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Degradation Dynamics and Persistence of Quinolphos and Methomyl In/On Okra (*Ablemoschus esculentus*) Fruits and Cropped Soil

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Abstract Dissipation of Quinalphos (Ekalux 20 AF) and Methomyl (Lannate 12.5 L) residues were studied in/on Okra (var. Pusa Sawani) fruits and cropped soil at Baruipur, West Bengal, India. The insecticides were applied at 21 days after sowing by foliar spray at the recommended and double the recommended dose (i.e. 500 and 1,000 g a.i. ha^{-1} in both the cases). Four sprays were given at 15 days interval in all the cases. The initial build-up residue on Okra fruits was to the magnitude of 3.20 and 7.50 μg g^{-1} for Quinalphos, 5.61 and 8.42 μg g^{-1} for Methomyl at lower and higher doses respectively. The half-lives ($t_{1/2}$) in Okra fruit were found to be 1.25–1.43 days for Quinalphos and 0.88–0.94 days for Methomyl. The safe waiting period (T_{MRL}) determined were 6.7 and 5.3 days at the lower dose of Quinalphos. The corresponding waiting period for Methomyl were 5.7 and 4.9 days. Decontamination process like washing and cooking dislodged 25.50%–81.50% residue depending on insecticides and doses, whereas 20.00%–69.60% surface residue was removed by washing alone. The residues of both insecticides in soil persisted for 6–8 days depending on dose. The half-lives in soil were found to be 1.07–1.20 days for Quinalphos and 0.97–1.25 days for Methomyl.

Keywords Okra · Quinalphos · Methomyl · Residue · Decontamination

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The maximum yield loss of Okra (*Abelmoschus esculentus*) per year are due to the attack of Okra shoot and fruit borer (*Earias vittella* L.) and Jassids (*Amrasca bigutulla bigutulla* Ishida) (Easwaramurthi et al. 1976; Awata et al. 1984). There are various chemicals to control them effectively. Quinalphos (O,O-diethyl O-quinoxalin-2-yl-phosphorothioate) [$C_{12}H_{15}N_2O_3PS$] and Methomyl (S-methyl-1-*N*-[(methylcarbamoyl) oxy] thioacetimidate) [$C_5H_{10}N_2O_2S$] both are used as selective insecticides to control Okra shoot and fruit borer and Jassid with high efficiency. Among the plant protecting chemicals Quinalphos (LD_{50}: 62–137 mg kg^{-1}) and Methomyl (LD_{50}: 17–24 mg kg^{-1}) are very toxic (Banerjee et al. 2006). Accumulation of toxic residues in fruits can be minimized to some extent by fixing the safe waiting period between the time of application and packing up (harvesting) of fruits (Kumari et al. 2004). Information regarding residue (Awasthi et al. 1984) data of Quinalphos and Methomyl in Okra fruits is meager under West Bengal agro-climatic condition, particularly during pre-kharif period (Feb–June). The present investigation was conducted to determine the dissipation pattern as well as the residue level of Quinalphos and Methomyl present in cropped soil, fresh, washed and both washed followed by cooked fruits for consecutive two seasons under West Bengal (East-Indian) climatic condition. Here various processes to decontaminate the residues are also discussed.

Materials and Methods

A two season field study was conducted at University Research Farm, University of Calcutta, Baruipur, 24-Pgs (S), West Bengal, India for consecutive two seasons (pre-kharif i.e. Feb–June in 2003 and 2004) on Okra [variety—"Pusa Sawani"]. The commercial formulations of Quinalphos (Ekalux 20 AF) and Methomyl (Lannate 12.5 L) were applied at 21 days after sowing as foliar spray at 500 g a.i. ha^{-1} (T_1), 1,000 g a.i. ha^{-1} (T_2) for Quinalphos and 500 g a.i. ha^{-1} (T_3), 1,000 g a.i. ha^{-1} (T_4) for Methomyl along with untreated control (T_5). Four sprays were given at 15 days interval along with untreated control (T_5) in both the cases. Each treatment including control was replicated thrice in a randomized block design (RBD). The size of each plot was 5 × 4 m. The residual fate of the insecticide formulations (i.e. Quinalphos and Methomyl) were studied on the four substrates i.e., fresh fruits, only washed fruits (for 1 min), both washed followed by cooked (5 min) fruits and cropped soil. All samples were collected at 0 (3 h after application), 2, 4, 6, 8 and 10 days interval after last application for dissipation study. All solvents were analytical grade and redistilled before use. Water was double glass distilled before use.

For Quinalphos (Ekalux 20 AF) soil samples were collected at a depth of 0–15 cm with the help of soil auger and representative amount of sample (100 g) was kept in a conical flask with 200 mL mixture of acetone:water (7:3, v/v) for 6 h. Then it was homogenized for 3 min using Remi Automix Blender. Then 10 g of celite was added in to the homogenate and again homogenized for 1 min. Then the homogenate was filtered through a buchner funnel using Whatman No. 1 filter paper followed by washing with 2 × 30 mL of acetone. The filtrate was concentrated in a rotary vacuum evaporator at 40°C and transferred to a separatory funnel along with 100 mL distilled water and 20 g of NaCl. Then it was partitioned with (100 + 50 mL) n-hexane. The hexane phase was discarded. Then the aquash portion was partitioned with (100 + 50 + 50 mL) chloroform and combined organic layer was collected through anhydrous sodium sulphate. The organic layer was concentrated to dryness in a rotary vacuum evaporator at 40°C and volume was made up to 10 mL with distilled ethyl acetate for GLC analysis.

For Methomyl (Lannate 12.5 L) soil samples were collected as described earlier. Here soil samples were soaked in 200 mL ethyl acetate for 6 h instead of acetonitrile:water mixture. Then it was blended for 5 min using Remi Automix Blender. Then it was filtered through a buchner funnel using Whatman No. 1 filter paper followed by washing with 2 × 100 mL of ethyl acetate. The filtrate was then mixed with 5 mL of water followed by concentration in a rotary vacuum evaporator at 40°C. Then the concentrate was transferred to a separatory funnel along with 100 mL of distilled water and 20 g of NaCl. Then it was acidified by adding 5 mL of 1 (N) H_2SO_4 followed by partition with (3 × 50 mL) n-hexane. The hexane phase was discarded. Then the aquash phase was partitioned with (3 × 50 mL) chloroform and combined organic layer was collected through anhydrous sodium sulphate. The organic layer was concentrated to dryness in a rotary vacuum evaporator at 40°C and volume was made up to 10 mL with acetonitrile for HPLC analysis.

For both the insecticides representative fruit samples (50 g each) were blended with 150 mL acetonitrile:water (9:1, v/v) in a Remi Automix Blender for 3 min and filtered through a buchner funnel using 100 mL acetonitrile:water (9:1, v/v) as washing solvent. Then the similar steps were followed as described above.

Final analysis of Methomyl (Lannate 12.5 L) residues in cropped soil, fresh, washed and washed followed by cooked fruit samples were done by HPLC (Shimadzu Model No. SPD M 1O A) equipped with Photo Diode Array Detector. The C-18 reverse phase column (15 cm × 4.6 mm i.d.) along with guard column was used. The mixture of acetonitrile and water (4:6, v/v) was used as mobile phase for the detection of Methomyl residue. The other parameters like flow rate, wavelength (λ_{max}), retention time, limit of quantification (LOQ) and limit of detection (LOD) were 1 mL min^{-1}, 240 nm, 3.17 ± 0.2 min, 0.05 μg g^{-1} and 0.01 μg g^{-1} respectively.

Final analysis of Quinalphos (Ekalux 20 AF) residues in cropped soil, fresh, washed and washed followed by cooked fruit samples were done by GC (Agilent Technologies 6890N Network GC system) with electron capture detector (ECD) coupled with Chemito 5000 data processor. The glass column (1.8 m × 2 mm i.d.) packed with DC-200 (3%) WAW on Chromosorb WHP (80–100 mesh) was used. The temperatures were: Oven 180°C, Injector 220°C, Detector 300°C. Flow rate of carrier gas (nitrogen) was 60 mL min^{-1}. The retention time, limit of detection (LOD) and limit of quantification (LOQ) were 4.04 ± 0.2 min, 0.01 μg g^{-1} and 0.05 μg g^{-1} respectively.

A recovery study was carried out in order to establish the reliability of the analytical method and to know the efficiency of the extraction and clean up steps employed for the present investigation. Cropped soil and fruit samples were spiked with 0.25, 1.0, 5.0 ppm analytical standard of Quinalphos and Methomyl separately and the average recoveries were 82%–84% and 86%–89% for Quinalphos and Methomyl respectively.

Results and Discussion

The residue data at different days interval, dissipation percentage, regression equation, half life and safe waiting

Table 1 Dissipation of Quinalphos in/on Okra cropped soil (pooled data for 2 years)

Interval from last spray (days)	Residue in ppm [M* ± SD] (% of dissipation)	
	T_1 (500 g a.i. ha^{-1})	T_2 (1,000 g a.i. ha^{-1})
0	1.75 ± 0.19 (–)	3.17 ± 0.10 (–)
2	0.79 ± 0.05 (54.82)	1.50 ± 0.13 (52.63)
4	0.32 ± 0.04 (81.71)	0.66 ± 0.07 (79.14)
6	0.05 ± 0.01 (97.12)	0.13 ± 0.03 (95.81)
8	BDL (–)	0.04 ± 0.01 (98.72)
10	BDL (–)	BDL (–)
Regression equation	Y = 2.39 − 0.28X	Y = 2.63 − 0.25X
Half-life in soil (d)	1.07	1.20

BDL = below detectable limit (<0.01 ppm)

M* = Mean of three replicate

Table 2 Dissipation of Methomyl in/on Okra cropped soil (pooled data for 2 years)

Interval from last spray (days)	Residue in ppm [M* ± SD] (% of dissipation)	
	T_3 (500 g a.i. ha^{-1})	T_4 (1,000 g a.i. ha^{-1})
0	2.83 ± 0.31 (–)	3.84 ± 0.33 (–)
2	0.88 ± 0.14 (68.90)	1.72 ± 0.14 (55.20)
4	0.32 ± 0.09 (88.69)	0.76 ± 0.07 (80.20)
6	0.04 ± 0.01 (98.58)	0.32 ± 0.07 (91.66)
8	BDL (–)	0.08 ± 0.01 (97.91)
10	BDL (–)	BDL (–)
Regression equation	Y = 2.53 − 0.31X	Y = 2.74 − 0.24X
Half-life in fruits (d)	0.97	1.25

BDL = below detectable limit (<0.01 ppm)

M* = Mean of three replicate

Table 3 Dissipation of Quinalphos in/on Okra fruits (pooled data for 2 years)

Interval from last spray (days)	Residue in ppm [M* ± SD] (% of dissipation)	
	T_1 (500 g a.i. ha^{-1})	T_2 (1,000 g a.i. ha^{-1})
0	3.20 ± 0.30 (–)	7.50 ± 0.14 (–)
2	1.30 ± 0.36 (59.37)	4.10 ± 0.20 (45.33)
4	0.80 ± 0.36 (75.01)	1.80 ± 0.83 (76.02)
6	0.20 ± 0.12 (93.75)	0.60 ± 0.21 (92.31)
8	0.06 ± 0.02 (98.12)	0.08 ± 0.02 (98.93)
10	BDL (–)	BDL (–)
Regression equation	Y = 2.66 − 0.24X	Y = 2.81 − 0.21X
Half-life in fruits (d)	1.25 days	1.43 days
Waiting period (T_{MRL})	5.28 days	6.7 days

BDL = below detectable limit (<0.01 ppm)

M* = Mean of three replicate

Table 4 Dissipation of Methomyl in/on Okra fruits (pooled data for 2 years)

Interval from last spray (days)	Residue in ppm [M* ± SD] (% of dissipation)	
	T_3 (500 g a.i. ha^{-1})	T_4 (1,000 g a.i. ha^{-1})
0	5.61 ± 0.47 (–)	8.42 ± 0.24 (–)
2	2.19 ± 0.30 (60.96)	3.90 ± 0.39 (53.68)
4	0.86 ± 0.03 (84.67)	1.13 ± 0.20 (86.57)
6	0.10 ± 0.04 (98.21)	0.43 ± 0.09 (94.89)
8	BDL (–)	0.01 ± 0.01 (99.88)
10	BDL (–)	BDL (–)
Regression equation	Y = 2.96 − 0.34X	Y = 3.14 − 0.32X
Half-life in fruits (d)	0.88 days	0.94 days
Waiting period (T_{MRL})	4.87 days	5.74 days

BDL = below detectable limit (<0.01 ppm)

M* = Mean of three replicate

period values in cropped soil, fresh, washed and washed followed by cooked fruits samples for Quinalphos and Methomyl following two different applications have been presented in Tables 1–6.

The initial deposits (4 h after spraying) of Quinalphos in fruits were found 3.20 and 7.50 ppm at lower (T_1) and higher (T_2) doses respectively irrespective of any season. Whereas, for Methomyl they were 5.61 and 8.42 ppm at lower (T_3) and higher (T_4) doses respectively. More than 50% of the initial deposit was dissipated within 48 h except double the recommended doses of Quinalphos. The half-life values ($t_{1/2}$) were found to be 0.88 and 0.94 days for Methomyl and 1.25 and 1.43 days for Quinalphos. The corresponding waiting periods (T_{MRL}) were found to be 5.28 and 6.7 days for Quinalphos and 4.87 and 5.74 days for Methomyl.

The initial deposit of Quinalphos in cropped soil was found 1.75 and 3.17 ppm for the lower and higher doses respectively. Whereas, for Methomyl they were 2.83 and 3.84 ppm at lower and higher doses respectively. The half-life ($t_{1/2}$) values in cropped soil were found to be 1.07–1.20 days for Quinalphos and 0.97–1.25 days for Methomyl. On an average after washing 20.00%–69.60% of Quinalphos, 25.58%–65.44% of Methomyl residues were recorded. Cooking after washing caused a residues reduction of 25.50%–76.52% for Quinalphos and 31.39%–81.50% for Methomyl.

So, we can conclude that the harvesting of Okra should be done at least 7 days after last application of insecticides. The fruits can be harvested for cooking purposes on and from 6th day after last application of insecticides as the data shows no residual toxicity at 6 days after last application of insecticides in both the

Table 5 Residues of Quinalphos in Okra after washing and cooking (pooled data for 2 years)

Dose (g a.i. ha^{-1})	Interval from last spray (days)	Original or initial residues in ppm [M* ± SD]	Residue in ppm [M* ± SD] (% of loss)	
			Washing	Washing & cooking
T_1 (500)	0	3.20 ± 0.30	1.38 ± 0.05 (56.87)	0.91 ± 0.10 (71.55)
	2	1.30 ± 0.36	0.78 ± 0.04 (52.02)	0.68 ± 0.15 (47.35)
	4	0.80 ± 0.36	0.52 ± 0.12 (28.00)	0.59 ± 0.04 (26.20)
T_2 (1000)	0	7.50 ± 0.14	2.28 ± 0.32 (69.60)	1.76 ± 0.11 (76.52)
	2	4.10 ± 0.20	1.82 ± 0.04 (55.60)	1.63 ± 0.15 (60.24)
	4	1.80 ± 0.83	1.44 ± 0.35 (20.00)	1.34 ± 0.09 (25.50)

BDL = below detectable limit (<0.01 ppm)

M* = Mean of three replicate

Table 6 Residues of Methomyl in Okra after washing and cooking (pooled data for 2 years)

Dose (g a.i. ha^{-1})	Interval from last spray (days)	Original or initial residues in ppm [M* ± SD]	Residue in ppm [M* ± SD] (% of loss)	
			Washing	Washing & cooking
T_3 (500)	0	5.61 ± 0.47	2.22 ± 0.04 (60.42)	1.16 ± 0.04 (79.25)
	2	2.19 ± 0.30	1.10 ± 0.05 (49.77)	0.89 ± 0.03 (59.28)
	4	0.86 ± 0.03	0.64 ± 0.12 (25.58)	0.59 ± 0.05 (31.39)
T_4 (1000)	0	8.42 ± 0.24	2.90 ± 0.30 (65.44)	1.69 ± 0.02 (81.50)
	2	3.90 ± 0.39	2.12 ± 0.25 (45.64)	1.55 ± 0.05 (56.66)
	4	1.13 ± 0.20	0.76 ± 0.03 (32.74)	0.69 ± 0.32 (38.93)

BDL = below detectable limit (<0.01 ppm)

M* = Mean of three replicate

cases (i.e. for Quinalphos and Methomyl) irrespective of their doses.

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