Assessment Of Pesticide Residues In Chausa And Amarpali Varieties Of Mango (Mangifera Indica L.) By GC-MS Of Ghaziabad

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Abstract

In India extensive use of pesticides in the agriculture causing the adverse effect. The hazardous residues of pesticides in fruits and vegetables are loaded on the upper limit. The contamination of pesticides present in fruits and vegetable is directly affecting the human health. The aim of the present study was to access the effect of pesticide residue on the public health. Commonly used pesticides are dichlorvos, diazinone, fenitrothion, malathion, chlorpyrifos and ethion. The pesticides limit were studied in the mango varieties i.e. amarpali and chausa. The samples were collected from fruits from the market of Ghaziabad. First of all the collected samples were washed, peeled and prepared for further analysis of GC-MS. Standard methods and validation for detection of pesticide residues were used. Most of the samples were contaminated from the different types of pesticides. In the present study we found that the amarpali had dichlorvos, diazinone, fenitrothion, malathion, chlorpyrifos and ethion 0.030, 0.00051, not detected (0.00), 0.006, 0.0068, and 0.0001 mg /Kg respectively. The chausa had dichlorvos, phorate, diazinone, fenitrothion, malathion, chlorpyrifos and ethion 0.0024, 0.00076, 0.0013, 0.0076, 0.0035, and 0.001 mg /kg respectively. The entire samples were under permissible limits as per FAO/WHO recommendation. The permissible limit of pesticides residue in fruits, vegetable and food items for public health is required constantly.

Key word - Mango, Fruits, Pesticides, Varieties, humanhealth.
Introduction:

Fruits and vegetables are the rich source of carbohydrate, protein, fibres, vitamins and organic acids such as malic acid, citric acid (Virendra et al 2021). Fruits and vegetable are primarily required in the diet because of their nutrients, minerals and trace elements (Virendra et al 2021). The antioxidants which can we extracted from various parts of plants as well as fruit pulp, peel and seed. (Ranina et al 2015). India is an agricultural country. Agriculture has an important role in GDP. India holds second rank in the world in the field of fruits and vegetables. Globally, India has the first position in Mango market. According to National Horticulture Board (year 2021-22) India produced 107.24 million metric tonnes of fruits and 204.84 million metric tons of vegetables. FAO estimated that annual production is in between 20 to 40 percent. The crop is protected by pesticide to fight against the harmful pests and pathogens during the vegetative growth. (report of WHO 1990, Abimbola et al 2023). This practice is very common because the farmer want to save the crop from insect, rodents, pathogens and weeds. Some farmers use the pesticides and chemical fertilizers for good yield therefore, the pesticides load is increasing day by day. By which the human health is affected vigorously. (Bradberry et al 2004, Lorenzin et al 2007 and WHO-2018. 2021).

There are more than 1000 varieties of mango. Now a day it is losing its quality due to the presence of pesticides residues effect the human health (Jeager et al 1999). The metabolized chemicals of pesticides are carcinogenic for respiratory tract, cardiovascular disease, skin and endocrine gland. (Garcia, 2003, Semchuk, 1992 et al and Bassil et al 2007). The reproduction system, nervous system and Lymphoma are also affected by fruit and vegetables pesticide. (Wesseling, et al 2002 and Rauh et al 2015). There are some other chronic diseases are also seen in the modern time. Due to heavy pesticides in daily food many diseases viz. high blood pressure, diabetes and chronic kidney failure are found (Salameh, et al 2006, Weisenburger et al 2006 and Karami-Mohajeri, et al 2011).

Material and methods

Sample collection:

Two varities of mango (Amrapali and Chausa) were collected as a samples from vegetable and fruits market of Ghaziabad District Uttar Pradesh. After collecting sample about 1 kg sample was separated, washed and store in the refrigerator until ready for use.

Chemical and reagents:

All chemical was used HPLC grade acetonitrile (ACN), acetate, methanol, milli Q water, Anhydrous Na₂SO₄, anhydrous MgSO₄, sodium citrate, Primary secondary amine (PSA), pesticide analytical slandered (purity 99.9 %) were used in during analysis.
Instrument analysis:

An Agilent 7890 GC was connected to Agilent 5977B Inert plus GC/MSD. The HP (5 % Phenyl methyl polysiloxane) column was used. The Mass hunter software use for run the samples and data analysis software was used for analysis the pesticide. Quantification of pesticide was done by peak area using the standards method. GC condition for analysis of pesticide was contain capillary column maximum temperature 325°C, normal length 30m, diameter 250μL, initial flow 1.0 ml/minute, back inlet, back detector (FPD), hydrogen flow 75.0 ml/minute oxidizer flow 100.0 ml per minute air oxidizer gas type. Oven initial temperature 100 °C maximum temperature 350 °C with initial time 2.00 minute and equilibration time is 1.00 minute, mode is split initial temperature was 200°C, split ratio 5:1 total flow 53.4 ml/minute gas type nitrogen was used.

Preparation of analytical standard solution:

Combined stock Standard solution for six pesticides such as dichlorovos, diazinone, fenitrothion, malathion, chlorpyrifos and ethion were prepared. In n-hexane (HPLC grade) working standard solution were prepared of five concentration 0.001, 0.0025, 0.05, 0.01 and 0.02, mg/kg all the working solution were store at 4°C in the refrigerator and inject in GCMS, obtained retention time (Table -1) a multiple component Curve (Fig. -1) and Table -1

Sample preparation:

Collected 1 kg of randomly from the selected mangoes of each varieties, washed with water and Chopped to obtain of mango pulp and taken 5 g of sub sample mixed thoroughly in 50 ml centrifuge tube and spike 100 ppb. Add 10 ml milli Q water and add 10 ml acetonitrile (ACN), Shake for 10 minutes with mechanical shaker. Add 6 gm anhydrous magnesium sulphate and 1.2 gram Sodium Citrate in centrifuge tube. Vortex centrifuge tube for 1 minute, centrifuge it for 15 minute at 4000 rpm, take 5 ml upper solvent layer in to 15 m centrifuge tube. Add 250 mg magnesium sulphate, 125 mg Primary-secondy amine (PSA) and 125 mg C18. Vortex for 1 minute, Centrifuge for 15 minute at 5000 rpm than take 2 ml upper layer in to test tube and dry under nitrogen, reconstitute up to 0.500 ml (500 µL) with Acetonitrile and inject on GC-MS.

Validation:

The method was validated combined calibration curve by linearity method, precision, which include recovery limit of detection (LODs), limit of quantification (LOQs) and Combined stock Standard solution for six pesticides such as dichlorovos, diazinone, fenitrothion, malathion, chlorpyrifos and ethion were obtained by injecting of reference standard solution matrix matched calibration curved. Accuracy and precision were evaluated by means of recovery experiments carried out using spike Mango (Amrapali and Chausa verities) matrices at five concentration (0.001, 0.0025, 0.005, 0.01 and 0.02 mg/kg). Relative standard deviation (RSD) was evaluated at all fortification level in all matrices. The accuracy and precision
were expressed as a percentage accuracy and RSD respectively. LOD was estimated based on characteristics ions of lowest fortified concentration and LOQ was estimated based on lowest fortified concentration.

**Results and discussion:**

The result for the concentration of six pesticide in the both selected varieties which worth colleted from Ghaziabad market. The concentration of selected pesticides is 0.01, 0.0025, 0.005, 0.01, and 0.02 with obtained abundance of selected pesticides (table 1) obtain responce by GC-MS draw combined calibration curve for validation of data. (Mozzaquatro et al., 2022). The GC-MS condition were optimized to obtain separate peak of six pesticides such as dichlorovos, diazinone, fenitrothion, malathion, chlorpyrifos and ethion retention time (RT) is 10.67, 23.94, 26.73, 27.14, 27.51 and 34.02 minute respectively (Table-2), Fig-3 and Fig -4 The fortified Amrapali and Chausa varities of Mango sample were extracted with suitable solvent to standardize method. The observations of data was obtain after calculation by GC-MS (Table-1).The validification of the analysed methods was used by the acuuracy, precision and linearty. The Limit of detection (LOD) and Limit of quantification (LOQ) of multiple pesticides was determined by injecting slandered solutions of different concentration levels. (Constantinou, 2021). (Table -2).

After dataanalysis amarpali variety of mango contained dichlorovos, diazinone, fenitrothion, malathion, chlorpyrifos and ethion 0.030, 0.00051, not detected (0.00), 0.006, 0.0068, and 0.0001 mg /Kg respectively. The Chausa variety of mango contained dichlorovos, diazinone, fenitrothion, malathion, chlorpyrifos and ethion 0.0024, 0.00076, 0.0013, 0.0076, 0.0035, and 0.001 mg /Kg

In the present study all sample were contaminated by the pesticides and observed that, dichlorovos was maximum residue in amrapali variety (0.0028 mg/kg) and minimum residual value in Chausa variety (0.0024 mg / kg), diazinone was maximum in residual value in Chausa variety (0.0076 mg/ kg) and minimum in amrapali (0.0050 mg / kg) fenitrothion was not detected in amrapali and very less residue was found in Chausa variety (0.0013 mg/ kg), malathion was present maximum in Chausa (0.0076 mg / kg) and minimum in amrapali (0.006 mg / kg), chlorpyrifas was present maximum in amrapali (0.0068 mg / kg) and minimum in Chausa (0.0035 mg / kg), ethion was present same value but very less in both variety sample result near to similar my previous study (Virendra et al 2023 ) and (Arif et al., 2018 and Hoffman et al 2000) (Table-3).

It was observed that all the samples were contaminated with pesticides under the MRLs (Maximum Residual Limit).of different sample of varieties of mango. Many scientist did the work on the pesticides on different fruits and vegetables and showed their effects on human health (Frenik et al., 2011, Cheng et al., 2017, Kne, 2012 and Bretveld et al. 2006 ).
Table 1 - The observations of concentration (mg/kg) and abundance of selected pesticides

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Concentration</th>
<th>Dichlorovos</th>
<th>Diazinone</th>
<th>Fenitrothion</th>
<th>Malathion</th>
<th>Chlorpyritos</th>
<th>Ethion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.001</td>
<td>690</td>
<td>1697</td>
<td>1378</td>
<td>3789</td>
<td>790</td>
<td>1689</td>
</tr>
<tr>
<td>2</td>
<td>0.0025</td>
<td>1689</td>
<td>2589</td>
<td>2586</td>
<td>6488</td>
<td>1598</td>
<td>3588</td>
</tr>
<tr>
<td>3</td>
<td>0.005</td>
<td>3849</td>
<td>5900</td>
<td>5896</td>
<td>13769</td>
<td>3689</td>
<td>7538</td>
</tr>
<tr>
<td>4</td>
<td>0.01</td>
<td>6489</td>
<td>10909</td>
<td>10747</td>
<td>28489</td>
<td>7368</td>
<td>15888</td>
</tr>
<tr>
<td>5</td>
<td>0.02</td>
<td>13489</td>
<td>20688</td>
<td>20984</td>
<td>56969</td>
<td>14878</td>
<td>30074</td>
</tr>
</tbody>
</table>

Fig 1 - Combined stock Standard calibration curve

\[ R^2 = 0.998 \]
Table-2 - Values of Retention Time (RT), LOD and LOQ.

<table>
<thead>
<tr>
<th>Sr. no</th>
<th>Pesticide</th>
<th>RT</th>
<th>LOD(mg/kg)</th>
<th>LOQ(mg/kg)</th>
<th>Max. intake limit (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Dichlorovos</td>
<td>10.67</td>
<td>0.0021</td>
<td>0.0065</td>
<td>0.005</td>
</tr>
<tr>
<td>2.</td>
<td>Diazinone</td>
<td>23.94</td>
<td>0.0018</td>
<td>0.005</td>
<td>0.02</td>
</tr>
<tr>
<td>3.</td>
<td>Fenitrothion</td>
<td>26.73</td>
<td>0.0014</td>
<td>0.0044</td>
<td>0.005</td>
</tr>
<tr>
<td>4.</td>
<td>Malathion</td>
<td>27.14</td>
<td>0.0011</td>
<td>0.003</td>
<td>0.02</td>
</tr>
<tr>
<td>5.</td>
<td>Chlorpyrifos</td>
<td>27.51</td>
<td>0.0008</td>
<td>0.002</td>
<td>0.01</td>
</tr>
<tr>
<td>6.</td>
<td>Ethion</td>
<td>34.02</td>
<td>0.0011</td>
<td>0.0033</td>
<td>0.002</td>
</tr>
</tbody>
</table>

LOD – Limit of detection, LOQ – Limit of quantitation, RT – Retention time

Table-3 - Observed Values of sample mg/kg

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Pesticide</th>
<th>Max. intake limit (mg/kg)</th>
<th>Observed value (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Amarapali</td>
<td>Chausa</td>
</tr>
<tr>
<td>1.</td>
<td>Dichlorovos</td>
<td>0.005</td>
<td>0.0030</td>
</tr>
<tr>
<td>2.</td>
<td>Diazinone</td>
<td>0.02</td>
<td>0.0050</td>
</tr>
<tr>
<td>3.</td>
<td>Fenitrothion</td>
<td>0.005</td>
<td>ND</td>
</tr>
<tr>
<td>4.</td>
<td>Malathion</td>
<td>0.02</td>
<td>0.006</td>
</tr>
<tr>
<td>5.</td>
<td>Chlorpyrifos</td>
<td>0.01</td>
<td>0.0068</td>
</tr>
<tr>
<td>6.</td>
<td>Ethion</td>
<td>0.002</td>
<td>0.001</td>
</tr>
</tbody>
</table>

ND=not detected
Fig-3. GCMS retention time Graph of selected Pesticides in Amrapali variety

Fig-4. GCMS retention time Graph of selected Pesticides in Chausa variety
Fig.: –4 Graphical representation of selected pesticide residues in sample

Conclusion

The fruits and vegetables containing pesticides are accumulated in the human body. The various diseases which are caused by pesticides such as cancer, damage CNS (central nervous system), ANS (autonomous nervous system), blood pressure, hypertension immune system disorder and diabetes are found. It is necessary to check these toxicity levels in fruits and vegetables to minimize the negative impact on human health. Therefore, we should promote the organic and bio-fertilizers for farming. According to the recommendation of FAO and WHO, the organic farming is secured for health.

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