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Assessment and management of pesticide residual toxicity in grapes and strawberry

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Abstract
This study aimed to quantitatively and qualitatively analyze the pesticide residues (PR) in selected fruits with and without pre-treatment. Two fruits (grapes and strawberry) were selected randomly from a local market in Coimbatore district. Pesticides were quantified by Gas Chromatograph with and without treatment (washing by dipping in 2% salt solution for 10 min, mechanical peeling and juicing) concurrently. QuEChERS method was used for preparation of samples for analysis of pesticide residue. The samples without pre-treatment showed the presence of Organo Phosphorus (OP) pesticides. The amount of Ethion in the grape sample was 15.99 ppm and MePrimphose was 22.98 ppm, which is above the MRL (i.e. > 0.05), while strawberry was reported to have Ethion (3855.56 ppm). The samples analysed after pre-treatment showed no detectable level of pesticide residue. The study puts forward the importance of organic foods and kitchen garden for elimination of these toxicities to human health.

Keywords: pesticide residual analysis, gas chromatography, MRLs, fruits

Introduction
India has been bestowed with wide range of climatic and physio-geographical conditions and as such is most suitable for growing various kinds of fruits. During 2012-13, its contribution in the world production of fruits was 12.6 per cent. In India, total production of fruits during 2013-14 was 84.4 million tonnes. Pesticides are chemical substances used to kill animal, insect, plant and fungal pests in agricultural, domestic and institutional settings (Sanborn *et al.* 2002). Interest on pesticide toxicity has particularly increased over the past years owing to increasing evidence of carcinogenic, mutagenic and teratogenic effects in experimental animals and exposed humans (Hrelia *et al.* 1996). This study aimed to quantitatively and qualitatively analyze the pesticide residues (PR) in selected fruits with and without pre-treatment.

Methods
Selection and Collection of samples
Two fruit samples namely grapes *(Vitis vinifera)* and strawberry *(Fragaria × Ananassa)* were selected manually based on visual appearance from the local fruit market. These samples were chosen for the study as per the list of fruits with highest level of residual pesticides, published by FDA, 2014.

Sample preparation
QuEChERS method was used for preparation of samples for analysis of pesticide residues (Anastassiades *et al.* 2003) [1]. The samples collected for the pesticide residual analysis were weighed before pre-preparation. The samples were cut into pieces and ground to a paste to obtain juice. Quick, Easy, Cheap, Effective, Rugged, and Safe, the QuEChERS ("catchers") method is based on work done and published by (Anastassiades *et al.* 2003) [1]. QuEChERS was developed using an extraction method for pesticides in fruits and vegetables, coupled with a clean-up method that removes sugars, lipids, organic acids, sterols, proteins, pigments, and excess water. This technique offers a user-friendly alternative to traditional liquid-liquid and solid phase extractions. The process involves two simple steps. First, the homogenized samples are extracted and partitioned using an organic solvent and salt solution. Then, the supernatant is further extracted and cleaned using a dispersive solid phase extraction (dSPE) technique.

Analysis of pesticide residues
The analysis of pesticide residues in the collected samples was carried out as two different sets. One set of analysis was carried out in the fresh fruit sample. Another set of analysis was carried out after a pre-treatment (washing by dipping in 2% salt solution for 10 min, and juicing). The fruit sample is ground using juicer mixer and the juice is filtered. The peel and other residues are discarded and the juice is used for pesticide residual analysis (Kaushik *et al*. 2009) [7, 9].

Qualitative and Quantitative analysis of pesticide residues by Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS)
Estimation of pesticide residues was undertaken using Gas chromatograph (GC) equipped with electron capture detector and flame thermionic detector (Shimadzu 2010 Plus) and the amount of residue was quantified using GC-MS. The results achieved were compared with the FSSAI (Food Safety and Standards Authority of India) MRLs. The concentration is expressed in milligrams of pesticide residue per kilogram of the commodity.

Results and Discussions
Analysis of pesticide residual in fruits samples without any pre-treatment
Residues in food and drink are an important source of on-going everyday low-level exposure to mixtures of pesticides, particularly residues in fresh fruit and vegetables, and drinking water. (Benbrook 2008).The major contaminant detected in the fruits samples were the organophosphates. The samples analyzed contained no detectable level of the monitored OrganoChloride Pesticides and synthetic pyrethroids. The presence of organophosphate residues in the fruits samples is an indicative of the change in usage of pattern of insectides in Tamil Nadu and India. The strawberry sample shows the presence of Ethion in very high concentration (3855.56 ppm) which is very much higher than MRLs (Maximum Residual Limit). The organochlorides and synthetic pyrethroids were found to be below the detectable level 0.01 and 0.1 respectively.

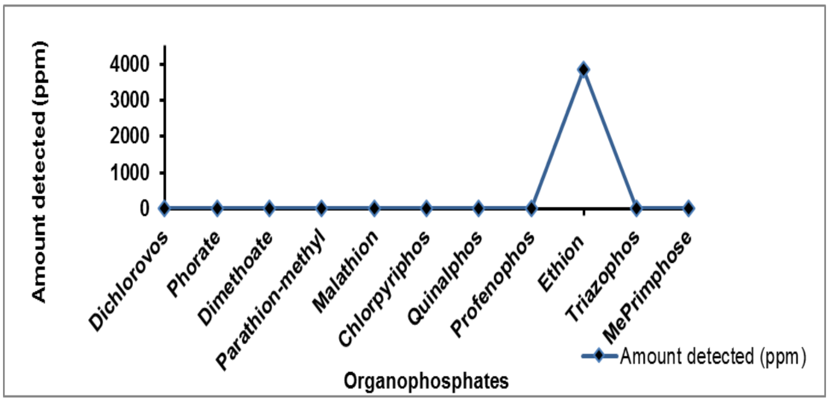

Fig 1: Analysis of pesticide residual in fresh Strawberry sample

Among the organophosphate compounds, Ethion (15.99 ppm) and MePrimphose (22.98 ppm) were detected in grape sample, which is found to be above the MRL (i.e > 0.05). The presence of organophosphates in grapes obtained from local market has also been reported by Bempah *et al.* (2011) [2], Ramesh and Murthy, 2013 and Parveen *et al.* (2013) [11].

Table 1: Analysis of pesticide residual in grapes sample without any pre-treatment

Organochlorine compounds	Amount detected (ppm)	Synthetic pyrethroids	Amount detected (ppm)	Organo phosphates	Amount detected (ppm)
α-HCH	BDL (<0.01)	Bifenthrin	BDL (<0.1)	Dichlorovos	BDL (<0.05)
β-HCH	BDL (<0.01)	Fenpropathrin	BDL (<0.1)	Phorate	BDL (<0.05)
γ-HCH	BDL (<0.01)	λ-Cyhalothrin	BDL (<0.1)	Dimethoate	BDL (<0.05)
δ-HCH	BDL (<0.01)	β - Cyfluthrin	BDL (<0.1)	Parathion-methyl	BDL (<0.05)
Dicofol	BDL (<0.01)	α-Cypermethrin	BDL (<0.1)	Malathion	BDL (<0.05)
Endosulfan-α	BDL (<0.01)	Fenvalerate	BDL (<0.1)	Chlorpyriphos	BDL (<0.05)
Endosulfan-β	BDL (<0.01)	Fluvalinate	BDL (<0.1)	Quinalphos	BDL (<0.05)
Endosulfan sulfate	BDL (<0.01)	Deltamethrin	BDL (<0.1)	Profenophos	BDL (<0.05)
p,p'-DDD	BDL (<0.01)			Ethion	15.99
p,p'-DDT	BDL (<0.01)			Triazophos	BDL (<0.05)
p,p'-DDE	BDL (<0.01)			MePrimphose	22.98

Analysis of pesticide residual in fruits samples after pre-treatment
The pesticide residual analysis in fruits samples carried out after pre-treatment showed no detectable level of organochloride, Synthetic pyrethroids or organophosphates. This shows that traditional processing techniques like dipping in salt water, and juicing (mixer) in fruits leads to removal of pesticide residues to a greater extent. Similar results were also reported by Gouri, 2012.

It was reported that washing the fruits with different household compounds reduced the residues by 20-89 per cent. Geetanjali *et al.* (2009) [7] reported that, the pulp or pomace by-products, which often include the skin, retain a substantial proportion of lipophilic residues. Thus moderately to highly lipophilic pesticides such as parathion, folpet, captan and synthetic pyrethroids are poorly transferred into juices and the residues are further reduced by clarification operation such as centrifugation or filtering.

Acute health problems which are sometimes misdiagnosed or not recognized as being associated with pesticide toxicity, include blurred vision, headaches, salivation, diarrhoea, nausea, vomiting, wheezing, eye problems, skin conditions, seizure, coma, and even death. Mild to moderate pesticide poisoning mimics intrinsic asthma, bronchitis, and gastroenteritis. Pesticides are especially harmful to children because of their developing physiology. And, relative to their size, they are exposed to higher amounts of pesticides (Kumar *et al.* 2013) [10].

Decreased fertility in both sex, demasculinization (antiandrogenic effects), elevated rate of miscarriage, altered sex ratio, and change in the pattern of maturity are among the most reported reproductive dysfunctions induced by chronic exposure to pesticides (Frazier, 2007) [6].

Conclusion

The study showed that OrganoPhosphorus pesticides (OPP's) are widely used in the world as an alternative in the recent years to pest control with organochlorine pesticides which leads to long term health hazards. The levels of Ethion, MePrimphose Quinalphos, Profenophos, and Fenthion residues in the samples were higher. The samples contained maximum residues of organophosphates that could be partially eliminated by traditional treatments. The solution to this concern lies in promoting practices like Integrated Pest Management (IPM), organic farming, biopesticides and crop diversification.

Recommendations

- Farmers to be educated on the judicial use of pesticides (Crop Specific) and the toxicity of pesticide residues to health
- Encourage them on the use of bio pesticides
- Decontamination methods may be developed at the household level
- Encourage people to have their own Kitchen garden

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