Assessment of agrochemical residues in banana fruit by using gas chromatography and QuEChers technique

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Abstract. Present study is performed to analyze the residues of agrochemicals in banana fruit sold in the Chandigarh region. Aim is to check whether the agrochemical waste of residues is within the maximum residue levels (MRLs) or not. Market survey was conducted in the fruit ripening godowns and it was observed that different toxic agrochemicals are being used in the banana cultivation and only 15% of working people were aware of chemicals and their harmful effects. The occurrence of some toxic agrochemical residues like endosulfan, carbendazim, chloropyripos, chlorthiophos was analyzed in the banana fruit samples taken from different markets areas of chandigarh. Multi-residue analysis was performed in peel and pulp differently for 10 different samples by gas chromatography mass spectrometer (GC MS). Chlorthiophos (organophosphorus pesticide) was found in three peel samples having range 0.004 – 0.23 mg kg⁻¹ and one pulp sample have concentration 0.005 mg kg⁻¹. Carbendazim concentration was in two peel samples have concentrations 0.002 and 0.07 mg kg⁻¹. Endosulfan, chloropyrifus were absent in all samples whereas presence of carbendazim and chlorthiophos were found within MRL guidelines of Food and Agriculture Organization (FAO).

1. Introduction

The banana is a tropical fruit that has a good nutritional value for consumption. Banana fruit with the scientific name as ‘Musa Paradisiaca’ is a fruit that has leading consumption in the huge Indian market. It is a reach source for the intake of useful vitamins and minerals with a low proportion of fat. It is a most common product used in different countries around the world in its raw, home cooked or juice form. It is a natural antioxidant food that acts as a good source against many diseases [1–3].

1.1. Production and usage of agrochemicals in India

The agrochemicals production initiated in Calcutta. Production of technical grade pesticides ranges from 5000 MT to 102240 MT. The Indian pattern of pesticides use is quite different from rest of world as it uses 76% of the pesticides as insecticide. The use of fungicides and herbicides is not much heavy in the Indian region. In India, the main crops that are using the pesticides are cotton crops with 45% weightage, with paddy and wheat using comparatively less pesticides [4,5].
1.2. Agrochemical Residues

Agrochemical Residues are the specified substances in food that are produced by the use of agrochemicals. It can also be identified as a derivative of an agrochemical, which can be a conversion product or waste product which are toxic in nature. If such toxic substances are present in the surrounding of inhabitants of an ecosystem, these can cause harm to the life of inhabitants [6,7]. Agrochemical residues generally emerge due to the over usage or inappropriate spraying on crops and grass. According to about 50 – 70 % of fruits and vegetables gets contaminated and affected with the insecticide residues and about 11 % had residues limit more than MRL [8,9].

2. Literature review

Many research articles are present in different databases for this study. Few of these articles are discussed to identify the research done in the field. Studied 59 samples of vegetables and raw fruits including banana to check Triazine herbicides, Organochlorine, fungicides, and Organophosphate insecticides. The analysis showed that about 7% of vegetables and fruits had no pesticides and these are good for consumption, and about 25% of vegetables and fruits were containing one or more pesticides that were below the specific value of MRL, and about 3% of vegetables and fruits failed to comply the conditions [10,11].

studied 11 pesticides including ethoprophos, chlorpyrifos-methyl, fenitrothion, dimethoate, malathion, chlorpyrifos, diazinon, malaoxon, fenamiphos, buprofezin and phosmet in 57 samples of banana that were taken from the local markets of the Canary Islands in Spain. The study was performed by the Quechers approach which was developed for the analysis of pesticides in food, including the use of gas chromatography (GC) with nitrogen – phosphorus detection (NPD.

studied 8 samples of fruits including banana taken from the local markets of Nawabshah district, Sindh for Organophosphate (OP), pesticides, Pyrethroid and Organochlorine (OC) study by Gas Chromatography (GC) [12–14]. The results show that all fruit samples other than banana were found contaminated the apple samples were found to exceeding the Maximum Residue Limits (MRL) [15–18].

The occurrence of chloropyripos and endosulfan, carbendazim in a sample of 10 bananas taken from the Tamilnadu state’s south part in India. In 7 out of 10 samples, the carbendazim was found at a concentration ranging from 0.002-0.11 mg kg⁻¹. In 3 out of 10 samples, the carbendazim was found in a negligible amount, whereas endosulfan and chloropyripos was not found in any of these samples. HPLC-UV was used to carry out the experiment and samples were confirmed by GC-MS. The 7 out of 10 samples contained carbendazim which did not exceed the FAO and WHO guidelines values for MRLs (Maximum Residue Limit).

3. Research Gap

As per the available literature, only few agrochemicals have been analyzed in banana and no research has been done on banana available in the market of Chandigarh city. No study has been done on effect of ripening chemicals of banana and on the Health hazard index (HHI) of pesticide residues in banana. Further only the presence of carbendazim has been studied and chlotothiophus, acetylene and monocrotophos has not been researched, which are also present in banana.

4. Objectives

- To conduct the market study for finding the extent of use of agrochemicals in banana fruit.
- To study and analyze the process of extraction of pesticide using an efficient solvent followed by clean-up procedure.
- To determine the level of agrochemical residues (endosulfan, chlorpyrifos, chlorothiophos, carbendazim, acetylene, monocrotophos) in the banana of Chandigarh city.
- To analyze the residues of ripening chemicals in banana.
- To estimate Health Hazard index of daily intake of pesticide residues.
5. Materials and methods

5.1. Study area

The present study was carried out on assessment of agrochemical residues in banana in Chandigarh markets. Banana samples were taken from different local markets of Chandigarh i.e. sector 15 Sahji Mandi, Nayagaon, Sector 11 market, and sector 17 market, see figure 1.

![Figure 1. Banana godown used for study in Chandigarh market.](image)

5.2. Sample Collection

The banana samples were collected from the markets of Chandigarh and nearby villages. Study was conducted from November 2018 to September 2019. The samples of banana were collected in sterilized poly bags and these poly bags were brought to the laboratory as soon as possible (within 24 h of the collection) and kept in the refrigerator at a controlled temperature of 4ºC until the tests were conducted. The sampling of banana and its preservation protocols were used according to the recommendations of the food safety and standards authority of India.

5.3. Chemicals and reagents

The analytical standards for pesticides were obtained from Merck, Germany. The stock standard solution of every pesticide was prepared in n-hexane and acetone solution with a ratio of 9:1 and kept at -20ºC in controlled conditions. All analytical reagents used in the test were of GC grade with a purity of about 99.8% and the equipment used for the test were clean and free from any type of chemical contamination.

Gas Chromatography (GC) operating conditions are given in Table 1.

| Instrument | Gas chromatography |
|------------|--------------------|
| Column     | Col-Elite-1 HT-30M, 0.250mm x 0.10 um film |
| Injector temperature | 225 ºC |
| Detector temperature | 275 ºC |

5.4. Sample preparation and extraction

The QuEChERS technique was adopted in this study. It includes different types of sampling techniques and cleaning techniques. The QuEChERS was actually designed for the analysis of pesticides and agrochemicals in fruits and vegetables. Now this technique includes a huge range of agricultural products which can be easily analyzed using this technique. In following way sample preparation and extraction is done, see figure - 2
- Collect samples and freeze them to -20°C in controlled conditions.
- Homogenize the sample.
- Then extract and clean the sample with dispersive or cartridge SPE which is used specifically for clean-up.
- Extraction and clean up reagents are given in Table 2 and 3.

![Sampling of F&V (Markets and farms)](image1)

![Pesticide extraction (QuEChERS method)](image2)

![Health hazard prediction](image3)

![Estimated daily intake of pesticides](image4)

![Pesticides residue analysis (GC-MS/MS)](image5)

**Figure 2.** Sample preparation process used in this study.

### Table 2. Extraction reagent and its functions

| Reagent          | Function                                           |
|------------------|----------------------------------------------------|
| Magnesium sulphate | Facilities solvent portioning and improves recovery of polar analytes |
| Acetic acid      | For adjust pH                                     |
| Buffers          | Prevents change of pH                             |

### Table 3. Clean-up reagents and its functions

| Reagent        | Function                 |
|----------------|--------------------------|
| Aminopropyl    | Removes sugars and fatty acids. |
| Chloro-filter  | Worked as sorbent        |
5.5. Pesticide residue analysis in GC-MS/MS

The residues of Pesticides were analyzed with the help of a gas (GCMS-TQ8040 Shimadzu, Japan), see figure – 3. The samples collected were automatically injected into column. The Ultrapure helium was used as a carrier gas and the collision gas was taken as argon. MS interface temperature and ion source temperature were 250ºC and 200ºC respectively.

![Figure 3. GC-MS assembly used in this study for sample analysis.](image)

6. Results and Discussion

Following are the details of pulp and peel of samples taken from different markets of Chandigarh as given in table 4.

| S.No. | Sample taken from       | Peel sample ID | Pulp sample ID |
|-------|-------------------------|----------------|----------------|
| 1     | Naya Gaon (Shop 1)      | PEEL 1         | PULP 1         |
| 2     | Naya Gaon (Shop 2)      | PEEL 2         | PULP 2         |
| 3     | PEC market (Sample 1)   | PEEL 3         | PULP 3         |
| 4     | PEC market (Sample 2)   | PEEL 4         | PULP 4         |
| 5     | PEC market (Sample 3)   | PEEL 5         | PULP 5         |
| 6     | Sector 11, Medical market | PEEL 6     | PULP 6         |
| 7     | Sector 15 ( shop 1)     | PEEL 7         | PULP 7         |
| 8     | Sector 15 ( shop 2)     | PEEL 8         | PULP 8         |
| 9     | Sector 15 ( shop 3)     | PEEL 9         | PULP 9         |
| 10    | Sector 17               | PEEL 10        | PULP 10        |

After analyzing the samples on GCMS, following results came:
1. Chlorthiophos (organo phosphorus pesticide) was found in 3 peel samples (PEEL 1, PEEL 2, PEEL 5) and 1 pulp sample (PULP 2).
2. Carbendazim was found in 2 Peel samples (PEEL 6, PEEL 8).
3. Endosulfan, Chloropyrifus was absent in all 20 samples.

After getting the area of required compounds, standards of the particular will be analyzed to find the concentration of the required compounds. Following chromatogram represents the standards of compounds.

After comparing the area of compounds with standard compound solution, concentration of compound is calculated.

Following table - 5 shows the readings of compounds present in the tested banana sample.

| S.No. | Sample ID | Agrochemical compounds | Concentration (Mg Kg⁻¹) |
|-------|-----------|------------------------|------------------------|
| 1     | Peel 1    | Chlorthiophos          | 0.23                   |
| 2     | Peel 2    | Chlorthiophos          | 0.004                  |
| 3     | Peel 5    | Chlorthiophos          | 0.094                  |
| 4     | Peel 2    | Chlorthiophos          | 0.005                  |
| 5     | Peel 6    | Carbendazim            | 0.07                   |
| 6     | Peel 8    | Carbendazim            | 0.002                  |

All the concentrations obtained in the table 5 are within the acceptable limits and below MRL.

7. Conclusion

The present study analyses the residues of agrochemicals in banana fruit sold in the Chandigarh region and has come up with the following findings.

- Most of the workers had very less knowledge about pesticide recommendations and pesticide residues in banana fruit. Ethylene gas is used as ripening agent in Chandigarh Banana godowns.
- All the samples obtained from Chandigarh markets were not having agrochemicals present in them however some samples showed their presence which indicates that banana which were brought from different places may not have been protected from pesticides or the farmers might have used pesticides carefully to limit the permissible level of application.
- Residues of Carbendezim and chlorothiopus found in the samples of Banana, which had concentration less then MRLs.
- All the samples obtained from Chandigarh markets found free from banned agrochemicals i.e. calcium carbide and endosulfan.
- Recovery data for the pesticide residues represents the efficiency of GCMS for the the analysis of pesticide residues.
- There are no health hazards found in banana fruit but it is recommended to have continuous monitoring of pesticides in Banana.

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