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Research Article

Persistence of Profenophos and Quinolphos on Cultivated Cucumber and its Removal

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ABSTRACT
Two sprays of profenophos 50% EC and quinolphos 25% EC were applied on cultivated cucumber (*Cucumis sativus* L.) at the rate of 500 and 250 g a.i. ha^{-1}, respectively. The first spray at fruit formation stage followed by second spray at seven days interval and the samples of cucumbers were collected at regular intervals of 0 (2 h after application), 1, 3, 5, 7, 10 and 15 days after second spray. Residues were quantified by using gas chromatography. The initial disappearance of profenophos and quinolphos appeared to follow first order kinetics with different rates of reactions of 0.19and 0.33 day^{-1} for cucumber respectively. The corresponding half-lives ($t_{1/2}$) were 3.65 and 2.10 days. To reduce the safe waiting period, efforts were made to decontaminate the residues from cucumber by various household processing methods (viz. washing, washing plus cooking, 2% salt water washing and peeling). Various household processing substantially reduced the residues from cucumber in the range of 41.53-84.17% for profenophos and 60.0- 83.05% for quinolphos. The maximum reduction (84.17%, 83.05%) was observed by 2% salt water washing, so the consumers are suggested to follow dipping of cucumber in 2% salt water, as best risk mitigation method.

Keywords: Profenophos, quinolphos, residues, cucumber, risk mitigation methods

INTRODUCTION

Good knowledge of the pesticides fate in agriculture is necessary to properly assess human exposure and the environmental impact of these contaminants. Vegetables are considered the cheap source of energy, rich sources of essential biochemical's and nutrients such as carbohydrates, carotene, proteins, vitamins, calcium, iron, ascorbic acid and palpable concentration of trace minerals.[1] These vegetables will continue to remain the basic source of energy for the developing countries. Cucumber is one of the most preferred and extensively cultivated vegetable in the states of Andhra Pradesh and Telalgana in India. Commercial production of cucumber is highly depends on usage of different pesticides for crop protection purpose, for the management of various sucking insect pests and mainly fruit borer in India, as per the Insecticide Act 1969, 30 insecticides are registered and recommended for use. Generally, cucumber farmer resort to insecticides application once in a week for crop protection purposes, and also harvest the crop at weekly intervals, and hence there is a scope for the presence of pesticide residues on marketable cucumbers, sometimes above the legal limits i.e. maximum residue limit (MRL). This is clear, as the National Monitoring data shows that the presence of residues in vegetables frequently and on some occasions above MRL. This is a serious concern for consumer for food safety, and there is a need to verify the simple, household method for removal of pesticide residues in cucumber, since during last few years, the Indian food habits are changing, increase in raw vegetable consumption as salad and is very particular in case of cucumber. To deal food safety issues, besides sensitizing farmers for good agricultural practices (GAPs), simple household risk mitigations for pesticide residues removal in cucumber are to be verified for consumer safety. Profenophos and quinolphos are an organophosphorous insecticides widely used to control various insect pests on vegetables crops in India. There are numerous studies in the literature that have examined profenophos and quinolphos behaviour in field vegetables [2,3,4,5]. As well as to find more efficient washing reagents for removing its residues from cucumbers to reduce the health hazards.[2,6] However, there is a lack of published data in India for the fate of these insecticides on field grown cucumber fruits

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and in the processed products. Therefore, the present work was designed to study the persistence of profenophos and quinolphos in cucumber fruits. Emphasis on the safety periods for this insecticide in the tested vegetables was considered. Also, this study aimed to throw light on the influence of different washing solutions and some house hold processing on the removal of such residues from the field treated vegetables.

MATERIALS AND METHODS

Insecticide and chemical reagents: Profenophos : (o-(4-bromo-chlorophenyl)-o-ethyl-S-propyl phosphorothioate), 250mg, (Batch / Lot number; SZBA 264 XV) 96.9%, purity and Quinolphos; (*O,O*-diethyl *O*-quinoxalin-2-yl phosphorothioate), 250mg, (Batch / Lot number; SZBA 249 XV) 99.4%, purity technical grade standards were procured from sigma Aldrich, Germany, which was used for GC standardization and fortification and recovery studies in the present study. Formulated products were purchased from local vender and were employed in the field experiment. Chemicals and sorbents (Acetonitrile, hexane, primary secondary amine (PSA), sodium sulphate, magnesium sulphate, sodium chloride) used were obtained from E. Merck and Agilent companies.

Field experiment and sampling: A field experiment was conducted on cucumber crop (Dharwad green) at the student's farm college of Agriculture, Acharya N.G. Ranga Agricultural University, Rajendranagar Hyderabad. During the period December, 2012 to March, 2013. Field trial was laid out in the randomized block design (RBD) and replicated three times. Plot size 3.35 x 3.35 with net size 3.00x3.00 spacing between different plots was 30 x 60 cm. Number of plants per row was 9 and rows /bed were 5. So, the total plants per bed were 9x5=45. Profenophos (Curacron 50% EC and quinolphos (Hitalux 25% EC) was applied on cucumber crop at 500 and 250 g a i/ha, respectively along with untreated control at fruiting stage. Each treatment including control was replicated thrice. The formulations was diluted with water and sprayed on cucumber crop whereas control plots were sprayed with water only. Cucumber fruit samples were collected at regular intervals, 0 (2 h after spray), 1, 3, 5, 7, 10, and 15 days after treatment in three replicates. Two Kg's of samples from each plot were collected in polythene bags and brought immediately to the laboratory then samples were made in to two portions, one portion was processed for dissipation studies and another one is processed with different house hold processing methods for the removal of profenophos and quinolphos residues.

Climatic conditions: The weather parameters for the season (December, 2012- March, 2013) were temperature, minimum 24.07 ^{0}C, maximum 24.47 ^{0}C; relative humidity 75%; rain fall 21.72 mm; at the experimental site.

Household Risk Mitigation Methods: The cucumber samples collected from three pesticides sprayed plots were divided in to five portions, one portion was processed as such second after plain water washing, third portion with 2% salt water washing, fourth after peeling and fifth one after washing followed by boiling / cooking. In treatment one, each replicated sample (100g) was washed under running tap water for 2 min. In the second treatment, the cucumbers (100g) were washed thoroughly under tap water for 2 min followed by boiling in 500 ml water for 5 min, and the water was discarded. The next treatment, cucumbers were dipped in 500 ml of 2% salt solution at room temperature, (28±1 ^{0}C) for 5 min and washed under tap water for 2 min. In the forth treatment, the cucumbers outer layer was peeled with peeler. The field samples analyzed without any house hold techniques are designed as unprocessed control.

Extraction and clean-up: Extraction and clean- up procedure was performed as per AOAC Official Method 2007.01 QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) with little modifications. Representative 2 kgs of cucumber fruits were collected randomly from profenophos and quinolphos sprayed plots in polythene bags. The samples were homogenized with robot coupe blixer. Homogenized 15±0.1g sample was taken in 50ml centrifuge tube, and 30±0.1 ml acetonitrile was added. The sample was homogenized at 14000-15000 rpm for 2-3 min using heidolph silent crusher. The samples was then added with 3±0.1g sodium chloride and mixed by shaking gently followed by centrifugation for 3 min at 2500-3000 rpm to separate the organic layer. The top organic layer of about 16 ml was taken into the 50 ml centrifuge tube and added with 9±0.1g anhydrous sodium sulphate to remove the moisture content. 8 ml of extract was taken in to 15 ml tube, containing 0.4±0.01g PSA sorbent (for dispersive solid phase d-SPE cleanup) and 1.2±0.01g anhydrous magnesium sulphate. The sample tube was vortexed for 30sec then followed by centrifugation for 5min at 2500-3000 rpm. The extract of about 2 ml was transferred into test tubes and evaporated to dryness using turbovap with nitrogen gas and reconstituted with 1ml n-Hexane: Acetone (9:1) for GC analysis with ECD detector under standard operational conditions.

Residue determination: Determination of profenophos and quinolphos residues in cucumber fruits was analyzed on Shimadzu – 2010 GC (gas chromatography) (Serial Number: C11324405589 SA) equipped with capillary column, MR- 1 (30mts, 0.25 mm ID, 0.25 µm Film thickness of diphenyl/ 95% dimethyl polysiloxane) and electron capture detector (ECD). The operating parameters of the instrument were: Column oven temperatures 150 ºC-2 min hold-250ºC-@10ºC/min-23 min; TOTAL 35 min, injection port temperature 280^{0}C and detector temperature was 300^{0}C. Flow rate of nitrogen (carrier gas) was 1ml/min through column; makeup gas flow is 35ml/min and split ratio is 1: 10. Under these operating conditions the retention times of quinolphos and profenophos were found to be 5.27 and 19.20 minutes, respectively (Figs. 1&2).

Recovery studies: In order to estimate the efficiency of the method, a recovery experiment was conducted by fortifying the untreated cucumber samples with analytical grade profenophos and quinolphos at the rate of 0.05, 0.25 and 0.5 mg kg^{-1}, and processed by following the methodology as described above. The result revealed that percent mean ± SD recoveries for cucumber samples at these three levels were 90.6±1.15, 90.6±2.30 and 100±2.0 for profenophos, 89.40±4.03, 92.90±3.46 and 111.66±5.85

for quinolphos (Table-1). The results have been reported as such without applying any correction factor. The minimum limit of detection (LOD) was 0.01mg kg^{-1} and limit of quantification (LOQ) for profenophos and quinolphos in cucumber fruits were found to be 0.05 mg kg^{-1}.

RESULT AND DISCUSSION

The residual data in Table 2 showed that the initial deposits of profenophos and quinolphos in/ on cucumber fruits were 7.20 and 4.19 ppm respectively. A rapid degradation was noticed after one day of application with values of 62.78, 41.05% for profenophos and quinolphos, respectively. The progression of time after the application resulted more dissipation of residues. The first five days was critical, showing the highest rate of dissipation of profenophos and quinolphos from cucumber fruits, being 92.36 and 92.13%, respectively. On the seventh day of experiment cucumber fruits collected from the profenophos sprayed plots shown the reduction of 99.03%, on 10th day it is reached to 100% dissipation, where as quinolphos residues from cucumber fruits were shown the reduction of 97.85 % on 10th day, it was shown the 100% dissipation on 15th day after spraying (Fig. 3). The initial disappearance of profenophos and quinolphos appeared to follow first order kinetics with different rates of reactions of 0.19 and 0.33 day^{-1} for cucumber fruits, respectively. The corresponding half-lives ($t_{1/2}$) were 3.65 and 2.10 for profenophos and quinolphos in on cucumber fruits respectively (Table-3).

The residual data could be concluded that, 0.07 ppm of profenophos residues was detected on cucumber fruits, 7 days after application, while in the case of quinolphos 0.09 ppm levels of residues were detected on cucumber fruits , 10 days after application. This indicated that only 10 and 15 days were long enough to reduce the residues of profenophos, and quinolphos below the determine levels (0.05 ppm) on cucumber fruits. The codex maximum residue limits (MRLs) for profenophos residues in/on several commodities ranged from 0.05 to 10 mg/kg, where as quinolphos, the maximum residue limits are ranged from 0.01 to 2 mg/ kg on different vegetable commodities. However, the list lacks the MRLs for profenophos and quinolphos on cucumber fruits. Therefore, cucumber fruits could be marketed with apparent safety for human consumption.

Profenophos and quinolphos residues in/on different vegetable commodities are reported in earlier studies; the initial deposits of profenophos in /on unwashed hot pepper, sweet pepper and eggplant were 11.62, 10.67 and 4.50 ppm, respectively. These levels were dissipated to 0.025, 0.31 and 0.15 ppm on 14 and 10 days from hot pepper, sweet pepper and eggplant, respectively.[4]Tomatoes treated with profenophos could be marketed, 8 days after application, while green beans could be consumed safely 11 days after spraying.[7] The profenophos residues in/on unwashed tomato and okra fruits were 10.18 and 11.56 ppm, respectively. These values were decreased to 0.04 and 0.025 ppm after 15 days of spraying.[5] The initial deposits of quinolphos residues were 4.42 and 9.72 ppm which is dissipated to 0.07 and 0.17 ppm by 8 days after application in/on cabbage heads.[2]

When the pre-harvest intervals between treatments and harvest are not respected by the farmers, the risk of having higher pesticide levels is not negligible. In this case, the higher levels of pesticides can involve considerable economic losses if the maximum residue limits established by FAO/WHO are surpassed. So, the effect of washing by different solutions or using some household processing in removing the pesticide residues from plants may be a solution to overcome this problem.[4]

Effect of various household risk mitigation methods: Profenophos and quinolphos initial residues and its removal percent as affected with different washing solutions and processing treatments on cucumber fruits were shown in Table 4. The residues of profenophos and quinolphos on raw unprocessed cucumber fruits after application were 7.2 and 4.19 ppm, respectively. The washing of treated fruits under running tap water reduced these residue levels to 4.21 and 1.67 ppm, respectively, with corresponding percent removal of 41.53 and 60.14, respectively. The result obtained by several authors,[2,4,8] indicated that washing profenophos and quinolphos treated vegetables fruits with tap water removed a considerable amounts of residues. Washing plus cooking, it further increased to a range of 1.94 ppm (73.06% reduction) and 0.71 ppm (83.05% reduction) of profenophos and quinolphos respectively. While cucumber fruits were washed with 2% salt water the initial residues found on unwashed fruit to 1.14 ppm (84.17% reduction) for profenophos. In case of quinolphos the reduction was 0.89 ppm (78.76% reduction), the method of washing plus cooking is not effective in case of quinolphos when compare with 2% salt water washing. When the outer layer of cucumber was peeled with peeler the reduction levels are 3.06 ppm (57.50% reduction) and 1.45 ppm (65.39% reduction) for profenophos and quinolphos in/on cucumber fruit, respectively. This was followed by tap water washing. These data indicated that the tested different washing solutions or home processing procedures had varied effects on reducing or removing of profenophos and quinolphos residues from the tested cucumber fruits depending upon the type of mitigation methods (Fig. 4). The removal studies are reported in the literature by different authors.[2,4,5,8,9,10] They found that washing with water and / or other solutions as well as the cooking process resulted in a great reduction of pesticide residues from treated vegetable fruits and lead to the residue level lower than the maximum residue limits (MRLs).

CONCLUSION

Thus, the present study provides residue data which may be useful for establishing the MRL and pre harvesting intervals for profenophos and quinolphos residues in/on cucumber fruits under Indian field conditions and suggests the need of implementation of these safety intervals before harvesting and marketing such vegetable fruits. Moreover, a comparison of the overall effect of different household mitigation methods indicated that levels of profenophos and quinolphos residues can be reduced significantly by washing plus cooking and 2% salt water washing. The reduction in residue levels makes these procedures worthwhile for adopting by the consumer. The effectiveness of different risk mitigation methods was observed in the order of tap water washing is less effective than peeling whereas washing plus cooking and 2% salt water washing have shown the equal effect in the removal of profenophos and quinolphos residues from cucumber fruits. Hence, to reduce the risk associated with these residues while consuming the raw cucumber, washing with 2% salt water is the best risk mitigation method before consumption.

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