32.40	1.48	1.34 ± 0.29	18.30
	0.35			1.53		
	0.47			1.01		
5	0.19	0.22 ± 0.04	66.70	0.39	0.35 ± 0.04	73.90
	0.26			0.35		
	0.21			0.31		
7	0.17	0.18 ± 0.02	72.40	0.29	0.32 ± 0.04	80.50
	0.17			0.30		
	0.20			0.37		
10	0.17	0.16 ± 0.01	75.40	0.33	0.29 ± 0.02	82.40
	0.16			0.24		
	0.15			0.30		
15	0.17	0.16 ± 0.01	75.40	0.22	0.22 ± 0.01	86.60
	0.17			0.22		
	0.15			0.23		

BDL: Below detectable level of 0.01 mg/kg

Table 3 Residues (mg/kg) of quinalphos in the pulp of kinnow mandarin fruits

Days after treatment	Single dose (2 mL/L water)		Double dose (4 mL/L water)	
	Replicates	Mean ± SD	Replicates	Mean ± SD
Before application	BDL	BDL	BDL	BDL
	BDL		BDL	
	BDL		BDL	
0	0.04	0.05 ± 0.01	0.19	0.16 ± 0.03
	0.06		0.16	
	0.05		0.13	
1	0.02	0.02 ± 0.01	0.04	0.03 ± 0.01
	0.01		0.03	
	0.03		0.03	
3	BDL	BDL	BDL	BDL
	BDL		BDL	
	BDL		BDL	

BDL: Below detectable level of 0.01 mg/kg

dose were found to be 1.42 and 3.66 mg/kg, respectively, and these residue levels reduced to 0.043 and 0.072 mg/kg, respectively, 21 days after last application (Padadopoulou-Mourkidou et al. 1995).

Pesticides were estimated in peaches and apple in Piedmont areas by employing HPLC and found that about 30% peaches samples were positive for quinalphos and maximum contamination was found to the extent of

0.309 mg/kg (Brana and Quaglino 1990). About 200 samples of citrus fruits viz, lemon grape fruits and oranges were analysed from markets of Valencian Community (Spain) for 12 organophosphorus compounds including quinalphos. It was revealed that quanilphos did not exceed its MRL value in any of the fruit samples (Torress et al. 1997).

These results are clearly indicative of the fact quinalphos does not penetrate into the fruit pulp. However, low residue levels detected in the pulp seems only due to physical transference through hand during peeling of the fruits. Moreover, low dissipation rate of quinalphos in the rind may be due to fibrous nature of the peel where the insecticide can be adsorbed, high moisture content and also due to waxy texture of the rind that the insecticide is not easily vaporized and degraded completely.

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