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Pesticidal contamination status and decontamination of various pesticide residues in fruits by household preparations

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ABSTRACT

The residual concentration of some pesticides in seasonal fruits was monitored. Locally available fruits were purchased from main market and nearby villages and analyzed by gas chromatography. In decontamination the apple and papaya fruits were spiked with some amount of pesticides (9-12mg/kg). Spiked samples were analyzed before and after of different household processing to evaluate the effect of processing. In apple and papaya fruits cumulative effect of washing with hot water showed the residue reduction by 75.9-92.4% followed by 80.8-91.1 % with salt water and 65.8-82.0 with 0.1 % citric acid solution washing and 47.5-71.2 % with tap water washing.

KEYWORDS

Monitoring;
Fruits;
Fungicide;
Insecticides;
Household preparations;
Decontamination.

INTRODUCTION

High demand for good quality products and urgent need for self sufficiency in food production is responsible for increasing use of pesticides in Asia, Africa, Central and South America[1] . India is the third largest consumer of pesticides in the world and highest among the South Asian countries. Total 173 pesticides have been registered under insecticide act 1968 in India[2]. During cultivation of fruits insecticides are used to control the pests and fungicides to control the diseases. Pesticides are directly spraying on crops and some of them may persist in the form of residues in fruits and vegetables after their harvest[3]. Improper use of pesticides on crops can cause the harmful effects of pesticide residues such as immune system problems and birth defects. Because of their small size and higher metabolism, mainly children's may be exposing to negative health effects from pesticide exposure through the food.

The study of monitoring and decontamination of pesticide residues is necessary to generate a baseline data to face the challenges of food safety and to support the policy makers. Keeping in this view, present study was designed to determine the organochlorine, organophosphate and fungicide residues in fruits from different places of Jalgaon district in order to find out the extent and magnitude of these pesticide residues and to generate a data on various household processing for decontamination of pesticide residue such as washing with water, hot water, salt water and citric acid solution. Earlier study reveals that several household processing can reduce the residue in food commodities[1,4-7].

EXPERIMENTAL

Part 1 : Monitoring study

Composite sample of two kg each of the fruit was collected from different local market sites and nearby villages of the Jalgaon city. Selection of fruits viz. banana (musa sapientum), apple (musa domestica), grapes (citrus grandis) and papaya (carica papaya) were based on their easy availability and relative importance in view of healthy diet. Samples were picked up and collected in polythene bags and transferred to the laboratory. Extraction of pesticide residue was carried out with the help of multiresidue method in fresh samples. Each fruit sample was chopped and homogenized in high speed blender and mixed with 10gm anhydrous sodium sulphate. This sample was extracted with 100ml acetone by mechanical shaking for 1 hour by using the technique of Kumari et al.[8]. Extract was filtered through Whatman filter paper No.40. Filtered extract was diluted 4-5 times with 10% NaCl solution and partitioned thrice with 50, 25, 25 ml ethyl acetate. Organic phases were combined.

Cleanup: All samples were cleaned up by florisil column method[9] before analysis by GC. The first layer is of glass wool was plugged at the bottom. To the top of glass wool, a layer of florisil (20gm) was allowed to settle in a column. After that a layer of anhydrous sodium sulphate (5cm) was added and followed with top layer of charcoal (2cm). The column containing adsorbents were washed with ethyl acetate and allowed to settle before transferring of sample. Flow rate at 1ml/min was adjusted. Filtrate was evaporated in a rotary vacuum evaporator up to dryness and redissolved in acetone (2ml) to make final volume and analyzed on GC.

Part 2 : Processing of fruits

For decontamination study apple and papaya fruits were procured from the local market and sprayed with known amount of pesticides in laboratory. Apple samples were spiked with cypermethrin (10mg/kg) and chlorpyriphos (9mg/kg). Papaya samples were spiked with endosulfan (10mg/kg) and quinalphos (12mg/kg). After spraying samples were kept for 3 hours and divided in to four equal parts for further four processing treatments.

1. Fruit samples were washed under running tap water for 5 minutes with slight rotation by hands and dried on blotting paper.
2. Fruits were kept in tray and washed with hot water (55-65°C) for 2 to 3 minutes.
3. Fruit were washed with 10% NaCl solution at room temperature followed by washing with tap water and dried on blotting paper.
4. Sample were dipped and washed with 0.1% citric acid solution followed by washing with tap water.

After processing these samples were subjected to the extraction and cleanup procedure.

GC analysis: Pesticide residues analyzed by gas chromatograph (Chemito, GC-8610) with Ni^{63} selective electron-capture detector (ECD). The capillary column used was BPX-5 of 5% diphenyl/95% dimethyl fused silica capillary column (30mX0.53 mm ID, 0.25μm film thickness), carrier gas was nitrogen (N_2); flow rate: 30ml min^{-1} through column. The conditions for GC maintained during the analysis were injection temperature 240°C, oven temperature 180^{0}C, Ramp-I 220°C with hold time 7°C/min., Ramp-II 250°C with hold time 8°C/min., detector temperature 300°C.

RESULT AND DISCUSSION

Monitoring study

Analytical data related to residues status of pesticides in four different fruits were determined in TABLE 1. The analytical method used in present study was gas chromatography by using electron capture detector. The residual concentration of a pesticide was an average of three replicates and comprise of OC (A-endosulfan, B-endosulfan), OP (dimethoate, malathion, chlorpyriphos, quinalphos), Pyrethroids (cypermethrin), fungicide (propiconazole) are presented in TABLE 1. In this study all fruit samples were found to be contaminated with above pesticides.

Eight apple samples from local markets and nearby villages analyzed for the presence of pesticide residues. All apple fruits were contaminated with chlorpyriphos and quinalphos; six were contaminated with A-endosulfan, B-endosulfan and dimethoate, seven with malathion. Cypermethrin was detected in five samples.

All the grapes samples in market were contaminated with pesticides such as chlorpyriphos, A-endosulfan, dimethoate, cypermethrin, propiconazole, quinalphos and malathion. Chlorpyriphos was detected in five samples. A-endosulfan and propiconazole each

TABLE 1 : Pesticide residues* (mg/kg) in fruits

Fruits→ Pesticides↓	Apple (8)[a] average residues±SD	Grapes (7)[a] average residues±SD	Papaya (6)[a] average residues±SD	Banana (7)[a] average residues±SD
Chlorpyriphos	0.09±0.02(8)[b]	0.036±0.016(5)	0.40±0.03(6)	0.403±0.023(5)
A-endosulfan	0.11±0.04(6)	0.004±0.001(4)	0.19±0.002(5)	ND
B-endosulfan	0.079±0.07(6)	ND	0.05±0.003(5)	ND
Dimethoate	0.28±0.05(6)	0.737±0.07(6)	0.11±0.021(4)	ND
Cypermethrin	0.36±0.006(5)	0.018±0.009(7)	0.06±0.004(6)	0.065±0.082(5)
Propiconazole	ND	0.311±0.04 (4)	ND	0.069±0.022(5)
Quinalphos	0.05±0.01(8)	1.081±0.07 (7)	0.006±0.001(5)	0.093±0.019(3)
Malathion	0.026±0.01(7)	0.022±0.031(7)	0.46±0.007(3)	ND

***Average of three replicates, a=No. of samples analyzed, b=No. of samples contaminated, MRL value (mg/kg) for as Chlorpyriphos: 0.5, Endosulfan: 2.0, Dimethoate: 2.0, Malathion: 4.0[16] Cypermethrin: 0.5, Propiconazole: 0.1[17]**

were found in four samples. Six were contaminated with dimethoate. Cypermethrin, quinalphos and malathion each was found in seven samples. All residue levels were below the tolerance limit, except four samples contaminated with propiconazole were showed the residue above MRL.

In case of papaya six samples were analyzed to determine the residue level. It revealed that all are contaminated with chlorpyriphos and cypermethrin, four with dimethoate, three with malathion. Five were contaminated with both A and B-endosulfan, quinalphos. But all the residue levels were below the prescribed MRL values.

In banana fruit, level of contamination was less as compared to other fruits. Out of seven samples five were contaminated with chlorpyriphos, three with quinalphos. Cypermethrin and propiconazole were found in five samples. In banana all residue levels were also below the prescribed MRL values. In earlier studies the contamination was found in grapes, apples with more than 10 pesticides having the frequent detection of dicofol and dimethoate, thus in fruits contamination rate is slightly higher than vegetables[10]. Apple fruits were also extensively contaminated from conventional farming and residue was detected in 59.5% of the fresh apple sample[11]. It reveals that malathion was the frequently used pesticide for both vegetables and fruits showing the higher concentration in vegetables as compared to fruits[12].

Processing of fruits

The average percent recoveries of different pesticide compounds from fruit samples spiked at 0.5 and 1.0mg/kg observed in the range of 84 to 96%. The reduction data for pesticide residues in Papaya and Apple fruits by various household processes was given in TABLE 2.

Apple: Apple samples were spiked at 10, 9mg/kg for cypermethrin, chlorpyriphos, respectively and showing the initial deposits of 8.9, 7.9mg/kg respectively for these pesticides.

Papaya: The initial deposits of 8.2 and 10.8 mg/kg was observed for endosulfan and quinalphos at the spiking level of 10 mg/kg and 12 mg/kg respectively (TABLE 2).

Washing with tap water: Washing of apple treated with cypermethrin under the running tap water shows the lowering of initial deposits from 8.9 to 3.9mg/kg

TABLE 2 : Reduction of pesticide residues in Papaya and Apple fruits by different household processes

Fruits	Pesticides	Spiking level mg/kg	Residue* before washing mg/kg	Residue after washing mg/kg	Residue after hot water washing mg/kg	Residue after salt water washing mg/kg	after citric acid solution washing mg/kg
Apple	Cypermethrin	10	8.9±0.005	3.9±0.041	1.2±0.020	1.7±0.031	2.4±0.002
	Chlorpyriphos	9	7.9±0.02	2.8±0.012	0.6±0.10	0.70±0.053	1.42±0.11
Papaya	Endosulfan	10	8.2±0.01	4.3±0.04	1.90±0.042	1.3±0.02	2.80±0.024
	Quinalphos	12	10.8±0.003	3.1±0.021	2.60±0.03	1.85±0.005	2.92±0.019

***residue is represented as average ±SD, average are mean of three replicates**

TABLE 3 : % reduction of pesticide residues due to household processing's

Fruits	Pesticides	%Reduction after washing	%Reduction after hot water washing	%Reduction after salt water washing	%Reduction after citric acid washing
Apple	Cypermethrin	56.1	86.5	80.8	73.03
	Chlorpyriphos	64.5	92.4	91.1	82.0
Papaya	Endosulfan	47.5	76.8	84.1	65.8
	Quinalphos	71.2	75.9	82.8	72.9

showing a reduction of 56.1% (TABLE 3).

Chlorpyriphos residue was reduced from initial deposit of 7.9 to 2.8 mg/kg and shows the reduction of 64.5%.

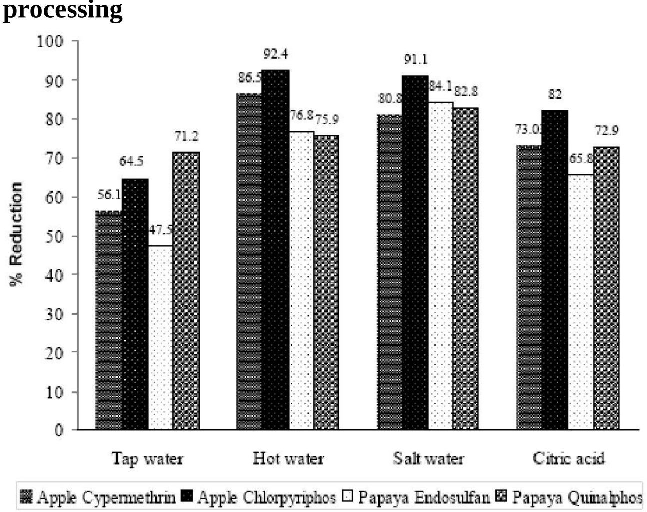
In case of papaya fruits tap water washing reduce the initial deposits from 8.2 to 4.3mg/kg and causing the reduction up to 47.5%. Quinalphos residue on papaya also shows the reduction from 10.8 to 3.1mg/kg. In earlier studies washing was found effective for reduction of residues in vegetables but it depends on a number of factors such as location of residues, age of residue, water solubility, temperature and type of washing[4].

Hot water washing: Apple fruit samples were washed with hot water shows the reduction of initial deposits from 8.9 to 1.2mg/kg and having the percent reduction 86.5% of cypermethrin. Chlorpyriphos residue was reduced from initial deposits of 7.9 to 0.6mg/kg thus showing a 92.4% reduction.

In papaya samples treated with endosulfan and quinalphos the initial deposits of 8.2 and 10.8 were reduced to 1.90 and 2.60mg/kg respectively showing the reduction of 76.8 and 75.9% respectively.

Salt water washing: After washing the apple fruits sprayed with cypermethrin resulted in a reduction of initial deposits from 8.9 to 1.7mg/kg and showing a reduction of 80.8 %. Chlorpyriphos residue on apple was reduced from 7.9 to 0.70mg/kg thus showing the reduction of 91.1%.

Figure 1 : % Reduction in pesticide residue after household processing



Papaya spiked with endosulfan, when washed by using salt water, showed a reduction of 84.1% from the initial deposit of 8.2mg/kg. Quinalphos residue was also reducing from initial deposit of 10.8 to 1.85mg/kg having the reduction of 82.8%.

Citric acid solution washing: The initial deposit of cypermethrin and chlorpyriphos were reduced from 8.9 to 2.4mg/kg and 7.9 to 1.42mg/kg respectively thus causing a reduction of 73.03% and 82.0% respectively.

When papaya fruits treated with endosulfan were subjected to citric acid solution washing, it shows the reduction from 8.2 to 2.80mg/kg thus leading a reduction up to 65.8%. In case of quinalphos 72.9% reduction takes place and residue reduced from initial deposit of 10.8 to 2.92mg/kg.

Thus, a comparison of the reduction due to all household processes showed that in apple, washing with hot water is more effective to dislodge the residue of both cypermethrin and chlorpyriphos followed by other solvents such as salt water, citric acid solution and tap water. In case of papaya fruit endosulfan and quinalphos residue were reduced significantly by washing with salt water as compared to hot water, citric acid and tap water washing.

So the present study concludes that, almost all fruit samples were contaminated with insecticide and fungicide residue but the residual concentration is within the safe limits. In earlier studies, rinsing of vegetables was also effective for various pesticides[13]. It revealed that certain types of household preparations was significantly reduce the pesticide residues in vegetables[1,4,5,6,14] and in fruits such as processed apple, reduction of azinophos-methyl, chlorpyriphos, esfenvalerate, methomyl residues was also reported[15].

CONCLUSION

Monitoring study concludes that, all fruit samples were contaminated with pesticide residue but all residue levels were within the safe limits. In decontamination the overall comparison of household processing's showed that hot water and salt water is more effective for breakdown of residues. Cypermethrin and chlorpyriphos residue reduction was occurred in order of hot water>salt water>citric acid>tap water. In papaya, endosulfan and quinalphos were in the order of salt water>hot water>citric acid>tap water. Thus reduction is very important in view of consumers health affected by the residue hazards and application of pesticides should be avoided before harvesting period of fruits.

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