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Evaluation of different household practices to decontaminate organophosphate insecticide residues from *Amaranthus tricolor* L.

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ABSTRACT: *Amaranthus tricolor* L (Amaranth) is a major leafy vegetable extensively cultivated in Kerala. Efficiency of different decontaminating methods viz., washing, cooking, 2% common salt, 2 % vinegar, 1% turmeric, 2% tamarind and 1% veggie wash (produced by Kerala Agricultural university, Vellayani), in the removal of organophosphate insecticide residues from amaranth, sprayed with different organo phosphate insecticides *viz.,* chlorpyriphos 20% EC, dimethoate 30 EC, ethion 50% EC, malathion 50 % EC, profenofos 50% EC and quinalphos 25% EC, indicated that dipping in 1% veggie wash for 20 minutes followed by three further washings plus cooking was found to be most effective in removal of OP insecticide residues (83%), followed by 1 % veggie wash for 20 minutes, 1% veggie wash for 10 minutes plus cooking and 2% vinegar (78, 76 and 74% respectively).

KEY WORDS: Amaranth, pesticide, residues, decontamination.

INTRODUCTION

Amaranth is extensively cultivated as a green and leafy vegetable in many temperate and tropical regions. It has excellent nutritional value because of their high content of essential micronutrients such as â-carotene, iron, calcium, zinc, phosphorous, vitamin C and folic acid (Schonfeldt and Pretorius, 2011). In India, it is cultivated largely in the southern states. It is raised throughout the year in paddy lowlands, garden lands and homesteads. The crop cultivated throughout the year. Farmers use chemical pesticides of a wide range and often in excessive dosage and at close intervals. This tendency leads to high residues on products reaching the market. Nair *et al.,* (2013) reported that most of the agricultural commodities tested had multiple residues containing three to six pesticides. Department of Agriculture, Government of Kerala and Kerala Agricultural University through the Plan Scheme "Production and marketing of safe to eat (pesticide free) vegetables, fruits and food products for sale through government outlets" revealed that out of 34 red amaranthus samples analyzed during the period of January – December 2013, 14 samples were found with insecticide residues. In these detected insecticides, most of the residues belong to organophosphate group (PAMSTEV, 2014). However, owing to their widespread use together with their unique physical, chemical and biological properties, these insecticides have raised serious concern among the public regarding their adverse

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effects on human health and environment. So there is need to remove pesticide residues from commodity at consumer level. Standardization of simple and cost effective methods to remove residues from amaranth has been reported here.

MATERIALS AND METHODS

A preliminary survey was conducted to assess the pesticide residues in amaranth in Kalliyoor and Pappanchani of Thiruvananthapuram district during March 2014 – June 2014. Ten farmers each from two locations engaged in commercial cultivation of red amaranth were selected randomly for the survey. The red amaranth plants grown organically in grow bags in premises of PRRAL, Vellayani were used for the standardisation of household practice to decontaminate residues. An insecticide mixture emulsion (100 ppm) was prepared by using required quantities of each insecticide mixed in one litre water. The insecticides used were dimethoate 0.3 ml L^{-1} (ROGOR), malathion 0.2 ml L^{-1} (CELTHION), chlorpyriphos 0.5 ml L^{-1} (CLASSIC-20), quinalphos 0.3 ml L^{-1} (EKALUX), profenophos 0.2 ml L^{-1} (CURACRON) and ethion 0.2 ml L^{-1} (FOSMITE). The amaranth plants were sprayed with this insecticide mixture using a hand sprayer (l L). Sprayed plants were kept under covered conditions to protect from rain. Treated plants were harvested at one day after spraying. Individual treated plants were subjected to different decontamination practices and some plants were kept as un processed control for comparison. Preparation of working standards and analysis of each sample processed according to specific procedure for vegetables and samples were analysed under specific working parameters of Gas Chromatograph (Nair *et al.,* 2013). The residues in processed and control (unprocessed) samples were extracted in acetonitrile and clean-up was done with QuEchERS method. The different decontamination treatments used in this experiment are mentioned in Table 3.

RESULTS AND DISCUSSION

Out of 20 samples tested, 17 samples were contaminated with pesticide residues. As there were no MRLs notified by FSSAI for amaranth, EU-MRLs were taken for reference. Among twenty surveyed samples, 13 samples had residues of quinalphos (0.04-1.20 ppm) and 4 samples exceeded the EU-MRL (0.05 ppm). Chlorpyriphos was found in three samples and the levels detected in all the three were above EU-MRL level. Profenofos, bifenthrin, ethion and fenvalerate were found in one sample each as above EU-MRL. Among surveyed samples, lambda-cyhalothrin and cypermethrin were found in one sample each and they were below EU-MRL (Table 1).

The recovery and repeatability of these insecticides are presented in Table 2. The effect of different household decontamination practices in removal of OP pesticide residues from amaranth are summarized in Table 3. The treatments varied significantly on their effect to remove dimethoate residues. KAU veggie wash (0.19 ppm) was found to be superior over all the treatments. Common salt (0.34), tamarind (0.42) and vinegar (0.42) were found to be next best treatments, whereas, turmeric (0.55) and water (0.66) were found to be less effective.

In removal of malathion residues KAU veggie wash (0.05) was found as superior and this was on par with vinegar (0.07). These treatments were followed by common salt (0.09), water (0.11) and turmeric (0.11), these three treatments were statistically on par. In removal of malathion turmeric (0.12) found as inferior among all the treatments. Vinegar (0.07) was found to be superior among all treatments in removal of chlorpyriphos residues from amaranth. The next best treatments were veggie wash (0.80), common salt (0.81) and water (0.90). These were followed by tamarind (1.00) and turmeric (1.34). All these treatments were statistically differ with untreated check. In case of quinalphos highest reduction of residue removal was observed when subjected to KAU veggie wash (0.40). More or less similar amount of residues were removed hen subjected to common salt (0.44), tamarind (0.51) and vinegar (0.54). All the above treatments were statistically not different. Water (0.67) and turmeric (0.70) exhibited less removal;

Table 1. Extent of pesticide residues in farm-gate samples collected from selected farmers

Farmer	Pesticides detected	Amount of residues found (Conc. in ppm)	EU – MRL	Below / Above MRL
1	Chlorpyriphos	1.009	0.05	Above
	Quinalphos	1.05	0.05	Above
2	Quinalphos	0.04	0.05	Below
3	Chlorpyriphos	0.09	0.05	Above
	Quinalphos	0.04	0.05	Below
4	—			
5	—			
6	Quinalphos	0.08	0.05	Above
7	Profenophos	0.02	0.01	Above
8	Quinalphos	1.20	0.05	Above
	Fenvalerate	0.08	0.02	Above
9	——			
10	Lambda cyhalothrin	0.025	1.00	Below
11	Cypermethrin	0.19	0.70	Below
	Quinalphos	0.05	0.05	Below
12	Quinalphos	0.04	0.05	Below
13	Quinalphos	0.87	0.05	Above
14	Ethion	0.03	0.01	Above
15	Bifenthrin	0.09	0.05	Above
	Quinalphos	0.05	0.05	Below
16	Quinalphos	0.03	0.05	Below
17	Quinalphos	0.04	0.05	Below
18	Quinalphos	0.05	0.05	Below
19	Quinalphos	0.03	0.05	Below
20	Chlorpyriphos	1.00	0.05	Above

ppm - parts per million, EU- European Union, MRL- Maximum Residue Limit

however, these treatments were statistically on par with tamarind and vinegar.

Among all treatments, the superior treatment for removing profenophos residues was KAU veggie wash (0.66) and next best treatment was common salt (0.68) which was statistically on par with KAU veggie wash. These treatments were followed by vinegar (0.94), tamarind (1.06) and turmeric (1.19), these three treatments did not show any significant variation. However, water (1.38) was the least effective treatment. In removal of ethion residues KAU veggie wash (0.64) removed highest amount of residues. Even though it was highest in removal of ethion, it was statistically on par with tamarind (0.90) and common salt (0.98). These treatments

Table 2. Recovery and repeatability of organo phosphate insecticides in amaranth at different fortification levels

Sl. No	Insecticides	Level of fortification					
		LOQ (0.05 mg kg $^{-1}$)		5 x LOQ (0.25 mg kg $^{-1}$)		10 x LOQ (0.5 mg kg $^{-1}$)	
		Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
1	Dimethoate	93.39 ± 6.19	6.63	95.72 ± 2.33	2.44	87.86 ± 15.28	17.39
2	Malathion	91.41 ± 8.83	9.66	95.24 ± 2.23	2.35	80.92 ± 8.72	10.78
3	Chlorpyriphos	92.07 ± 6.43	6.98	97.86 ± 1.52	1.55	88.60 ± 11.61	13.11
4	Quinalphos	86.65 ± 0.77	0.88	94.52 ± 2.41	2.55	87.88 ± 10.41	11.84
5	Profenophos	91.81 ± 4.59	5.00	95.66 ± 0.96	1.00	92.26 ± 9.54	10.34
6	Ethion	93.51 ± 4.43	4.74	95.31 ± 3.27	3.43	92.00 ± 6.95	7.56

Number of replications at each level (n) = 3; SD = Standard Deviation; RSD = Relative SD

were followed by vinegar (1.20) and turmeric (1.33). Whereas water treated samples contained 1.83 ppm residues.

Decontamination treatments including tamarind (2 %), vinegar (2 %), common salt (1 %) and KAU veggie wash (1%) and cooking process such as washing plus cooking and cooking after washing with KAU veggie wash (1%) showed significant effect in reducing organophosphate insecticide residues from amaranth when compared to dipping in tap water alone. The extent of removal of insecticide residues through dipping in water depend upon the solubility of the insecticides in water and the type of insecticide formulation. The ten insecticides analysed in this study were emulsifiable concentrates (EC) and water miscibility of these formulations were low. After one day of spraying when plants were subjected to dipping in water for 10 minutes followed by three normal washing, a wide range of pesticide residues were removed. When the amount of residues removed in washed samples were compared with those in un processed sample residues, maximum reduction was recorded in the case of malathion (80.56%). Among all the insecticides tested, lowest per cent removal was observed in dimethoate followed by ethion. In the case of dimethoate, systemic nature of the insecticide might be the reason for lower extent of removal. The effectiveness of washing on removal of residues depended upon the location of the pesticide present whereas the surface residues are responsive to washing, systemic residues present in tissue will be less amenable (Holland *et al.,* 1994).

Maximum removal of all pesticide residues was noticed in amaranth plants dipped in KAU veggie wash (1%) for 20 minutes plus washing and cooking and dipping in KAU veggie wash (1%) for 20 minutes followed by washing alone except in the case of chlorpyriphos. In the case of systemic insecticides, washing plus cooking could remove residues to a maximum extent of 86.27 per cent (Veggie wash + cooking) than other treatments. The extent of residue removal by this treatment was higher than dipping in water followed by cooking probably because of ionisation of residues in acidic solution. The pH of veggie wash (1%) was 3.16. These results agree with the observations of Vemuri *et al.* (2015) who reported synergic effect of treatment with acidic solution and cooking which together dislodged 99 to 100 per cent residues of dimethoate, methyl parathion, quinalphos, endosulphan and profenophos. Dipping amaranth plants in 1 per cent KAU veggie wash followed by

Table 3. Extent of removal of organo phosphate insecticides residues from amaranth

TREATMENTS	Mean per cent removal of insecticides (%)											
	Dimethoate		Malathion		Chlorpyriphos		Quinalphos		Profenophos		Ethion	
	Residues (ppm)	% removal	Residues (ppm)	% removal	Residues (ppm)	% removal	Residues (ppm)	% removal	Residues (ppm)	% removal	Residues (ppm)	% removal
T1- Water*	0.66^{e}	49.74^{d}	0.11^{d}	80.56^{c}	0.90^{c}	56.18^{d}	0.67^{b}	51.29^{c}	1.38^{d}	51.78^{d}	1.83^{c}	37.39^{d}
T2-2%Tamarind*	0.42^{c}	67.84^{c}	0.12^{d}	77.71^{d}	1.00	51.05^{e}	0.51^{b}	62.95^{b}	1.06^{c}	63.11^{c}	0.90^{a}	69.04^{b}
T3- 2% Common salt*	0.34^{b}	73.54^{b}	0.09^{c}	83.24^{c}	0.81^{c}	60.66^{c}	0.44^{a}	67.60^{b}	0.68^{b}	76.17^{b}	0.98^{a}	66.43^{b}
T4-1% Turmeric*	0.55^{d}	57.93^{d}	0.11^{d}	79.61^{c}	1.34^{d}	34.56^{f}	0.70^{b}	48.89	1.19^{c}	58.41^{c}	1.33^{b}	54.32^{c}
T5-2% Vinegar*	0.42^{c}	67.80^{c}	0.07^{b}	86.26^{b}	0.07^{a}	96.61^{a}	0.54^{b}	60.47^{c}	0.94^{c}	67.27^{c}	1.20^{b}	58.93^{c}
T6-1% KAU Veggie wash*	0.19^{a}	85.63^{a}	0.05^{b}	90.67^{b}	0.80^{c}	61.20^{c}	0.40^{a}	72.08^{b}	0.66^{b}	77.15b	0.64^{a}	77.93^{a}
T7-1% KAU Veggie wash* + cooking	0.18^{a}	86.27^{a}	0.02^{a}	96.47^{a}	0.27^{b}	86.45^{b}	0.24^{a}	81.36^{a}	0.38^{a}	86.60^{a}	0.63^{a}	78.59^{a}
T8- Washing* + cooking	0.30^{b}	76.94^{b}	0.08^{c}	84.86^{c}	0.80^{c}	61.15^{c}	0.39^{a}	71.62^{b}	0.69^{b}	76.00^{b}	1.10^{b}	62.30^{b}
Untreated	1.32	—	0.55	—	2.06	—	1.37	—	2.87	—	2.92	—
CD (0.05)	0.087	8.330	0.023	5.839	0.107	5.049	0.201	9.556	0.255	9.150	0.508	9.435
MRL (EU)	0.02		0.02		0.05		0.05		0.01		0.01	

* subjected to dipping in treatment solutions for 10 minutes followed by three normal washings

three washings with tap water also could remove residues up to the level of removal observed in dipping in KAU veggie wash (1%) plus cooking. The residue removal ranged from 61 to 90 per cent (Table 3). Whereas dipping in plain water alone removed residues only up to 56 per cent except in the case of malathion (80.56 %). This treatment had significant variation with dipping in water alone for all insecticides removal. The composition and pH may be the reason for the effectiveness (Mathew, personal communication, 2014). No such relevant studies were conducted earlier, but a study conducted by Rasheed (2013) pointed out a good adsorption efficiency (70 - 90 %) of lingo-cellulosic wastes of plant origin like coffee grounds, melon seeds and orange peels for o-nitrophenol and p-nitrotoluene. Thus, it could be inferred that, insecticide residues degraded at such a low pH and got adsorbed on to mucilage/lingo-cellulose fraction of veggie wash.

Up to 96.61 per cent of residues of chlorpyriphos were removed when amaranth plants were subjected to dipping in vinegar (2 %) for 10 minutes followed by three normal washing with tap water. Vinegar was found as the better option for chlorpyriphos sprayed amaranth plants as it removed up to 40 per cent more residues when compared to simple washing with tap water. Highest removal of organophosphate insecticides tested was in the case of chlorpyriphos (96.61%) whereas only 50 per cent of residue was removed by dipping in water. At the same time, no treatment other than vinegar (2%) could remove chlorpyriphos up to 90 per cent. The percentage of removal of the organophosphate group of insecticide was maximum in vinegar and this was attributed by polar nature of the insecticide belonging to this group. Varghese (2011) reported that the polar nature of insecticides is the deciding factor in removal by vinegar. These results agreed with those obtained by Nair (2013) who reported that dipping of curry leaf in 2 % vinegar for 15 minutes resulted in up to 93 per cent of organo phosphate residues and up to 66 per cent residue removal at one day after spraying.

The combination of washing with water (dipping of amaranth plants in water for 10 minutes) and cooking for 10 minutes (closed pan) had given satisfactory removal of residues of organophosphate insecticides. These results may be influenced by the physico-chemical properties of the pesticides when subjected to heat treatment. Abou-Arab (1999) found that home canning reduces organophosphates more than organo chlorine pesticide residue levels. The synergic effect of washing and cooking resulted in 39 to 100 per cent removal of pesticide residues from different food samples (Yang *et al.,* 2012). The loss of pesticide residue during heat processing may be due to evaporation, co-distillation., thermal degradation which vary with the chemical nature of the individual pesticide (Sharma *et al*., 2005 and Balinova *et al.,* 2006)

In the case of 2 % common salt treatment the results agree with those of Nair *et al.,* (2014) who reported that up to 68 per cent of organophosphate and 50 per cent of synthetic pyrethroid insecticide residues were dislodged in okra by subjecting to 2 per cent common salt for 15 minutes. The cause and effect of the reduction in 2 % NaCl washing solutions is still not known and needs further investigation. Dipping of amaranth plants in tamarind (2 %) solution for 10 minutes followed by three washings with plain water also removed impartially good amount of residues. Singh *et al*. (2007) reported that tamarind pulp had significant amount of organic acids, of which tartaric acid (98 %) is the major one having a pH of 2.7. Varghese and 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. In the case of chlorpyriphos, turmeric (2 %) was inferior (34.56 %) over dipping in water (56.18 %) and superior over dipping in water (37.39 %) in the case of ethion (54.32 %). These results were not in agreement with the findings of Vijayasree *et al.,* (2012) and Nair (2013) who reported that turmeric solution (1%) was effective in removal of insecticide residues from curry leaves and okra respectively.

The efficiency of treatments differed with respect to different insecticidal chemistries and also with the properties of commodity tested. The effect of processing depends upon many factors such as water-octanol partition coefficients, water solubility, heat stability, vapour pressure etc. In all above treatments more removal noticed in organophosphate insecticide residues than in synthetic pyrethroid insecticides it may be because of higher solubility for organophosphate insecticides than synthetic pyrethroids and also because of polarity of compound (PPDB, 2015). Washing could remove more effectively in the case of surface residues. Washing is very effective in removal of residues located on surface of commodity. In the case of surface residues thermal treatment is also effective. This was supported by results of Dikshit (2001). From the above results it is clear that dipping in 1 per cent KAU veggie wash for 20 minutes followed by cooking and dipping in 1 % KAU veggie wash for 20 minutes followed by washing (without cooking) are recommendable treatments to remove significant amounts of pesticide residues from amaranth.

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