Available online at http://www.ijims.com
ISSN: 2348 – 0343

Monitoring and decontamination of pesticide residues in okra (Abelmoschus esculentus Moench)

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Abstract

A monitoring study was carried out in okra for a period of six months to assess the level of pesticide residues of three different chemical groups ie organochlorines, organophosphates and synthetic pyrethroids. Okra samples showed residues of malathion and profenophos. To evaluate the effect of different decontaminating solutions in the removal of pesticide residues, okra var. Varsha Upahar was sprayed with a mixture of pesticides which were frequently detected in okra. Estimation of residues was done using Gas Chromatograph equipped with Electron Capture Detector. The results indicated that dipping in tamarind (2 %) solution for 15 minutes followed by washing in tap water was found to be more effective in reducing all pesticides tested when compared with other treatment solutions. This study helped to standardize simple cost effective strategies to eliminate harmful pesticides from okra which could be practiced by home makers.

Key words: Okra, Decontamination, Pesticide, Residue

Introduction

Pesticides are recognized as important for food production, but their use might cause potential health risks from both occupational and non-occupational exposures. Different pesticides have been implicated in chronic neurotoxicity, endocrine disruption, immune impacts, genotoxicity, mutagenicity and carcinogenesis through routes that include consumption of dietary residues. Several studies conducted in Kerala had led to a conclusion that the direct health effects of pesticide residues entering the human system through contaminated food are much more serious than the indirect effects through food chain and environment[1]. It is expected that fruits and vegetables contain higher pesticide residue levels compared to other foods of plant origin, such as bread based on cereal processing, because they are mainly consumed raw or semi-processed [2].

Okra (Abelmoschus esculentus (L) Moench) or bhendi also known as ladies finger is an important vegetable crop being native of tropical Africa. In a monitoring study conducted at central Aravalli region of Rajasthan during 2012, it was found that 32.00 % okra samples were contaminated with residues of methyl parathion, monocrotophos, cypermethrin and quinalphos [3]. Samples of okra collected from farmer's field of Andaman Nicobar Islands, were tested for the presence of organochlorine (OC), organophosphorus (OP) and synthetic pyrethroid (SP) compounds. From the samples tested, 34.00 per cent contained pesticide residues. Among the OC compounds, alpha endosulphan, beta endosulphan, and endosulphan sulfate were detected in 14.50 per cent (crucifer, okra, green chilli and cucurbit) of the samples. SP residues viz., alpha cypermethrin, fenvalerate I, fluvalinate I, deltamethrin, and lambda cyhalothrin were detected in 32 per cent of the samples. The residues of OP compounds such as chlorpyriphos, profenophoss, monocrotophos, triazophos, ethion, dimethoate and acephate were found in 54 per cent of the samples[4].

Food contaminated with toxic pesticide is likely to be associated with severe effects on human health. Hence, great significance has to be given to monitor pesticide residues in agricultural commodities and to standardize simple cost effective methods which can be practiced by home makers to eliminate pesticide residues. In the light of the above facts a study was

carried out to measure the residues of organochlorines, organophosphates and synthetic pyrethroid pesticide residues in okra and to assess the effect of different decontamination techniques on the removal of pesticide residues.

Materials and methods

Certified Reference Materials (CRM) of different pesticides used in the present study having purity ranging from 95.10 to 99.99 per cent were purchased from M/s Sigma Aldrich and stored in a freezer at low temperature, with light and moisture excluded. Solvents used in the study were all glass distilled before use. Sodium sulphate, sodium chloride and magnesium sulphate were pre-washed with acetone, dried at room temperature and then activated in hot air oven at 450 ^{0}C for 5 h.

A weighed amount of analytical grade material of each pesticide was dissolved in a minimum quantity of distilled acetone and diluted with n-hexane: toluene (1:1) to obtain a stock solution of 1000 mg kg^{-1} The intermediate standards and working standards of 0.5, 0.1, 0.075, 0.05, 0.025 and 0.01 mg kg^{-1} were prepared by suitably diluting the stock solution in n-hexane and used as standard check in analysis, linearity and recovery studies.

The analytical method for estimation of residues of pesticides in okra has been validated by conducting recovery studies using control samples. Twenty five gram each of control samples of blended okra fruits was taken in 200 ml centrifuge tubes in three replicates each were spiked with organochlorine, organophosphate and synthetic pyrethroid pesticides at the required fortification levels ie. LOQ, 5 x LOQ and 10 x LOQ, adding an appropriate volume of working standard of 10 mg L^{-1}. This mixture was then shaken, in order to attain a proper homogeneity of pesticides in the samples. The tubes containing fortified samples were left open for a while, just to allow the evaporation of excess solvent. A volume of 50 ml acetonitrile was added to the mixture and then homogenized at 14000 rpm for one min. Ten gram of sodium chloride was added to the mixture and centrifuged at 2000-2500 rpm for 4 min. From this, 16 ml supernatant was transferred to a 50 ml centrifuge tube containing 6.0 g sodium sulphate and vortexed. A total of 12 ml supernatant was then transferred to a 15 ml centrifuge tube containing 1.2 g magnesium sulphate and 0.2 g Primary Secondary Amine (PSA) and vortexed again at full speed for 30 s and centrifuged at 2500 rpm for 3 min. After that, 4.0 ml of upper layer was evaporated to dryness using Turbovap at 50^{0}C. The dry residue was reconstituted to one ml using n-hexane and analyzed in a Gas Chromatograph equipped with ^{63}Ni Electron Capture Detector (ECD), fitted with DB-5 capillary column (dimethyl polysiloxane, 30m x 0.25mm i.d. x 0.5µm film thickness) was used for the analysis. Ultra high Purity (99.999 %) nitrogen was used as carrier gas with a column flow rate of 0.79 ml min^{-1} and linear velocity 26.00 cm S^{-1}. A column temperature programme was developed to get proper separation of all pesticides used in the analysis. The operating parameters of the instrument were: oven temperature 170^{0}C (5 min) →1.5^{0}C min^{-1} →220^{0}C (10 min) →4^{0}C min^{-1}→280^{0}C (7 min), injection port at 250^{0}C and detector at 300^{0}C and the total run time as 70 min and split ratio 1: 10.

Monitoring study

Okra samples (2 kg) were collected from local markets of Thiruvananthapuram, Kerala, India at monthly intervals for a period of six months starting from January 2012 - June 2012. Each sample was processed and analyzed for the determination of organochlorines, organophosphates and synthetic pyrethroid group of pesticides. Samples were analyzed within 24 hr and stored at 4°C until the moment of extraction.

Decontamination study

Okra plants raised organically in the Instructional Farm, College of Agriculture, Vellayani was sprayed with an insecticide emulsion mixture containing malathion (Hilmala 50 EC 2.0 ml L^{-1}), chlorpyriphos (Radar 20 EC 2.0 ml L^{-1}), quinalphos (Ekalux 25 EC 1.60 ml L^{-1}), profenophos (Curacron 50 EC 3.0 ml L^{-1}) and cypermethrin (Cyperkill 25 EC 1.10 ml L^{-1}) in one litre using a hand sprayer. Okra fruits collected after 1st day and 3rd day of insecticide spraying were subjected to dipping in different decontaminating solutions.

The different decontaminating solutions used in this experiment are Tamarind 2 % (20g of tamarind pulp extracted in one litre water), Common salt 2 % (20g of common salt dissolved in one litre water), Turmeric powder 1 % (10g of turmeric powder dissolved in one litre water), Vinegar 2 % (20 ml of vinegar diluted in one litre water), Butter milk 2 % (20 ml of buttermilk diluted in one litre water), Luke warm water (36-40^{o}C) and Water (untreated control)

Samples (250 g okra fruits) were dipped individually in these treatment solutions for fifteen minutes followed by washing in tap water. Samples were then homogenized after chopping into small pieces and the representative sample (25 g) in three replicates was used for residue estimation.

Levels of pesticides present in processed and unprocessed commodity was estimated using the formula

$$\frac{\text{Peak area of sample} \times \text{Concentration of standard injected} \times \text{Volume of sample injected} \times \text{Dilution Factor}}{\text{Peak area of standard} \times \text{Volume of standard injected}}$$

Results and discussion

Recovery study

The analytical method was validated in terms of limit of quantification, linearity, precision and recovery. The fortification study was carried out by spiking the untreated curry leaves at 0.05, 0.25 and 0.5 mg kg-1 levels to determine the recovery levels and the average recoveries of the method for malathion, quinalphos, chlorpyriphos, profenophos and cypermethrin was 85.94 - 105.60 %, 73.05 – 85.94 %, 76.71 – 84.71 %, 85.84 -105.64 % and 84.86 – 96.16 %. The precision of the method in terms of relative standard deviations (RSD) ranged from 0.56 % to 10.43 %. The limit of quantification (LOQ) was found to be 0.05 mg kg^{-1} and limit of detection (LOD) being 0.01 mg kg^{-1}.

Monitoring study

Out of the six okra fruit samples analyzed during January to June 2012, two of them contained residues of pesticide (Table 1). Malathion residue was detected in one sample (0.038 mg kg^{-1}) falling below FSSAI MRL. One sample showed the presence of profenophos at 0.121 mg kg^{-1} and which has no FSSAI MRL in okra.

Decontamination study

The effect of decontaminating solutions of different household products on removal of pesticide residues in okra fruits at different intervals (1st and 3rd day) after spraying are summarized in Table 2 and 3.

All the decontaminating solutions significantly removed the residues of malathion, chlorpyriphos, quinalphos, profenophos and cypermethrin from okra fruits on 1st day and 3rd day after spraying. It was found that dipping in 2% tamarind solution and 2% common salt solution for 15 minutes followed by washing in tap water were more effective in removing the residues one day after spraying, recording a residue removal of 54.46.59 – 73.25 % and 54.38 – 68.24 % respectively. Similarly on the third day 2% tamarind solution was found to be the best treatment with a residue load of 52.18 – 65.65 % followed by common salt with 45.61 – 68.24 %. Dipping of okra fruits in luke warm water for 15 min followed by washing in tap water did not show much difference in removing residues from simple water wash. From the results it is presumed that all the decontamination solutions used in the study were more effective in reducing the residues of 1st day because residues are localized on the okra fruits which could be dislodged easily. On the passage of time, residues penetrate into the fruits and hence less removal was observed on the third day.

The literature pertaining to the efficacy of the various decontamination treatments used in the present investigation are scanty. However Varghese & Mathew (2013) reported that 2 % tamarind solution was the best decontaminating solution in removing residues of spiromesifen (90.03 %) and propargite (96.69 %) from green chilli fruits. Similar type of observation with phosphamidon and monocrotophos in bittergourd and cowpea pods has been reported by Kumar (1997). It was reported

that turmeric was a good decontaminating agent in removing chlorantraniliprole residues (79.81 - 87.40 %) from vegetable cowpea at 0^{th} day and 3^{rd} day after spraying [6]. Zohair (2001) reported that organophosphorus pesticides (pirimiphos-methyl, malathion, and profenophos) were eliminated more effectively by acidic, neutral and alkaline solutions and their removal depended on the kind and concentration of solutions. Washing of cauliflower treated with chlorpyriphos, quinalphos, endosulfan, fenvalerate and deltamethrin reduced28.92 %–78.64 % residues of these insecticides[8]. Tomatoes contaminated at level of 1 mg kg^{-1} upon washing with 10 % NaCl solution gave 42.90, 46.10, 27.20, 90.80, 82.40 and 91.40 per cent loss in HCB, lindane, p,p-DDT, dimethoate, profenophos and pirimiphos-methyl, respectively [9]. Liang and co workers (2012) reported that 63.40, 60.00, 50.00, 31.10 and 66.70 per cent reduction in the residues of trichlorfon, dimethoate, dichlorvos, fenitothion and chlorpyriphos respectively, were observed in cucumber when dipped in 2 % sodium chloride solution for 20 min. These results agree with those obtained by Zohair (2001) who reported that soaking of contaminated potatoes in neutral (NaCl) solution (5 and 10 %) for 10 min resulted in 100 percent removal of pirimiphos methyl residues. The cause and effect of the reduction in 2 % NaCl washing solutions is still not known and needs further investigation.

Conclusion

The study clearly revealed that dipping in 2 % tamarind solution for 15 min followed by washing in tap water was the best treatment to eliminate residues of majority of insecticides under present study. High extent of pesticide residues in agricultural commodities calls for improved management of residues at production, post harvest and marketing of food commodities especially of vegetables. Moreover, great significance has to be given to standardize simple cost effective strategies to eliminate harmful pesticides which could be practiced by home makers.

Acknowledgement

The authors are thankful to All India Network Project on Pesticide Residues and Kerala Agricultural University for providing necessary funds.

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Table 1: Pesticide residues in okra collected from market during January 2012 - June 2012.

Monitoring period	Insecticides detected	Concentration (mg kg^{-1})
January 2012	-	
February 2012	Malathion	0.038
March 2012	Profenophos	0.121
April 2012	-	
May 2012	-	
June 2012	-	

Table 2. Extent of removal of insecticide residues from okra fruits collected at 1st day after spraying*

Insecticides	Mean per cent removal of insecticides (%) ± SD						
	2% Tamarind	2% Vinegar	1% Turmeric	2% Common salt	2% Buttermilk	Luke warm water	Water
Malathion	68.92 ± 1.44 (0.25)	38.67 ± 2.83 (0.49)	70.56 ± 1.27 (0.24)	62.37 ± 1.36 (0.30)	67.75 ± 1.42 (0.26)	37.53 ± 1.67 (0.50)	37.67 ± 1.55 (0.50)
Chlorpyriphos	62.52 ± 3.29 (0.54)	50.67 ± 0.70 (0.72)	32.14 ± 1.19 (0.98)	54.38 ± 2.36 (0.66)	13.90 ± 1.48 (1.25)	18.68 ± 1.32 (1.18)	9.48 ± 0.40 (1.31)
Quinalphos	65.30 ± 3.69 (0.42)	54.79 ± 3.67 (0.55)	52.88 ± 2.88 (0.57)	63.14 ± 2.10 (0.45)	44.46 ± 1.15 (0.68)	39.67 ± 0.78 (0.74)	33.24 ± 2.20 (0.81)
Profenophos	73.25 ± 4.12 (0.80)	63.76 ± 3.01 (1.08)	50.60 ± 1.26 (1.47)	68.24 ± 2.41 (0.95)	52.71 ± 2.52 (1.41)	27.23 ± 1.67 (2.17)	23.64 ± 2.89 (2.28)
Cypermethrin	54.46 ± 1.22 (0.05)	57.23 ± 1.32 (0.05)	32.28 ± 1.16 (0.07)	54.61 ± 2.09 (0.05)	25.63 ± 1.17 (0.08)	18.17 ± 1.82 (0.09)	6.70 ± 3.04 (0.10)
CD (5%)	1.31						

Value in parentheses are concentration of insecticide residues in mg kg^{-1}

*subjected to dipping in different treatment solutions for 15 min.

Table 3. Extent of removal of insecticide residues from curry leaf collected at 3rd day after spraying*

Insecticides	Mean per cent removal of insecticides (%) ± SD						
	2% Tamarind	2% Vinegar	1% Turmeric	2% Common salt	2% Buttermilk	Luke warm water	Water
Malathion	57.10 ± 1.67 (0.13)	41.77 ± 1.56 (0.18)	63.89 ± 3.75 (0.11)	62.37 ± 1.36 (0.12)	66.70 ± 1.59 (0.10)	32.53 ± 2.89 (0.21)	25.88 ± 3.31 (0.23)
Chlorpyriphos	60.22 ± 1.15 (0.20)	47.30 ± 1.00 (0.26)	8.90 ± 1.36 (0.46)	54.38 ± 2.36 (0.23)	11.44 ± 1.34 (0.44)	17.84 ± 1.89 (0.41)	10.80 ± 0.40 (0.45)
Quinalphos	61.31 ± 1.09 (0.22)	51.48 ± 0.82 (0.28)	36.40 ± 1.39 (0.37)	56.14 ± 2.10 (0.25)	41.86 ± 1.15 (0.34)	32.41 ± 0.79 (0.39)	18.59 ±1.22 (0.47)
Profenophos	65.65 ± 2.48 (0.36)	52.77 ±1.44 (0.49)	41.68 ± 1.62 (0.61)	68.24 ± 2.41 (0.33)	48.33 ± 1.90 (0.54)	27.66 ± 2.64 (0.75)	21.66 ± 0.69 (0.81)
Cypermethrin	52.18 ± 1.16 (0.03)	50.25 ± 1.63 (0.03)	19.59 ± 1.06 (0.06)	45.61 ± 2.09 (0.04)	22.74 ± 1.77 (0.05)	15.49 ± 2.90 (0.06)	8.19 ± 2.65 (0.06)
CD(5%)	0.98						

Value in parentheses are concentration of insecticide residues in mg kg^{-1}

*subjected to dipping in different treatment solutions for 15 min.