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Analysis of Pesticide Residues in Water, Rice, Fruits and Vegetables

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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Original Research Article

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ABSTRACT

Pesticides have played a major role in increasing agricultural output by pest control and eliminating insect driven illnesses. Kerala's tragedy on endosulfan exposure made us to study pesticides in water, rice, fruits and vegetables from Thiruvananthapuram location. Rice (the main cereal consumed in Kerala), fruits, and vegetables, as well as water samples from wells and streams in the Thiruvananthapuram districts, were collected for analysis of residue levels in major food items consumed by people in Kerala. The research was carried out to measure the concentration of organochlorine, organophosphorus, and synthetic pyrethroid pesticides using gas chromatography. The water and food samples collected were analysed for pesticide residues and the quantities were estimated using GC-ECD/NPD. A standard mixture containing Pesticides (OCs, OPs, Pyrethroids, and carbamates) was run before the actual samples. The detection was used to estimate the residues of fifteen commonly used pesticides, namely organochlorine pesticides (endosulfan, dieldrin, aldrin, lindane, DDT), organophosphorus pesticides (chlorpyrifos, profenophos, quinalphos, dimethoate, phorate) and synthetic pyrethroid pesticides (cypermethrin, fenvalerate, deltamethrin, carbofuran). The study concluded that food exposure to pesticides would result in unacceptable health hazards and awareness of pesticide residues in foodstuffs, as well as to quantify the possible health. Hence, necessary to maintain the survey of pesticide residues in all food commodities in order to safeguard the consumers.

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1. INTRODUCTION

Pesticides are used by farmers around the world, including India, to avoid disastrous crop losses caused by pests and diseases. Thus, pesticides have been used in agriculture in India for several decades, not only to manage and to eliminate crop pests, but also to combat disease vectors in the public health sector. Pesticide pollution of water bodies, particularly those that are submerged, is becoming a serious problem. Numerous authorities identified the presence of pesticides in the subsurface water in agriculturally developed areas. Endosulfan residual (ppm) values were very high in blood, fruits, and tissues were detected from samples of Padre village in the Kasargod district of Kerala [1]. All farmers who regularly practise commercial farming use preventive methods for the protection of plants. According to another study carried out in Kerala [2], the application of the pesticide was found to start from transplantation. Of the approximately 15 chemicals in bitter gourd, eight were insecticides, four were fungicides, one was a weedicide, and the rest were stimulators for plant growth. During the seedling transplantation, phorate granules were found to be placed in the pit. At an interval of two weeks, the prophylactic use of pesticides was initially reversed, which fell to two days as the crop began flowering and the fruit set. Furthermore, Acetamaprid, Phorate and Dimethoate were sprayed six times each, while Quinalphos and Indoxacarb were sprayed four times each, and the remaining three to four times each. Farmers used pesticides as many as 50 times on bitter gourds during a 90-day crop cycle. Even if there are many reports from various parts of the globe, including India, very few areas are examined in comparison to the large number of sensitive areas. Moreover, the studies in India are mostly concentrated on major cities or industrialised areas, avoiding the most susceptible rural areas, including fields. Besides, the studies show that farmers are extremely unaware of the precautions or incapable of following supervised trials of pesticide applications. In the case of Kerala, the studies are too few or practically nil to develop a database of the usage of different deadly chemicals other than a few attempts, including the analysis of soil and food materials in Kasargod. It is obvious that there is a need to analyse food and environmental samples primarily in order to controlled usage of pesticides in agriculture and, indeed, by using pesticide-contaminated products, to limit the risks of human residue intake. This study has revealed the pesticide load imposed by pollution of water, rice, vegetables, and fruits. We assumed that this study would help to raise consumer and producers' awareness of the levels and possible health risks associated with the contamination of our food and environment.

2. METHODOLOGY

2.1 Analysis of Pesticide Residues from Samples

Many steps are involved in analysing pesticides in different selected fruits, vegetables, and water samples taken from various locations. After a sample has been composited, the following procedures are often taken in pesticide residue analysis:

2.2 Pesticide Residues Extraction from Sample Matrix

2.2.1 Extraction of residual pesticide from water

The collected samples were extracted through liquid removal [3] A separating burner collected a litre of water sample, and 75 mL of dichloromethane was used as a pesticide. With the aid of a dispenser bottle, dichloromethane (25 mL) has been added. By placing the deck on it, the separating funnel was closed. In and out of the movements of the separator funnel, the solvents were mixed softly (not strongly). Three times has been mixing. Every time the stopper was opened, the gases were removed from the separating funnel. In a round-bottom flak, a small funnel with a small cotton plug and anhydrous Na_2SO_4 at its openings was held in place in 10 minutes for phase separation. Downward separated oily layer was collected with a small funnel. The use of pasture pipettes for efficient separation has been used to add sodium chloride. The addition of dichloromethane (25 mL) and the lower organic layer separation have been repeated three times. There were a few drops of propylene glycol and approximately 3 ~ 4 glass beads in ethyl acetate solution (1:1). The contents were evaporated at a vacuum speed of 40°C in rotary evaporator. Finally, complete drying was done by using nitrogen gas. In 1 mL ethyl acetate, the contents were reconstituted.

Gas chromatography (GC) analysis were conducted using the Ahad K et al. method [4].

2.2.2 Extraction of residual pesticide from rice

The analytical method was based on AOAC [5]. Weighed the grinded rice sample of 20-50 g in duplicate is blended using 350 mL of water and acetonitrile (Ratio of 7:13). Mixed in a stainless-steel blender at high speed for about 5 minutes to get an uniform sample. Sample is filtered using Buckner funnel into a 500 mL flask with suction & transferred the filtrate to petroleum ether. The measured volume of extract/filtrate was added to 100 mL of petroleum ether and transferred to a one litre separator. Further sample was shaken vigorously for 2 minutes before adding 10.0 mL of saturated NaCl and 600 mL of H_2O. Added 15 g of anhydrous sodium sulphate (Na_2SO_4) & vigorously shaken. Concentrated the filtrate to 15 mL in Kuderna-Danish evaporative concentrator & directly transferred the solution to Florisil column for cleanup before analysis [6]

2.2.3 Extraction of residual pesticides from vegetables & fruits

Common approach to remove non-ionic pesticides from the plant matrix by using organic solvent with a homogenising device. For extraction of pesticide residues from vegetable & fruit samples, Ethyl acetate has been shown to be a good solvent compared to other solvents because of its high polarity and thermally volatile and labile compound. Kadenezki et al. [7] have made changes in extraction procedure to make it faster and economical.

Each chopped sample is weighed 1 kilogram & mix thoroughly. Transferred 200 g of chopped sample into a fast blender for homogenous sample. Into a 250 mL Erlenmeyer extraction flask taken 50 g of sample and mixed in a horizontal shaker for 2 hours and then added to a 75 mL ethyl acetate and 25 g anhydrous Na_2SO_4. A Whatman No.4 filter paper is used to filter the ethyl acetate extract [8-12].

2.3 Removal of Water from the Extract

2.3.1 Cleaning

2.3.1.1 Sample clean-up

Due to the non-selective nature of the exhaustive extraction techniques and the complexity of the sample matrices, complex extracts are generated that require additional purification to eliminate any interfering compounds recovered concurrently with pesticide residues. Florisil column adsorption chromatography was used for this purpose.

2.4 Analysis

2.4.1 Analysis of organochlorines and synthetic pyrethroid pesticide residues

Gas chromatography (Thermoquest-Trace GC) with the 63Ni selective Electron Capture Detector was used. This detector enables the identification of pollutants at trace levels as low as ppb in the presence of a large number of chemicals.

Instrumental parameters:

Column type : DB-17, 30 m x 0.25 mm and film 0.25 µm

Oven temperature : Initially 120°C with a hold time of 1 minute, then rise 205°C at a rate of 25°C/minute with a hold time of 1 minute, finally to 290°C at a rate of 2°C/minute with a hold time of 12 minutes

Carrier gas : Nitrogen

Flow rate : 0.4 mL/min

Mode : Splitless

Injector temperature : 270°C

Detector temperature : 320°C

Injection volume : 2 µL (For Standard and samples) (Syringe make: Hamilton, Capacity: 10 µL)

Makeup gas (N_2) flow : 60 mL/min

Peak identification was performed by the GC software (Chromcard 32-bit Ver 1.06 October 98) calibration table set up with a relative retention time window of 0.65%.

2.5 Analysis of Organophosphorous Pesticides

To examine the organophosphorus insecticides Gas chromatography (Nucon-5765 series) with Nitrogen Phosphorus detector was used.

Instrumental parameters:

Column type: DB-17, 30 m x 0.25 mm and film 0.25 µm

Oven temperature : Initially 120°C hold for 1 minute, then increased to 205°C at a rate of 25°C/minute hold for 1 minute finally increased to 270°C at a rate of 2°C/minute hold for 1 minute
Carrier gas : Nitrogen
Flow rate : 1.3 mL/min
Mode : Splitless
Injector temperature : 270°C
Detector temperature : 300°C
Injection volume : 2 µL (For Standard and samples) (Syringe make : Hamilton, Capacity: 10 µL)
Hydrogen flow : 8 mL/min
Air flow : 80 mL/min
Makeup gas (N2) flow : 25 mL/min

The samples were calibrated (retention period, area count) against a reference combination of 12 organophosphorus pesticides with known concentrations. The relative retention period of each peak was compared to that of standards to characterize it.

2.6 Quantitation

The amounts of residues in the sample extracts were determined using an external technique. The detector response of individual component was estimated using a reference combination containing a known concentration of pesticide. Sample concentration was calculated against the standard concentration. All of the analysis were done in triplicate, and the average concentrations were calculated [13-17].

Concentration of Pesticide Residues in mg/kg =

$$\frac{\text{Area response of sample peak}}{\text{Area response of std peak}} \times \frac{\text{Final volume in mL}}{\text{sample weight in g}} \times \frac{\text{std injected volume in µL}}{\text{sampling volume in µL}} \times \text{Standard Conc.}$$

2.7 Residual Pesticides in Water and Food Samples

Fresh vegetables and fruits samples were collected from the selected areas and were analysed to assess the residue levels of different Pesticides on these crops. The samples were extracted, cleaned up, and analysed using GC. We compared our results with MRLs established by the FAD/WHO CODEX Alimentarius Commission. Residue levels of less than the minimum detectable quantities are not reported and are indicated as zero.

2.8 Residual Pesticides in Water Samples Collected from Trivandrum

In Trivandrum, the samples were collected from Aruvikkara (WS1) dam and the fresh-water lake at Vellayani (WS2). The well samples were collected from wells in the Palode (WW1) and Kallara (WW2) areas of Trivandrum. Individual pesticide concentrations in water samples obtained from various places in Trivandrum are mentioned under Table 1. A comparison of residues in well and river water samples is shown in Fig. 1.

In water sample WW1, the residues of organochlorines were found in all except aldrin but the level and endosulfan and dieldrin were found above MRL, among organophosphates-chloropyrifos and dimethoate were detected and these were below the residue limit and all pyrethroids were detect and the concentration of fenvalerate and carbofuran were exceed the residue limit. In water sample WW2, the residues of organochlorines-endosulfan, lindane, and DDT were detected whereas the concentration of lindane was exceeded. Among organophosphates all were detected except chloropyrifos and phorate, and quinalphos was above MRL. All of the pyrethroids analysed were present in the samples except cismethrin. The concentration of fenvalerate and carbofuran were exceeded the limit.

In water sample WS1, the organochlorines residues of dieldrin and DDT were detected, and the concentrations exceeded MRL in case of dieldrin. Among organophosphates-profenofos, quinalphos, and chloropyrifos were detected, and the concentration of profenofos and quinalphos were found to be above MRL. All of the pyrethroids analysed were present in the samples except cismethrin. But the values were within the limit except for fenvalerate and carbofuran. In water sample WS2, residues of endosulfan and DDT were detected among organochlorine pesticides, but the values were below the residue limit.

All the organophosphates analysed were found to be present except for profenophos. Moreover, the concentration of phorate was found above MRL. All of the pyrethroids analysed were present in the samples except deltamethrin and cismethrin. The concentrations of fenvalerate and carbofuran exceeded the limit in the samples.

Table 1. Pesticide residues analyzed from the water samples (mg/L) collected from Trivandrum

Pesticides	WW1	WW2	WS1	WS2
Organochlorines				
Endosulfan	0.018*±0.08	0.003±0.005	0	0.002±0.008
Lindane	0.013±0.005	0.018*±0.04	0	0
Dieldrin	0.007*±0.003	0	0.024*±0.005	0
Aldrin	0	0	0	0
p,p'-DDT	0.023±0.005	0.01±0.005	0.017±0.008	0.019±0.008
Organophosphates				
Chlorpyrifos	0.013±0.002	0	0.033±0.004	0.045±0.003
Dimethoate	0.021±0.004	0.003±0.008	0	0.016±0.005
Quinalphos	0	0.037*±0.003	0.032*±0.006	0.018±0.04
Profenophos	0	0.013±0.004	0.027*±0.05	0
Phorate	0	0	0	0.035*±0.02
Synthetic pyrethroids				
Cypermethrin	0.038±0.006	0.024±0.005	0.053±0.03	0.004±0.006
Fenvalerate	0.005*±0.009	0.019*±0.04	0.042*±0.005	0.048*±0.008
Deltamethrin	0.002±0.002	0.023±0.009	0.018±0.006	0
Cismethrin	0.008±0.003	0	0	0
Carbofuran	0.028*±0.004	0.02*±0.01	0.038*±0.004	0.056*±0.006
∑Mean level	0.018±0.005	0.018±0.03	0.018±0.08	0.02±0.004

*N.B: *values above corresponding MRL. The MRLs (mg/kg) for endosulfan: 0.02, lindane: 0.02, dieldrin; 0.01, aldrin: 0.01, DDT: 0.05, chlorpyrifos: 0.5, dimethoate: 0.02, quinalphos: 0.05, profenophos: 0.02, phorate: 0.02, cypermethrin: 0.5, fenvalerate 0.02, deltamethrin 0.05 cismethrin: 0.05 and carbofuran: 0.02*

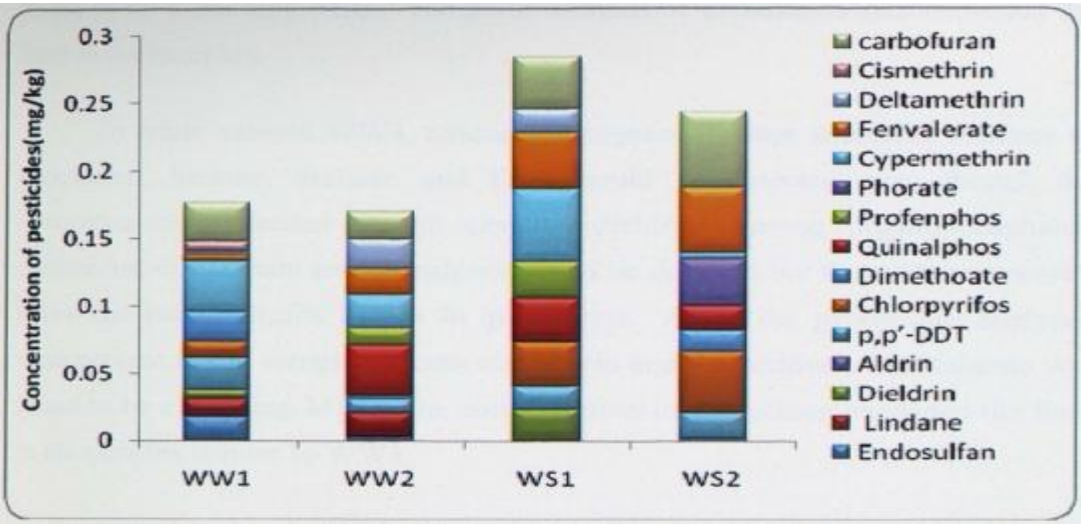

Fig. 1. Comparative level of pesticide contamination in the well and stream water samples (mg/L) collected from Trivandrum. WWl, WW2, WS1 and WS2 denote water samples from wells of Palode, Kallara areas and from Aruvikkara dam and fresh-water lake at Vellayani in Trivandrum were evaluated for Residual pesticides using Gas Chromatography

2.9 Residual Pesticides in Samples of Rice from Trivandrum

Rice samples for analysis were collected from Connemara market (RM1) and Chalai market (RM2) and also from paddy fields from Palode (RF1) and Kallara (RF2). Individual pesticide concentrations in rice samples obtained from various places in Trivandrum are mentioned under Table 2. A comparison of residues in well and river water samples is shown in Fig. 2.

In rice sample RF1, the residues of organochlorines-endosulfan and DDT, among organophosphates-profenophos and quinalphos and pyrethroids except cismethrin were present in the samples and were found to be below MRL. In rice sample RF2, the residues of

organochlorines-only DDT was detected and in organophosphates-dimethoate and profenophos were detected but profenophos was found above MRL. All of the pyrethroids were present except cismethrin and the residues of fenvalerate, found to be exceeding MRL.

In rice sample RM1, the residues of organochlorines-lindane, dieldrin and DDT were detected and concentrations were exceeded MRL in lindane and dieldrin. Among organophosphates-except Profenophos all are detected whereas Quinalphos and phorate found above MRL. In the case of pyrethroids, all of them were present in the samples except cismethrin and deltamethrin. The residual concentration of fenvalerate and carbofuran were found exceeded the limit. In rice sample RM2, the residues of organochlorines-all were detected except aldrin but the values of dieldrin was exceed the MRL. Among organophosphates, phorate, dimethoate and quinalphos were found and only phorate concentration was found above MRL and in pyrethroids-except deltamethrin and cismethrin all were present and the concentration of fenvalerate and carbofuran were exceeded the limit [18-20].

The result also shows that the maximum mean value for residual concentration was found in RM1 samples, followed by RM2, and then by RF1, which indicates that samples collected from market areas show comparatively more contamination than samples from fields. This indicates a high application of pesticides during storage.

2.10 Residual Pesticides of Organochlorine in Fruits & Vegetables Samples of Trivandrum

Table 3 & Fig. 3 depicts the residual pesticide range and mean concentrations of organochlorine pesticide present in vegetable & fruit samples. Endosulfan was found in mango, tomato, cabbage and carrot. All the results of tested samples reveal that residual level is lower compared to its permitted limits. The residues of lindane were present in almost all the samples except banana and the quantity exceeded the MRL in samples of grapes, mango, tomato, bitter gourd, and carrot. Similarly, dieldrin was detected in the samples of grapes, mango, tomato, and carrot except apple orange and banana. The concentrations were above MRL in all the detected samples except in spinach and cabbage. Aldrin residues were detected only in three samples namely banana, tomato, and spinach and the residues tomato samples were found above MRL. As per the record of test samples, DDT is observed in all fruit samples & vegetable samples except mango, spinach and carrot. The values were found to be above the MRL in the cases of grapes and bitter-gourd samples. The outcome clearly indicates that each of the varieties analysed was polluted with a minimum of two pesticide residues.

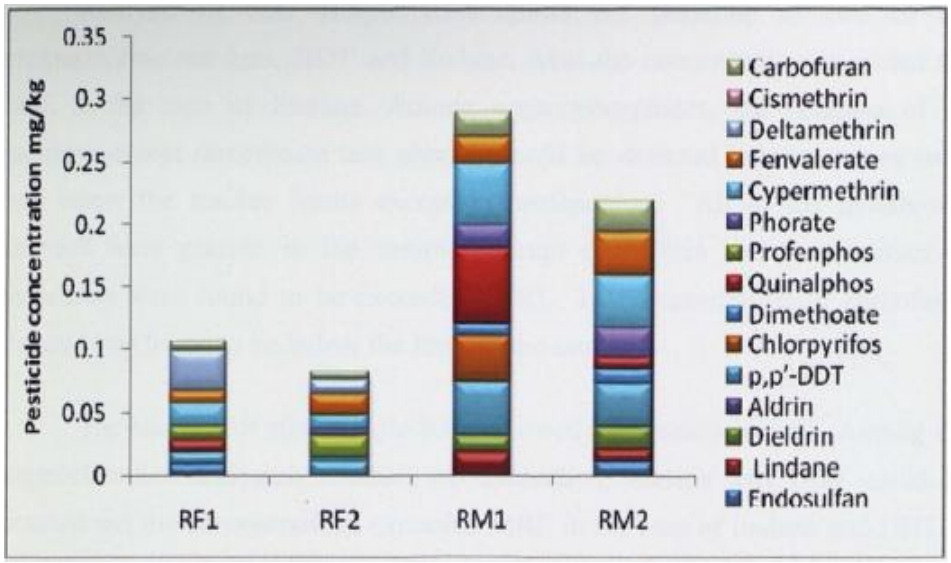

Fig. 2. Pesticide residues (mg/kg) obtained from the Rice samples collected from Trivandrum. RM1, RM2, RF1 and RF2 denote rice samples collected from Connemara market, Chalai market and also from paddy fields from Palode and Ka1lara were evaluated for Residual pesticides using Gas Chromatography

Table 2. Pesticide residues (mg/kg) present in the Rice samples collected from Trivandrum

Pesticides	RF1	RF2	RM1	RM2
Organochlorines				
Endosulfan	0.008±0.01	0	0	0.01±0.005
Lindane	0	0	0.018*±0.008	0.01±0.003
Dieldrin	0	0	0.013*±0.021	0.019*±0.009
Aldrin	0	0	0	0
p,p'-DDT	0.01±0.021	0.011±0.004	0.043±0.034	0.034±0.005
Organophosphates				
Chlorpyrifos	0	0	0.037±0.051	0
Dimethoate	0	0.003±0.003	0.01±0.002	0.012±0.003
Quinalphos	0.01±0.014	0	0.06*±0.006	0.009±0.007
Profenophos	0.011±0.013	0.017*±0.011	0	0
Phorate	0	0.005±0.005	0.019*±0.02	0.024*±0.011
Synthetic pyrethroids				
Cypermethrin	0.018±0.008	0.012±0.004	0.048±0.01	0.042±0.019
Fenvalerate	0.01±0.004	0.017*±0.032	0.022*±0.05	0.034*±0.016
Deltamethrin	0.032±0.005	0.011±0.021	0	0
Cismethrin	0	0	0	0
Carbofuran	0.008±0.009	0.007±0.06	0.02*±0.011	0.025*±0.018

*NB: *values above corresponding MRL. The MRLs (mg/kg) for endosulfan: 0.02, lindane: 0.02, dieldrin; 0.01, aldrin: 0.01, DDT: 0.05, chlorpyrifos: 0.5, dimethoate: 0.02, quinalphos: 0.05, profenophos: 0.02, phorate: 0.02, cypermethrin: 0.5, fenvalerate 0.02, deltamethrin 0.05 cismethrin: 0.05 and carbofuran: 0.02*

Table 3. Organochlorine residual pesticide present in fruit & vegetable samples from Trivandrum market areas

Fruit/Vegetable	Endosulfan	Lindane	Dieldrin	aldrin	p,p'-DDT
Apple	0	0.007±0.005	0	0	0.002±0.05
Orange	0	0.002±0.008	0	0	0.008±0.004
Grapes	0	0.12*±0.002	0.027*±0.023	0	0.058*±0.003
Banana	0	0	0	0.008±0.017	0.024±0.015
Mango	0.008±0.01	0.012*±0.2	0.017*±0.018	0	0
Tomato	0.002±0.05	0.029*±0.02	0.023*±0.042	0.012*±0.04	0.012±0.06
Bittergourd	0	0.085*±0.02	0	0	0.047*±0.021
Spinach	0	0.008±0.02	0	0.008±0.021	0
Cabbage	0.003±0.028	0.004±0.02	0	0	0.016±0.04
Carrot	0.01±0.04	0.02*±0.03	0	0	0

*N.B: Values are the mean of three samples analyzed in duplicate collected from each locations. *values above corresponding MRL. The MRLs (mg/kg) for endosulfan: 0.02, lindane: 0.02, dieldrin; 0.01, aldrin: 0.01 and DDT: 0.05*

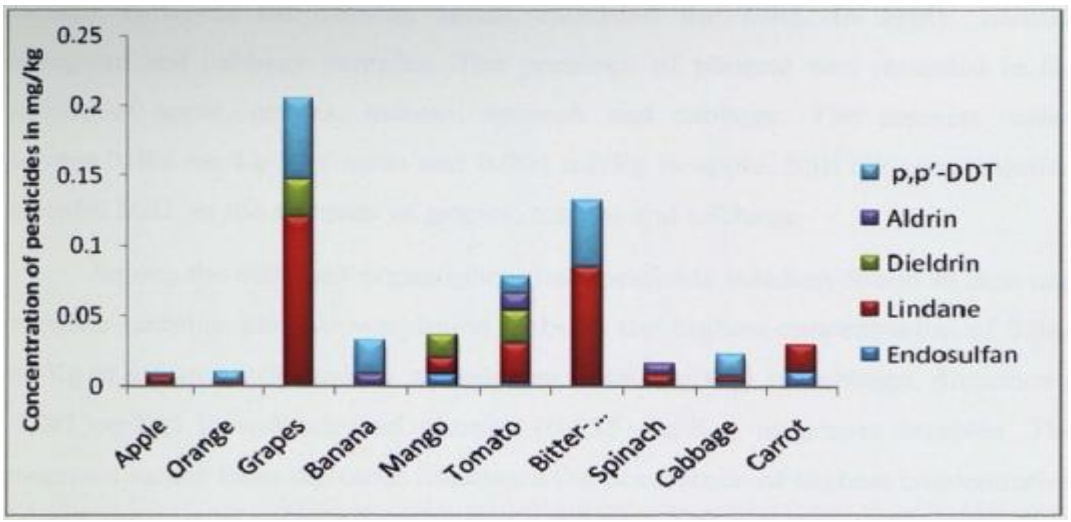

Fig. 3. Organochlorine pesticide residues obtained from the fruits and vegetable samples (mg/kg) collected from Trivandrum market areas

3. RESULTS AND DISCUSSION

To check the efficiency of the system, recovery studies were performed for the residues in each type of sample. Finally, the health risk was estimated according to the lifetime exposure to each of the pesticides analyzed.

3.1 Rice and Water Samples

Below data shown in Table 4, depicts the precision and recovery (express as RSD) results for 3 sets of samples. Data shown reveals average range of recovery for 0.1 and 0.5 mg/kg fortification level of the method fell within 75.2%-95.9% with % RSD in the range of 4.90-12.42 and within 81.8%-96.9% with %RSD in the range of 2.41-9.00 respectively. Table shows that the recovery rate for fifteen pesticides were within acceptable range.

3.2 Fruits/Vegetable Samples

Precision and recovery (express as RSD) results for 3 sets of samples are calculated, and outcome is reported in Table 5. The pesticide recovery rates were within an acceptable range.

Table 4. Analytical recoveries (%)±SD of pesticide residues in water and rice samples at various fortifying levels

Pesticides	Rice (mg per kg)		Water (mg per L)	
	0.1	0.5	0.1	0.5
Organochlorines				
Endosulfan	82.4±0.03	95.2±0.06	78.5±0.04	88.1±0.06
Dieldrin	86.6±0.04	88.5±0.04	93.2±0.05	94.1±0.08
Aldrin	85.8±0.02	89.3±0.05	84.6±0.06	95.2±0.05
Lindane	85.2±0.05	86.8±0.06	80.8±0.04	86.2±0.04
DDT	89.4±0.03	89.8±0.05	75.2±0.07	84.5±0.06
Organophosphates				
Chlorpyrifos	84.5±0.02	89.8±0.03	76.5±0.08	88.6±0.08
Profenophos	82.0±0.06	94.8±0.05	79.2±0.06	82.5±0.05
Chlordane	78.5±0.03	93.8±0.02	85.5±0.05	94.4±0.08
Phorate	83.2±0.05	86.8±0.05	79.2±0.02	88.2±0.03
Quinalphos	92.5±0.06	96.3±0.04	85.8±0.05	93.8±0.04
Synthetic pyrethroids				
Cismethrin	82.2±0.09	86.4±0.07	93.2±0.03	96.9±0.09
Cypermethrin	79.5±0.03	94.8±0.06	81.3±0.06	84.5±0.07
Fenvalerate	90.6±0.07	81.8±0.05	85.0±0.04	88.0±0.05
Deltamethrin	95.9±0.06	96.7±0.05	82.9±0.05	87.6±0.08
Carbofuran	92.7±0.08	94.8±0.06	90.2±0.08	93.8±0.09

Table 5. Analytical recoveries (%)±SD of pesticide residues in vegetables and fruit samples at different fortification levels

Pesticides	Tomato (mg/kg)			Grapes (mg/kg)			Carrot (mg/kg)		
	0.05	0.1	0.5	0.05	0.1	0.5	0.05	0.1	0.5
Organochlorines									
Endosulfan	85.3±0.03	87.2±0.04	88.5±0.04	86.1±0.02	88.5±0.04	96.1±0.07	87.2±0.06	91.3±0.02	96.5±0.03
Dieldrin	78.2±0.04	88.5±0.02	96.2±0.04	86.6±0.013	90.6±0.01	98.8±0.03	82.3±0.06	97.2±0.02	96.6±0.02
Lindane	79.3±0.03	87.1±0.04	98.1±0.05	88.8±0.005	92.5±0.006	91.5±0.04	88.1±0.04	92.4±0.05	93.4±0.04
DDT	85.1±0.06	91.3±0.02	95.6±0.04	79.2±0.02	84.7±0.005	89.3±0.01	78.4±0.07	88.6±0.03	87.9±0.04
Organophosphates									
Chlorpyrifos	90.1±0.02	92.4±0.04	94.2±0.02	81.2±0.015	88.4±0.004	93.8±0.08	79.5±0.02	89.8±0.04	87.2±0.03
Profenophos	84.7±0.04	89.2±0.03	93.9±0.014	79.2±0.031	88.8±0.03	96.3±0.04	87.6±0.01	96.9±0.05	97.5±0.04
Chlordane	90.1±0.06	90.4±0.05	95.1±0.032	81.3±0.06	89.9±0.043	93.2±0.01	86.8±0.05	88.8±0.04	87.6±0.08
Phorate	88.3±0.03	89.6±0.02	89.1±0.031	84.5±0.021	88.1±0.041	95.5±0.03	81.9±0.06	87.2±0.03	95.1±0.05
Synthetic pyrethroids									
Cypermethrin	86.5±0.07	90.1±0.06	93.2±0.023	87.9±0.032	91.4±0.032	94.6±0.05	83.7±0.02	86.5±0.04	88.6±0.09
Fenvalerate	80.1±0.06	91.1±0.03	94.5±0.021	85.8±0.041	92.2±0.021	94.1±0.07	85.5±0.04	89.1±0.05	90.4±0.07
Deltamethrin	79.2±0.01	84.24±0.05	91.5±0.013	78.8±0.026	82.3±0.03	89.2±0.07	79.1±0.03	86.1±0.04	88.6±0.08

Table 6. Estimation of endosulfan concentration that can be accumulated in humans and animals after consumption of the food types analyzed

Food Item	Daily Consumption*(X) L or kg/day	Concentration of residue (Y) mg/kg or L	Concentration of residue per day (X x Y) mg/kg or L	Concentration of residue accumulated (mg/kg)
Water	1.5	0.015	0.023	1 year
Rice	0.6	0.003	0.002	0.036x12x30=13
Fruits	0.1	0.031	0.005	15 years
Vegetables	0.15	0.037	0.006	13x15=195
Total			0.036	30 years
				13x30=390

The retention periods and peak areas of the pesticides under investigation were comparable to those found in relative standards. By using GC methodology, each pesticide lowest concentrations i.e., limit of detection were assessed and also checked reproducibility of each matrices; limit of detection for OC is 0.001 µg/g, for OP is 0.01 µg/g & for SP is 0.005 µg/g. To evaluate the interference of reagents blank was also analysed.

3.3 Calculation of Total Residues that can be Accumulated from all the Food Varieties

From the above results, it could be possible to calculate the total residues that can be accumulated in humans who are consuming water, rice, fruits, and vegetables. The average daily intake of food items based on the guidelines of FAO was used to calculate the total residues. Accordingly, the concentration of each pesticide accumulated from all the varieties analysed per day is calculated as given below for endosulfan (organochlorines) and shown in Table 6.

4. CONCLUSION

The present work provides information on residual pesticides in ground water, rice, fruits & vegetables, collected from different locations in Trivandrum. While pesticide usage has undoubtedly enhanced agricultural productivity in general, persistent pesticide residues have a tremendous negative effect on environment & on human health. Pesticide residues presence cause a threat to life of human posed by drinking water, dietary food & the residential risks. Recovery studies indicate a high degree of reproducibility for the procedure. The analytical technique for pesticide residues should be sufficiently sensitive that at the very least the lowest allowable limit is quantified [2]. The outcome of the study indicated that pesticide residues of organochlorine were in 36.2%, residues of organophosphate in 24.7%, and residues of synthetic pyrethroid were in 39.1% samples of water. Rice sample analysis revealed that market samples contain greater residues than field samples. This indicates that pesticides were used during storage to prevent pest infestation. This also leads to another possibility: that a large portion of the rice consumed in Kerala is imported, and that residues found in stores as a result of the rice lobby's excessive pesticide spraying. The study found that 75% of rice samples tested positive for contamination, with 28% of tested samples shows positive for residual pesticides above MRL and 47% of tested sample shows positive for residual pesticides below MRL. Alone 24.6 percent of analysed samples contains a detectable amount of pesticides being monitored. Due to the absence of a report on rice analysis in Kerala, this research emphasises the critical importance of rigorous regulations and constant monitoring of domestic and imported rice. The study found that 61% of fruits and vegetables samples tested positive for contamination, with 18.7% of samples were above the MRL and 42.3% of samples were below the MRL. Remaining 39% of samples evaluated did not contain detectable levels of the pesticides being monitored. Thus, the current investigation demonstrates that residues of pesticide were found in well-nigh all the samples of water, rice, fruit, & vegetable collected from various places around Thiruvananthapuram. Almost 70% of samples tested positive for contamination, with around 25% of samples testing positive for pesticide residues above the MRL. Based on the findings of these investigations, it is suggested that a more comprehensive research encompassing all food and water in Thiruvananthapuram of Kerala shall be conducted to ascertain the precise degree of pesticide contamination.

CONSENT

It is not applicable.

ETHICAL APPROVAL

It is not applicable.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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