CHAPTER 4
RESULTS AND DISCUSSION

4.1 Method Validation
4.1.1 Calibration Curve (Linearity)

The calibration graph of each pesticide was constructed using samples spiked with different concentrations of standard mixture solutions. The calibration standard mixture solutions over the different concentration range of interest were prepared by serial dilution of the mixed standard stock solution with ethyl acetate solvent then spiked to the fruit and vegetable samples. The detector response linearity was examined over different concentration ranges; the analyte peaks obtained were integrated and plotted as functions of concentration. The standard mixture solutions were analyzed in triplicates by GC-ECD and GC-MS at each concentration level. The linearity of the calibration plots was studied using calibration solutions prepared in the control/blank sample extract. The correlation coefficients of analytical curves were near 0.99, with linearity for each compound, which allows the quantitation of these compounds by the method. In the present work, the linearity of the method was determined by injecting 1 µL of spiked blank matrix extracts. Linear calibration graphs were constructed by least squares regression of concentration versus peak area and height ratio (analyte / I.S.) of the calibration standards (Fig:4.1 to Fig:4.4).

Table 4.1: Stock/standard (mg kg\(^{-1}\)) calibration solution preparation for chlorpyrifos, cypermethrin, endosulfan and monocrotophos

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Stock standard</th>
<th>mL to 10 mL Dilution</th>
<th>Calibration solution 1</th>
<th>Calibration solution 2</th>
<th>Calibration solution 3</th>
<th>Calibration solution 4</th>
<th>Calibration solution 5</th>
<th>Calibration solution 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorpyrifos</td>
<td>50.0</td>
<td>5.0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.125</td>
<td>0.0625</td>
<td>0.0325</td>
<td>0.01625</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>50.0</td>
<td>5.0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.125</td>
<td>0.0625</td>
<td>0.0325</td>
<td>0.01625</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>50.0</td>
<td>5.0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.125</td>
<td>0.0625</td>
<td>0.0325</td>
<td>0.01625</td>
</tr>
<tr>
<td>Monocrotophos</td>
<td>50.0</td>
<td>5.0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.125</td>
<td>0.0625</td>
<td>0.0325</td>
<td>0.01625</td>
</tr>
</tbody>
</table>
Figure 4.1: Calibration graph of chlorpyrifos

Figure 4.2: Calibration graph of cypermethrin
Figure 4.3: Calibration graph of endosulfan

Figure 4.4: Calibration graph of monocrotophos.
4.1.2 Recovery

The accuracy of an analytical method is the closeness of experimental results obtained by that method to true value. The accuracy of the method was estimated through recovery experiment. Recovery tests were carried out based on the addition of known amounts of pesticides to the vegetable samples. For this purpose, control samples (brinjal and okra) were spiked with a 1.0 mg kg\(^{-1}\), 2.0 mg kg\(^{-1}\) and 3.0 mg kg\(^{-1}\) of pesticides. The concentration of each pesticide in the final extracts was calculated. The average recoveries of pesticide residues in fruits and vegetables samples were 75.0 to 105.0%. The recoveries and linearity of the method was examined on pesticide-free vegetable samples. The percentage recovery was determined for triplicate samples at three concentration levels.

4.1.3 Recovery study of pesticide residues in vegetables by GC-ECD

Table 4.2: Recovery of pesticide in spiked vegetable samples, extracted with 1% acetic acid solution of acetonitrile cleaned up with PSA and magnesium sulphate and analysed by GC-ECD

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Spiking level Mg kg(^{-1})</th>
<th>Brinjal Recovery %</th>
<th>Brinjal RSD %</th>
<th>Okra Recovery %</th>
<th>Okra RSD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorpyrifos</td>
<td>1.0</td>
<td>104.2</td>
<td>6.0</td>
<td>75.1</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>86.1</td>
<td>7.5</td>
<td>95.1</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>95.3</td>
<td>8.8</td>
<td>104.5</td>
<td>6.9</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>1.0</td>
<td>103.1</td>
<td>7.6</td>
<td>80.1</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>98.1</td>
<td>5.8</td>
<td>102.9</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>102.8</td>
<td>9.6</td>
<td>88.8</td>
<td>6.6</td>
</tr>
<tr>
<td>Monocrotophos</td>
<td>1.0</td>
<td>95.1</td>
<td>6.6</td>
<td>90.1</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>76.5</td>
<td>7.8</td>
<td>102.2</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>104.2</td>
<td>9.7</td>
<td>91.8</td>
<td>5.9</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>1.0</td>
<td>82.1</td>
<td>6.7</td>
<td>91.0</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>103.1</td>
<td>6.2</td>
<td>101.3</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>93.1</td>
<td>9.8</td>
<td>93.1</td>
<td>7.3</td>
</tr>
</tbody>
</table>
Figure 4.5: Recovery of pesticide in spiked vegetable samples, extracted with acetonitrile and analysed by GC-ECD

The recovery study was carried out control samples spiked with 1.0, 2.0 and 3.0 mg kg\(^{-1}\) of solution (Fig.4.5) showing recovery of pesticides extracted with acetonitrile and analysed by GC-ECD. The recovery was in the range of 75.0 to 105\%
### 4.1.4 Recovery study of pesticide residues in vegetables by GC-MS

Table 4.3 Recovery of pesticide in spiked vegetable samples, extracted with 1% acetic acid solution of acetonitrile cleaned up with PSA and magnesium sulphate and analysed by GC-MS

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>Spiking level mgkg⁻¹</th>
<th>Brinjal</th>
<th>Okra</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Recovery %</td>
<td>RSD %</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>1.0</td>
<td>104.6</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>88.1</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>98.3</td>
<td>8.1</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>1.0</td>
<td>105.1</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>99.1</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>105.0</td>
<td>7.4</td>
</tr>
<tr>
<td>Monocrotophos</td>
<td>1.0</td>
<td>96.1</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>78.5</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>104.6</td>
<td>6.7</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>1.0</td>
<td>85.1</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>104.6</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>95.4</td>
<td>6.7</td>
</tr>
</tbody>
</table>
Figure 4.6: Recovery of pesticide in spiked vegetable samples, extracted with acetonitrile and analysed by GC-MS

The recovery study was carried out on control samples collected from experimental field, spiked with 1.0, 2.0 and 3.0 mg kg\(^{-1}\) of solution (Fig.4.6) showing recovery of pesticides extracted with acetonitrile and analysed by GC-MS. Better recovery was obtained by GC-MS.

Gas chromatography mass spectrometry method when compared to the gas chromatography electron capture detector results only it provides quantitative, elemental and peak retention time data, but lack of the specificity which is necessary for molecular structural identification. Mass spectrometry is a two-dimensional detection method and provides both peak retention time and mass spectrum. The full spectrum profile in the computer database is a finger print identification for final confirmation. Gas chromatography mass spectrometry is a powerful tool for residue identification and confirmation purposes. The sensitivity and selectivity of gas chromatography electron capture detector for a rapid and reliable quantitative result makes the mass spectra system a logical complementary instrument in trace residue confirmation in fruits and vegetables samples.
4.1.5 Quantitation ion, confirmation ion, calibration range, correlation coefficient and coefficient of variation

Table 4.4: Quantitation ion, confirmation ion and calibration range of monocrotophos, chlorpyrifos and endosulfan

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantitation ion</th>
<th>Confirmation ion</th>
<th>Calibration range (mg kg(^{-1}))</th>
<th>Correlation coefficient</th>
<th>Coefficient of variation (n = 5) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorpyrifos</td>
<td>97</td>
<td>314</td>
<td>0.02-1.00</td>
<td>0.993</td>
<td>6.0</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>181</td>
<td>127</td>
<td>0.02-1.00</td>
<td>0.991</td>
<td>5.8</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>373</td>
<td>237</td>
<td>0.02-1.00</td>
<td>0.990</td>
<td>5.9</td>
</tr>
<tr>
<td>Monocrotophos</td>
<td>127</td>
<td>98</td>
<td>0.02-100</td>
<td>0.994</td>
<td>6.3</td>
</tr>
</tbody>
</table>

4.1.6 Molecular formula, retention time, LODs and LOQs of chlorpyrifos, cypermethrin, endosulfan and monocrotophos

Table 4.5: Molecular formula, retention time, LODs and LOQs of chlorpyrifos, cypermethrin, endosulfan and monocrotophos

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular formula</th>
<th>RT (min)</th>
<th>LoDs (µg kg(^{-1}))</th>
<th>LoQs (µg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorpyrifos</td>
<td>C(<em>9)H(</em>{11})Cl(_3)NO(_3)PS</td>
<td>25.12</td>
<td>3.00</td>
<td>9.00</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>C(<em>{22})H(</em>{19})Cl(_2)NO(_3)</td>
<td>31.12</td>
<td>3.00</td>
<td>8.00</td>
</tr>
<tr>
<td>Endosulfan</td>
<td>C(_9)H(_6)Cl(_6)O(_3)S</td>
<td>26.72</td>
<td>4.00</td>
<td>12.00</td>
</tr>
<tr>
<td>Monocrotophos</td>
<td>C(<em>7)H(</em>{14})NO(_5)P</td>
<td>17.89</td>
<td>5.00</td>
<td>15.00</td>
</tr>
</tbody>
</table>
Figure 4.7: Mass spectra of chlorpyrifos
Figure 4.8: Mass spectra of cypermethrin

$C_{22}H_{15}Cl_2NO_3$
Figure 4.9: Mass spectra of endosulfan
Figure 4.10: Mass spectra of monocrotophos
Figure 4.11: Gas chromatogram of monocrotophos, chlorpyrifos, endosulfan and cypermethrin
4.2 Analysis of fruits and vegetables collected from local market

4.2.1 Analysis of pesticide residues in vegetable samples collected from local market

4. 2.1.1 Analysis of brinjal and cauliflower samples collected during 2010

Samples of brinjal and cauliflower were collected from the local market during the year 2010 and analysed for residues of chlorpyrifos and cypermethrin. A total 10 samples of cauliflower and brinjal were collected in which chlorpyrifos were detected in five samples and cypermethrin was detected in four samples. All samples of vegetables were detected one or other pesticide residues. Samples of brinjal was found more contaminated comparative to cauliflower.

Table 4.6: Amount of pesticide residues detected in cauliflower and brinjal samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chlorpyrifos mg kg(^{-1})</th>
<th>Cypermethrin mg kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cauliflower</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.024</td>
<td>ND</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>ND</td>
<td>0.002</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.027</td>
<td>ND</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Brinjal</td>
<td>ND</td>
<td>0.012</td>
</tr>
<tr>
<td>Brinjal</td>
<td>0.021</td>
<td>ND</td>
</tr>
<tr>
<td>Brinjal</td>
<td>ND</td>
<td>0.008</td>
</tr>
<tr>
<td>Brinjal</td>
<td>0.018</td>
<td>0.003</td>
</tr>
<tr>
<td>Brinjal</td>
<td>0.020</td>
<td>ND</td>
</tr>
</tbody>
</table>

MRL:FAO/WHO/Codex: cauliflower, chlorpyrifos 0.05mgkg\(^{-1}\), brinjal, cypermethrin 0.2 mg kg\(^{-1}\)

A total 10 samples of brinjal and cauliflower were analysed for chlorpyrifos and cypermethrin. A residues of chlorpyrifos in brinjal were detected (0.021 mg kg\(^{-1}\), 0.018 mg kg\(^{-1}\) and 0.020mgkg\(^{-1}\)) and cypermethrin residues detected (0.012 mg kg\(^{-1}\), 0.008 mg kg\(^{-1}\) and 0.003 mg kg\(^{-1}\)). Residues of chlorpyrifos in cauliflower were
detected (0.024 mg kg$^{-1}$ and 0.027 mg kg$^{-1}$) and cypermethrin residues detected (0.002 mg kg$^{-1}$). Higher residues of chlorpyrifos were observed in cauliflower (Table 4.6) whereas less cypermethrin residues were detected in cauliflower samples. Brinjal was found more contaminated than cauliflower samples.

4.2.1.2 Analysis of pesticide residues in brinjal, capsicum, cauliflower and okra samples collected during January 2010 to December 2010

Brinjal, capsicum, cauliflower and okra were collected from local market, Nanded, Maharashtra, India, from January 2010 to December 2010. A total of 288 vegetable samples, were periodically collected and analysed by using GC-MS for the determination of chlorpyrifos, cypermethrin and monocrotophos. The results obtained showed that vegetable samples analyzed contained detectable level of the pesticides residues below the maximum residue limit (MRL) except few samples. The samples of brinjal, capsicum, cauliflower and okra were contaminated with chlorpyrifos, cypermethrin and monocrotophos 59.3%, 59.3% and 66.6% respectively. The maximum contamination was found in brinjal and okra samples respectively. Capsicum was found least contaminated. The average recoveries of pesticide residues in brinjal, capsicum, cauliflower and okra samples were 75.0 to 105.0 % (Table 4.7-4.12).
Table 4.7: Amounts of chlorpyrifos residues detected in vegetables samples collected from local market, Nanded, extracted with 1% acetic acid solution of acetonitrile cleaned up with PSA and magnesium sulphate and analysed by GC-MS

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Sample collection period</th>
<th>No. of sample collected</th>
<th>Residue level mg kg$^{-1}$ in sample no.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Brinjal</td>
<td>Jan. 2010 to March 2010</td>
<td>6</td>
<td>0.025</td>
</tr>
<tr>
<td>Capsicum</td>
<td>Jan. 2010 to March 2010</td>
<td>6</td>
<td>N D</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>Jan. 2010 to March 2010</td>
<td>6</td>
<td>N D</td>
</tr>
<tr>
<td>Okra</td>
<td>Jan. 2010 to March 2010</td>
<td>6</td>
<td>0.012</td>
</tr>
<tr>
<td>Brinjal</td>
<td>April 2010 to June 2010</td>
<td>6</td>
<td>N D</td>
</tr>
<tr>
<td>Capsicum</td>
<td>April 2010 to June 2010</td>
<td>6</td>
<td>0.004</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>April 2010 to June 2010</td>
<td>6</td>
<td>N D</td>
</tr>
<tr>
<td>Okra</td>
<td>April 2010 to June 2010</td>
<td>6</td>
<td>0.024</td>
</tr>
</tbody>
</table>

A total 48 samples of brinjal capsicum, cauliflower and okra were collected from January 2010 to June 2010 and analysed for the detection of chlorpyrifos. Chlorpyrifos residues detected in 7 out of 12 samples of brinjal in the range of 0.008 mg kg$^{-1}$ to 0.040 mg kg$^{-1}$. Chlorpyrifos residues detected in 5 out of 12 samples of capsicum in the range of 0.004 mg kg$^{-1}$ to 0.040 mg kg$^{-1}$. Chlorpyrifos residues detected in 5 out of 12 samples of cauliflower in the range of 0.004 mg kg$^{-1}$ to 0.096 mg kg$^{-1}$. Chlorpyrifos residues detected in 9 out 12 samples of okra in the range of 0.008 mg kg$^{-1}$ to 0.028 mg kg$^{-1}$. In this brinjal was found more contaminated than other vegetables. Residues of chlorpyrifos were found in cauliflower above MRLs as
prescribed (0.05 ppm) for vegetables. Most of the samples of brinjal were found contaminated with chlorpyrifos followed by brinjal, capsicum and cauliflower samples (Table 4.7).

Table 4.8: Amounts of chlorpyrifos residues detected in vegetables samples collected from local market, Nanded, extracted with 1% acetic acid solution of acetonitrile cleaned up with PSA and magnesium sulphate and analysed by GC-MS

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Sample collection period</th>
<th>No. of sample collected</th>
<th>Residue level mg kg(^{-1}) in sample no.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Brinjal</td>
<td>July 2010 to Sept. 2010</td>
<td>6</td>
<td>0.020</td>
</tr>
<tr>
<td>Capsicum</td>
<td>July 2010 to Sept. 2010</td>
<td>6</td>
<td>0.007</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>July 2010 to Sept. 2010</td>
<td>6</td>
<td>0.022</td>
</tr>
<tr>
<td>Okra</td>
<td>July 2010 to Sept. 2010</td>
<td>6</td>
<td>N D</td>
</tr>
<tr>
<td>Brinjal</td>
<td>Oct. 2010 to Dec. 2010</td>
<td>6</td>
<td>0.015</td>
</tr>
<tr>
<td>Capsicum</td>
<td>Oct. 2010 to Dec. 2010</td>
<td>6</td>
<td>0.023</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>Oct. 2010 to Dec. 2010</td>
<td>6</td>
<td>0.012</td>
</tr>
<tr>
<td>Okra</td>
<td>Oct. 2010 to Dec. 2010</td>
<td>6</td>
<td>0.024</td>
</tr>
</tbody>
</table>

A total 48 samples of brinjal capsicum, cauliflower and okra were collected from July 2010 to December 2010 and analysed for the detection of chlorpyrifos. Chlorpyrifos residues detected in 8 out of 12 samples of brinjal in the range of 0.008 mg kg\(^{-1}\) to 0.028 mg kg\(^{-1}\). Chlorpyrifos residues detected in 7 out of 12 samples of capsicum in the range of 0.007 mg kg\(^{-1}\) to 0.024 mg kg\(^{-1}\). Chlorpyrifos residues detected in 8 out of 12 samples of cauliflower in the range of 0.004 mg kg\(^{-1}\) to 0.096 mg kg\(^{-1}\).
Chlorpyrifos residues detected in 9 out of samples of okra in the range of 0.010 mg kg\(^{-1}\) to 0.062 mg kg\(^{-1}\) (Table 4.8).

Table 4.9: Amounts of cypermethrin residues detected in vegetables samples collected from local market, Nanded, extracted with 1% acetic acid solution of acetonitrile cleaned up with PSA and magnesium sulphate and analysed by GC-MS

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Sample collection period</th>
<th>No. of sample collected</th>
<th>Residue level mg kg(^{-1}) in sample no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brinjal</td>
<td>Jan. 2010 to March 2010</td>
<td>6</td>
<td>0.035 0.042 0.058 N D N D 0.033</td>
</tr>
<tr>
<td>Capsicum</td>
<td>Jan. 2010 to March 2010</td>
<td>6</td>
<td>N D 0.045 N D N D 0.021 N D</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>Jan. 2010 to March 2010</td>
<td>6</td>
<td>0.034 N D 0.015 0.042 N D 0.016</td>
</tr>
<tr>
<td>Okra</td>
<td>Jan. 2010 to March 2010</td>
<td>6</td>
<td>0.012 0.078 0.084 N D 0.022 0.014</td>
</tr>
<tr>
<td>Brinjal</td>
<td>April 2010 to June 2010</td>
<td>6</td>
<td>N D 0.012 N D 0.044 0.050 N D</td>
</tr>
<tr>
<td>Capsicum</td>
<td>April 2010 to June 2010</td>
<td>6</td>
<td>N D N D 0.034 0.008 N D 0.040</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>April 2010 to June 2010</td>
<td>6</td>
<td>N D 0.012 N D N D 0.038 0.062</td>
</tr>
<tr>
<td>Okra</td>
<td>April 2010 to June 2010</td>
<td>6</td>
<td>0.065 0.026 N D 0.010 N D 0.012</td>
</tr>
</tbody>
</table>

A total 48 samples of brinjal capsicum, cauliflower and okra were collected from January 2010 to June 2010 and analysed for the detection of cypermethrin. Cypermethrin residues detected in 7 out of 12 samples of brinjal in the range of 0.012 mg kg\(^{-1}\) to 0.058 mg kg\(^{-1}\). Cypermethrin residues detected in 5 out of 12 samples of capsicum in the range of 0.008 mg kg\(^{-1}\) to 0.045 mg kg\(^{-1}\). Cypermethrin residues
detected in 7 out of 12 samples of cauliflower in the range of 0.012 mg kg\(^{-1}\) to 0.062 mg kg\(^{-1}\). Chlorpyrifos residues detected in 9 out of samples of okra in the range of 0.010 mg kg\(^{-1}\) to 0.084 mg kg\(^{-1}\) (Table 4.9).

Table 4.10: Amounts of cypermethrin residues detected in vegetables samples collected from local market, Nanded, extracted with 1% acetic acid solution of acetonitrile cleaned up with PSA and magnesium sulphate and analysed by GC-MS

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Sample collection period</th>
<th>No. of sample collected</th>
<th>Residue level mg kg(^{-1}) in sample no.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Brinjal</td>
<td>July 2010 to Sept. 2010</td>
<td>6</td>
<td>0.025</td>
</tr>
<tr>
<td>Capsicum</td>
<td>July 2010 to Sept. 2010</td>
<td>6</td>
<td>N D</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>July 2010 to Sept. 2010</td>
<td>6</td>
<td>0.015</td>
</tr>
<tr>
<td>Okra</td>
<td>July 2010 to Sept. 2010</td>
<td>6</td>
<td>0.012</td>
</tr>
<tr>
<td>Brinjal</td>
<td>Oct. 2010 to Dec. 2010</td>
<td>6</td>
<td>0.015</td>
</tr>
<tr>
<td>Capsicum</td>
<td>Oct. 2010 to Dec. 2010</td>
<td>6</td>
<td>0.050</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>Oct. 2010 to Dec. 2010</td>
<td>6</td>
<td>0.065</td>
</tr>
<tr>
<td>Okra</td>
<td>Oct. 2010 to Dec. 2010</td>
<td>6</td>
<td>0.012</td>
</tr>
</tbody>
</table>

A total 48 samples of brinjal capsicum, cauliflower and okra were collected from July 2010 to December 2010 and analysed for the detection of cypermethrin. Cypermethrin residues detected in 8 out of 12 samples of brinjal in the range of 0.004 mg kg\(^{-1}\) to 0.050 mg kg\(^{-1}\). Cypermethrin residues detected in 6 out of 12 samples of capsicum in the range of 0.012 mg kg\(^{-1}\) to 0.052 mg kg\(^{-1}\). Cypermethrin residues detected in 5 out of 12 samples of cauliflower in the range of 0.015 mg kg\(^{-1}\) to 0.065 mg kg\(^{-1}\).
Chlorpyrifos residues detected in 9 out of samples of okra in the range of 0.008 mg kg$^{-1}$ to 0.086 mg kg$^{-1}$ (Table 4.10).

Table 4.11: Amounts of monocrotophos residues detected in vegetables samples collected from local market, Nanded, extracted with 1% acetic acid solution of acetonitrile cleaned up with PSA and magnesium sulphate and analysed by GC-MS

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Sample collection period</th>
<th>No. of sample collected</th>
<th>Residue level mg kg$^{-1}$ in sample no.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Brinjal</td>
<td>Jan.2010 to March 2010</td>
<td>6</td>
<td>0.025</td>
</tr>
<tr>
<td>Capsicum</td>
<td>Jan. 2010 to March 2010</td>
<td>6</td>
<td>N D</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>Jan.2010 to March 2010</td>
<td>6</td>
<td>0.065</td>
</tr>
<tr>
<td>Okra</td>
<td>Jan. 2010 to March 2010</td>
<td>6</td>
<td>0.012</td>
</tr>
<tr>
<td>Brinjal</td>
<td>April2010 to June 2010</td>
<td>6</td>
<td>0.015</td>
</tr>
<tr>
<td>Capsicum</td>
<td>April2010 to June 2010</td>
<td>6</td>
<td>0.050</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>April2010 to June 2010</td>
<td>6</td>
<td>0.012</td>
</tr>
<tr>
<td>Okra</td>
<td>April2010 to June 2010</td>
<td>6</td>
<td>0.046</td>
</tr>
</tbody>
</table>

A total 48 samples of brinjal capsicum, cauliflower and okra were collected from January 2010 to June 2010 and analysed for the detection of monocrotophos. Monocrotophos residues detected in 10 out of 12 samples of brinjal in the range of 0.014 mg kg$^{-1}$ to 0.051 mg kg$^{-1}$. Monocrotophos residues detected in 5 out of 12 samples of capsicum in the range of 0.014 mg kg$^{-1}$ to 0.053 mg kg$^{-1}$. Monocrotophos residues detected in 7 out of 12 samples of cauliflower in the range of 0.012 mg kg$^{-1}$. 
to 0.065 mg kg$^{-1}$. Monocrotophos residues detected in 8 out of samples of okra in the range of 0.008 mg kg$^{-1}$ to 0.046 mg kg$^{-1}$ (Table 4.11).

Table 4.12: Amounts of monocrotophos residues detected in vegetables samples collected from local market, Nanded, extracted with 1% acetic acid solution of acetonitrile cleaned up with PSA and magnesium sulphate and analysed by GC-MS

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Sample collection period</th>
<th>No. of sample collected</th>
<th>Residue level mg kg$^{-1}$ in sample no.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Brinjal</td>
<td>July 2010 to Sept.2010</td>
<td>6</td>
<td>0.025</td>
</tr>
<tr>
<td>Capsicum</td>
<td>July 2010 to Sept. 2010</td>
<td>6</td>
<td>N D</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>July 2010 to Sep. 2010</td>
<td>6</td>
<td>N D</td>
</tr>
<tr>
<td>Okra</td>
<td>July 2010 to Sept. 2010</td>
<td>6</td>
<td>0.012</td>
</tr>
<tr>
<td>Brinjal</td>
<td>Oct. 2010 to Dec. 2010</td>
<td>6</td>
<td>0.015</td>
</tr>
<tr>
<td>Capsicum</td>
<td>Oct.2010 to Dec.2010</td>
<td>6</td>
<td>0.030</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>Oct.2010 to Dec.2010</td>
<td>6</td>
<td>0.012</td>
</tr>
<tr>
<td>Okra</td>
<td>Oct.2010 to Dec.2010</td>
<td>6</td>
<td>0.061</td>
</tr>
</tbody>
</table>

A total 48 samples of brinjal capsicum, cauliflower and okra were collected from July 2010 to December 2010 and analysed for the detection of monocrotophos. Monocrotophos residues detected in 9 out of 12 samples of brinjal in the range of 0.014 mg kg$^{-1}$ to 0.050 mg kg$^{-1}$. Monocrotophos residues detected in 6 out of 12 samples of capsicum in the range of 0.004 mg kg$^{-1}$ to 0.045 mg kg$^{-1}$. Monocrotophos in residues detected in 9 out of 12 samples of cauliflower in the range of 0.002 mg
Monocrotophos residues detected in 9 out of samples of okra in the range of 0.008 mg kg$^{-1}$ to 0.061 mg kg$^{-1}$ (Table 4.12).

In the above study was observed that residues of pesticides found more prevalent in cold season than in hot season it may be due to less degradation in cold season. The sample of vegetables collected from the local market was contaminated with pesticides but their frequency is significantly variable which may be due to rain, temperature, humidity and physic-chemical properties of soil bed. A study was conducted Beena Kumari and coworkers (2004) on farmgate vegetables and found that 26% samples contained residues above MRL values. The results obtained in our study are in agreement with respect to presence of contamination pesticide in vegetables samples and found the residues in most of the samples taken for study.

A study was conducted by Crentsil et al. (2012) to investigate the organochlorine, organophosphorus and synthetic pyrethroid pesticide residues in fruits and vegetables from markets in Ghana. For this purpose, a total of 309 fruits and vegetable samples, were collected and analyze by GC-ECD. The obtained results showed that the predominance of organochlorine followed by organophosphorus and synthetic pyrethroid pesticides in most of the analyzed samples. The detected concentrations of them were most significant in vegetable samples. The results obtained showed that 39.2% of the fruits and vegetable samples analyzed contained no detectable level of the monitored pesticides, 51.0% of the samples gave results with trace levels of pesticide residues below the maximum residue limit (MRL), while 9.8% of the samples were above the MRL.
residue limit (MRL), while 9.8% of the samples were above the MRL. On the basis of findings it was the urgent need to establish reliable monitoring programs for pesticides, so that any exceedance in concentration over environmental quality standards can be detected and appropriate actions taken.

Chauhan et al. (2012) conducted a monitoring study on pesticides residues in farmgate vegetables (like brinjal, okra, tomato, sweet-pepper, cabbage and cauliflower) at Uttarakhand, India during 2009 to 2010. It was observed that most of the vegetables have endosulfan residues above MRL(maximum residue limit) values followed by carbendazim, chlorpyrifos, imidachloprid and cypermethrin respectively. The results showed that amongst the different vegetable samples cauliflower and tomato had carbendazim residues higher than the recommended MRL’s whereas cabbage had endosulfan contamination higher than the recommended MRL values.

Another study was conducted by the Ananda Gowda and Somashekar (2012) analysed for 20 pesticide residues. Vegetable samples were found to be contaminated with the organochlorines (83.5%) dominated followed by organophosphates (67%) and pyrethroids (55%). However, 34% of the samples were found to contain the residues of organophosphate insecticides above their respective maximum residue limits (MRL). However, 34% of the samples were found to contain the residues of organophosphate insecticides above their respective maximum residue limits (MRL).

The present study is in agreement with earlier studies were made on the presence of pesticides residues in market samples. The study showed the residues of pesticides vegetables collected from the market were detected below MRL in most of the samples.
4.2.2 Analysis of pesticide residues capsicum and cauliflower collected during 2012

Capsicum and cauliflower samples were collected from the local market analysed for the detection of chlorpyrifos, endosulfan and monocrotophos. A total 10 samples of capsicum and cauliflower were analysed, chlorpyrifos were detected in four samples, endosulfan was detected in eight samples and monocrotophos were detected in six samples. All samples of vegetables were detected one or other pesticide residues.

Table 4.13: Amounts of pesticide residues detected in capsicum and cauliflower samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Monocrotophos mg kg(^{-1})</th>
<th>Chlorpyrifos mg kg(^{-1})</th>
<th>Endosulfan mg kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cauliflower</td>
<td>ND</td>
<td>ND</td>
<td>0.002</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.024</td>
<td>ND</td>
<td>0.003</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>ND</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.027</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>ND</td>
<td>ND</td>
<td>0.002</td>
</tr>
<tr>
<td>Capsicum</td>
<td>ND</td>
<td>0.012</td>
<td>0.008</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.021</td>
<td>ND</td>
<td>0.021</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.007</td>
<td>0.008</td>
<td>0.027</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.018</td>
<td>0.023</td>
<td>ND</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.020</td>
<td>ND</td>
<td>0.026</td>
</tr>
</tbody>
</table>

MRL FAO/WHO Codex: cauliflower, chlorpyrifos 0.05 mg kg\(^{-1}\), monocrotophos 0.2 mg kg\(^{-1}\).

A total 10 samples of capsicum and cauliflower were analysed for the detection of monocrotophos, chlorpyrifos and endosulfan. Monocrotophos residues was detected in the two cauliflower samples (0.024 mg kg\(^{-1}\) and 0.027 mg kg\(^{-1}\)) and four capsicum samples (0.021, 0.007, 0.018 and 0.020 mg kg\(^{-1}\) respectively). Chlorpyrifos residues was detected in the one cauliflower sample (0.002 mg kg\(^{-1}\)) and three capsicum samples (0.012, 0.008 and 0.023 mg kg\(^{-1}\) respectively). Endosulfan residues was detected in the four cauliflower samples (0.002, 0.003 and 0.001 mg kg\(^{-1}\) respectively) and four capsicum samples (0.008, 0.021, 0.027 and
0.026 mg kg\(^{-1}\) respectively) (Table 4.13).

4.2.3 Analysis of pesticide residues in fruits samples collected from local market

4.2.3.1 Analysis of pesticide residues in apple and grape samples collected during August 2012 to March 2013

A total of 10 samples of each apple and grape were collected from the local market Vasco-Da-Gama, Goa, India during the period of August 2012 to March 2013 according to the fresh samples availability in the market on a seasonal basis. The fruit samples were analysed for the detection of monocrotophos, chlorpyrifos, endosulfan and cypermethrin. Apple and grape samples were found contaminated 55.0% and 57.5% respectively. Residues were in the range of 0.08 mg kg\(^{-1}\) - 0.105 mg kg\(^{-1}\). The average recoveries of pesticide residues in grape and apple samples were 75.0 to 105.0%.

Table 4.14: Amounts of pesticides residue detected in apple samples collected during August 2012 to December 2012

<table>
<thead>
<tr>
<th>Monocrotophos mg kg(^{-1})</th>
<th>Chlorpyrifos mg kg(^{-1})</th>
<th>Endosulfan mg kg(^{-1})</th>
<th>Cypermethrin</th>
</tr>
</thead>
<tbody>
<tr>
<td>N D</td>
<td>N D</td>
<td>0.026</td>
<td>0.008</td>
</tr>
<tr>
<td>0.024</td>
<td>N D</td>
<td>0.012</td>
<td>N D</td>
</tr>
<tr>
<td>N D</td>
<td>0.008</td>
<td>0.008</td>
<td>0.032</td>
</tr>
<tr>
<td>0.045</td>
<td>N D</td>
<td>N D</td>
<td>0.025</td>
</tr>
<tr>
<td>0.015</td>
<td>0.042</td>
<td>0.022</td>
<td>0.012</td>
</tr>
<tr>
<td>N D</td>
<td>N D</td>
<td>0.105</td>
<td>N D</td>
</tr>
<tr>
<td>0.024</td>
<td>N D</td>
<td>0.044</td>
<td>N D</td>
</tr>
<tr>
<td>0.050</td>
<td>N D</td>
<td>N D</td>
<td>0.080</td>
</tr>
<tr>
<td>N D</td>
<td>0.085</td>
<td>0.052</td>
<td>N D</td>
</tr>
<tr>
<td>0.054</td>
<td>N D</td>
<td>0.022</td>
<td>N D</td>
</tr>
</tbody>
</table>

A total 10 samples of apple were analysed for the detection of monocrotophos, chlorpyrifos, endosulfan and cypermethrin. A Monocrotophos residue was detected in the six apple samples (0.024 mg kg\(^{-1}\), 0.045 mg kg\(^{-1}\), 0.015 mg kg\(^{-1}\), 0.024 mg kg\(^{-1}\), 0.050 mg kg\(^{-1}\) and 0.054 mg kg\(^{-1}\) respectively). A Chlorpyrifos residue was detected in the three apple samples (0.008 mg kg\(^{-1}\), 0.042 mg kg\(^{-1}\) and 0.085 mg kg\(^{-1}\) respectively). Endosulfan residues were detected in the eight apple samples (0.026
mg kg$^{-1}$, 0.012 mg kg$^{-1}$, 0.008 mg kg$^{-1}$, 0.105 mg kg$^{-1}$, 0.044 mg kg$^{-1}$ 0.052 mg kg$^{-1}$ and 0.022 mg kg$^{-1}$ respectively). Cypermethrin residues was detected in the five apple samples (0.008 mg kg$^{-1}$, 0.032 mg kg$^{-1}$, 0.025 mg kg$^{-1}$, 0.012 mg kg$^{-1}$ and 0.080 mg kg$^{-1}$ respectively) (Table:4.14).

Table 4.15: Amounts of pesticides residue detected in grape samples collected during December 2012 to March 2013.

<table>
<thead>
<tr>
<th>Monocrotophos mg kg$^{-1}$</th>
<th>Chlorpyrifos mg kg$^{-1}$</th>
<th>Endosulfan mg kg$^{-1}$</th>
<th>Cypermethrin mg kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.027</td>
<td>N D</td>
<td>N D</td>
<td>0.008</td>
</tr>
<tr>
<td>N D</td>
<td>0.088</td>
<td>0.012</td>
<td>0.040</td>
</tr>
<tr>
<td>0.018</td>
<td>N D</td>
<td>0.028</td>
<td>N D</td>
</tr>
<tr>
<td>0.022</td>
<td>N D</td>
<td>0.036</td>
<td>0.044</td>
</tr>
<tr>
<td>0.035</td>
<td>0.024</td>
<td>N D</td>
<td>0.028</td>
</tr>
<tr>
<td>0.027</td>
<td>N D</td>
<td>N D</td>
<td>0.028</td>
</tr>
<tr>
<td>N D</td>
<td>N D</td>
<td>0.002</td>
<td>N D</td>
</tr>
<tr>
<td>0.045</td>
<td>0.084</td>
<td>N D</td>
<td>N D</td>
</tr>
<tr>
<td>N D</td>
<td>0.052</td>
<td>N D</td>
<td>0.074</td>
</tr>
<tr>
<td>N D</td>
<td>0.105</td>
<td>0.086</td>
<td>N D</td>
</tr>
</tbody>
</table>

A total 10 samples of grape were analysed for the detection of monocrotophos, chlorpyrifos, endosulfan and cypermethrin. Monocrotophos residues was detected in the six grape samples (0.027 mg kg$^{-1}$, 0.018 mg kg$^{-1}$, 0.022 mg kg$^{-1}$, 0.035 mg kg$^{-1}$, 0.027 mg kg$^{-1}$ and 0.045 mg kg$^{-1}$ respectively). Chlorpyrifos residues was detected in the five grape samples (0.088 mg kg$^{-1}$, 0.024 mg kg$^{-1}$, 0.084 mg kg$^{-1}$ 0.052 mg kg$^{-1}$ and 0.105 mg kg$^{-1}$ respectively). Endosulfan residues was detected in the five grape samples (0.012 mg kg$^{-1}$, 0.028 mg kg$^{-1}$, 0.036 mg kg$^{-1}$ 0.002 and 0.086 mg kg$^{-1}$ respectively). Cypermethrin residues was detected in the seven grape samples (0.008 mg kg$^{-1}$, 0.040 mg kg$^{-1}$, 0.044 mg kg$^{-1}$, 0.028 mg kg$^{-1}$ and 0.074 mg kg$^{-1}$ respectively) (Table 4.15).

4.2.3.2 Analysis of pesticide residues in apple, grape and guava samples collected during July 2012 to April 2013

A total of 36 samples of fruits namely apples, grapes and guava were collected from the local market Nanded, India. The fresh samples of apple grape and guava collected in the year 2012 and 2013 for the detection of chlorpyrifos, cypermethrin and
monocrotophos. 75% of fruit samples were showed the presence of residues with one or more than one of pesticides. Total 9 samples (apple one, grape three and guava four samples respectively) were not detected any pesticides. The samples fruits were analysed for the detection of chlorpyrifos, cypermethrin and monocrotophos, residues was found in the range of 0.001-0.021 mg kg$^{-1}$.

Table 4.16: Amount of pesticide residues detected in apple sample collected from local market, Nanded, extracted with 1% acetic acid solution of acetonitrile cleaned up with PSA and magnesium sulphate analysed by GC-MS

<table>
<thead>
<tr>
<th>Sample collection period</th>
<th>No. of sample collected</th>
<th>Chlorpyrifos (mg kg$^{-1}$)</th>
<th>Cypermethrin (mg kg$^{-1}$)</th>
<th>Monocrotophos (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>July- 2013</td>
<td>1</td>
<td>0.008</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>ND</td>
<td>0.001</td>
<td>ND</td>
</tr>
<tr>
<td>August -2013</td>
<td>1</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.002</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>September-2013</td>
<td>1</td>
<td>ND</td>
<td>ND</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>ND</td>
<td>0.004</td>
<td>ND</td>
</tr>
<tr>
<td>October-2013</td>
<td>1</td>
<td>ND</td>
<td>0.002</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.011</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>November-2013</td>
<td>1</td>
<td>ND</td>
<td>0.002</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.002</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>December-2013</td>
<td>1</td>
<td>0.001</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>ND</td>
<td>0.002</td>
<td>ND</td>
</tr>
</tbody>
</table>

A total 12 samples of apple were analysed for the detection of chlorpyrifos, cypermethrin and monocrotophos. Chlorpyrifos residues was detected in the five samples (0.008 mg kg$^{-1}$, 0.002 mg kg$^{-1}$, 0.011mg kg$^{-1}$, 0.002 mg kg$^{-1}$ and 0.001 mg kg$^{-1}$ respectively). Cypermethrin residues was detected in the four samples (0.001 mg kg$^{-1}$, 0.004 mg kg$^{-1}$, 0.002 mg kg$^{-1}$ and 0.002 mg kg$^{-1}$ respectively). Monocrotophos residues was detected in the two samples (0.004 mg kg$^{-1}$ and 0.007 mg kg$^{-1}$ respectively) (Table 4.16).
A total 12 samples of grape were analysed for the detection of chlorpyrifos, cypermethrin and monocrotophos. Chlorpyrifos residues was detected in the four samples (0.021 mg kg\(^{-1}\), 0.002 mg kg\(^{-1}\), 0.008 mg kg\(^{-1}\), 0.011 mg kg\(^{-1}\) and 0.016 mg kg\(^{-1}\) respectively). Cypermethrin residues was detected in the three samples (0.001 mg kg\(^{-1}\), 0.002 mg kg\(^{-1}\), 0.002 mg kg\(^{-1}\) and 0.002 mg kg\(^{-1}\) respectively). Monocrotophos residues was detected in the two samples (0.004 mg kg\(^{-1}\) and 0.005 mg kg\(^{-1}\) respectively) (Table 4.17).

<table>
<thead>
<tr>
<th>Sample collection period</th>
<th>No. of sample collected</th>
<th>Chlorpyrifos (mg kg(^{-1}))</th>
<th>Cypermethrin (mg kg(^{-1}))</th>
<th>Monocrotophos (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>November-2012</td>
<td>1</td>
<td>N D</td>
<td>N D</td>
<td>N D</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.021</td>
<td>0.001</td>
<td>N D</td>
</tr>
<tr>
<td>December-2012</td>
<td>1</td>
<td>N D</td>
<td>N D</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.002</td>
<td>N D</td>
<td>ND</td>
</tr>
<tr>
<td>January-2013</td>
<td>1</td>
<td>N D</td>
<td>0.002</td>
<td>N D</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.008</td>
<td>N D</td>
<td>N D</td>
</tr>
<tr>
<td>February-2013</td>
<td>1</td>
<td>N D</td>
<td>0.002</td>
<td>N D</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.011</td>
<td>N D</td>
<td>N D</td>
</tr>
<tr>
<td>March-2013</td>
<td>1</td>
<td>N D</td>
<td>N D</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>N D</td>
<td>N D</td>
<td>N D</td>
</tr>
<tr>
<td>April-2013</td>
<td>1</td>
<td>N D</td>
<td>0.016</td>
<td>N D</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>N D</td>
<td>0.002</td>
<td>N D</td>
</tr>
</tbody>
</table>
A total 12 samples of guava were analysed for the detection of chlorpyrifos, cypermethrin and monocrotophos. Chlorpyrifos residues was detected in the three samples (0.002 mg kg$^{-1}$, 0.008 mg kg$^{-1}$ and 0.006 mg kg$^{-1}$ respectively). Cypermethrin residues was detected in the three samples (0.005 mg kg$^{-1}$, 0.004 mg kg$^{-1}$ and 0.007 mg kg$^{-1}$ respectively). Monocrotophos residues was detected in the three samples (0.012 mg kg$^{-1}$, 0.005 mg kg$^{-1}$ and 0.002 mg kg$^{-1}$ respectively) (Table 4.16)

Bena Kumari et al. (2006) conducted a study on monitoring on fruit samples of ber, grapes and guava. It was observed contamination with organochlorine, synthetic pyrethroid and organophosphate insecticides. Among organochlorines, HCH, DDT and endosulfan were detected in almost all the samples. Residues of HCH and DDT were found maximum in ber followed by grapes and guava whereas of endosulfan were maximum in guava followed by grapes and ber. All the fruit samples showed the
presence of residues with one or the other group of pesticides. Residues of none of the pesticides exceeded the MRL values in any sample.

Another study was conducted by Kanuajia et al. (2012) on analysis of pesticides residues in winter fruits (apple, grapes, banana cheeku, papaya, lemon). The obtained results showed that out of nine pesticides tested for most of the sample show very high levels of malathion, while other pesticides residues are within the established tolerance, BHC endosulphan dieldrin are within limits. It was suggested that intake of pesticides from fruit samples should be reduced by washing fruits with water.

Yawar et al. (2011) conducted a monitoring of 26 pesticides in commonly used fruits some commonly used fruits in Hyderabad region, Pakistan. A total 131 analyzed by GC-MS, the samples, 53 (40%) were found contaminated with pesticide residues while only 3 (2%) samples were exceeded the MRLs of some pesticides. Chlorpyrifos and dieldrin were detected in almost all analyzed samples. Residues of chlorpyrifos (1256 µg kg⁻¹) and endosulfan sulfate (1236 µg kg⁻¹) were found higher in orange and apple samples, respectively.

On the basis of the above results, it can be concluded that most of the fruits samples contained pesticides residues. The results obtained in the present study in agreement in term of detectable pesticides residues but below MRLs in the fruits samples collected from local market.

Seyed and Somashekar (2010), analysed for synthetic pyrethroid pesticides in grape samples collected from Southern India market. The obtained results showed that all the samples were contaminated with pesticides having higher levels of residues, beyond the MRL as defined by the FAO/WHO, and grapes committee. The screening also showed higher concentration of cypermethrin in comparison to fenvalerate residue.

The present study conducted analysis of fruits sample collected from different market. The pesticides residues were detected in most of the samples. The results obtained in earlier studies were in agreement with the study.
4.3 Comparative solvent extraction method for determination of pesticide residues in vegetables

4.3.1 Comparative solvent extraction of vegetable samples with ethyl acetate and cleanup with Florisil and charcoal and acetonitrile containing 1% of acetic acid cleanup with PSA and magnesium sulphate

A comparative study on solvent extraction method was carried out for the determination of chlorpyrifos, cypermethrin and monocrotophos in brinjal and okra samples.

Table 4.19: Extraction of chlorpyrifos residue using different solvent system in brinjal samples collected from supervised field sprayed with 100, 200 and 300 g a.i. ha\(^{-1}\)

<table>
<thead>
<tr>
<th>Days after treatment</th>
<th>Recovery of residues (mg kg(^{-1}))</th>
<th>Sample extracted with ethyl acetate residues(%)</th>
<th>Sample extracted with acetonitrile residues(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>dose (100 g a.i. ha(^{-1}))</td>
<td>dose (200 g a.i. ha(^{-1}))</td>
</tr>
<tr>
<td>0 (2hr)</td>
<td></td>
<td>0.358</td>
<td>0.678</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>0.223</td>
<td>0.404</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.127</td>
<td>0.238</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>0.049</td>
<td>0.101</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>0.033</td>
<td>0.045</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>0.008</td>
<td>0.017</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>0.002</td>
<td>0.008</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>BDL</td>
<td>0.002</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>-</td>
<td>BDL</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>BDL</td>
<td>BDL</td>
</tr>
</tbody>
</table>

A comparative study on solvent extraction method was carried out for the determination of chlorpyrifos, cypermethrin and monocrotophos in brinjal and okra samples residues were analysed by GC-MS. When a brinjal crop was treated with chlorpyrifos at dose of 100 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically from the experimental field, extraction carried out with ethyl acetate.
Residues of chlorpyrifos was detected 0.358, 0.223, 0.127, 0.049, 0.033, 0.008, 0.002 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11 and 13 respectively. The samples of brinjal when extracted with acetonitrile the residues of chlorpyrifos was detected 0.362, 0.229, 0.129, 0.051, 0.035, 0.009, 0.002 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11 and 13 respectively (Table 4.19).

When a brinjal crop was treated at dose of 200 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically, extraction carried out with ethyl acetate. Residues of chlorpyrifos was detected 0.678, 0.404, 0.238, 0.101, 0.045, 0.017, 0.008, 0.002 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13 and 15 respectively. The samples of brinjal when extracted with acetonitrile the residues of chlorpyrifos was detected 0.679, 0.409, 0.240, 0.104, 0.047, 0.018, 0.010, 0.002 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13 and 15 respectively (Table 4.19).

When a brinjal crop was treated at dose of 300 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically, extraction carried out with ethyl acetate. Residues of chlorpyrifos was detected 0.874, 0.501, 0.284, 0.136, 0.058, 0.024, 0.010, 0.006, 0.004 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15 and 17 respectively. The samples of brinjal when extracted with acetonitrile the residues of chlorpyrifos was detected 0.876, 0.509, 0.288, 0.139, 0.059, 0.026, 0.012, 0.007, 0.004 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15 respectively (Table 4.19).
A brinjal crop was treated with cypermethrin at dose of 100 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically from the experimental field, extraction carried out with ethyl acetate. Residues of cypermethrin was detected 0.339, 0.203, 0.106, 0.028, 0.014, 0.005 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9 and 11 respectively. The samples of brinjal when extracted with acetonitrile the residues of cypermethrin was detected 0.340, 0.207, 0.106, 0.029, 0.015, 0.005 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9 and 11 respectively (Table 4.20).

When a brinjal crop was treated with cypermethrin at dose of 200 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically, extraction carried out with ethyl acetate. Residues of cypermethrin was detected 0.657, 0.382, 0.221, 0.075, 0.028, 0.011, 0.004 mg kg\(^{-1}\) and BDL respectively in samples which were collected after
treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11 and 13 respectively. The samples of brinjal when extracted with acetonitrile the residues of cypermethrin was detected 0.661, 0.384, 0.224, 0.078, 0.030, 0.013, 0.004 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11 and 13 respectively (Table 4.20).

When a brinjal crop was treated at dose of 300 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically, extraction carried out with ethyl acetate. Residues of cypermethrin was detected 0.858, 0.483, 0.265, 0.102, 0.058, 0.038, 0.021, 0.010, 0.004 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13 and 15 respectively. The samples of brinjal when extracted with acetonitrile the residues of cypermethrin was detected 0.862, 0.488, 0.266, 0.107, 0.038, 0.023, 0.011, 0.004, mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13 and 15 respectively (Table 4.20).

Table 4.21: Extraction of monocrotophos residue using different solvent system in brinjal samples collected from supervised field sprayed with 100, 200 and 300g a.i. ha\(^{-1}\)

<table>
<thead>
<tr>
<th>Days after treatment</th>
<th>Sample extracted with ethyl acetate residues</th>
<th>Sample extracted with acetonitrile residues</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(dose (100 g a.i. ha(^{-1})) )</td>
<td>(dose (200 g a.i. ha(^{-1})) )</td>
</tr>
<tr>
<td>0 (2hr)</td>
<td>0.379</td>
<td>0.689</td>
</tr>
<tr>
<td>1</td>
<td>0.234</td>
<td>0.416</td>
</tr>
<tr>
<td>3</td>
<td>0.148</td>
<td>0.260</td>
</tr>
<tr>
<td>5</td>
<td>0.071</td>
<td>0.122</td>
</tr>
<tr>
<td>7</td>
<td>0.038</td>
<td>0.058</td>
</tr>
<tr>
<td>9</td>
<td>0.021</td>
<td>0.034</td>
</tr>
<tr>
<td>11</td>
<td>0.006</td>
<td>0.008</td>
</tr>
<tr>
<td>13</td>
<td>BDL</td>
<td>0.002</td>
</tr>
<tr>
<td>15</td>
<td>-</td>
<td>BDL</td>
</tr>
<tr>
<td>17</td>
<td>BDL</td>
<td>BDL</td>
</tr>
</tbody>
</table>
A brinjal crop was treated with monocrotophos at dose of 100 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically from the experimental field, extraction carried out with ethyl acetate. Residues of monocrotophos was detected 0.379, 0.234, 0.148, 0.071, 0.038, 0.021, 0.006 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11, and 13 respectively. The samples of brinjal when extracted with acetonitrile the residues of cypermethrin was detected 0.388, 0.236, 0.148, 0.073, 0.039, 0.024, 0.006 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, and 13 respectively (Table 4.21).

When a brinjal crop was treated with monocrotophos at dose of 200 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically, extraction carried out with ethyl acetate. Residues of monocrotophos was detected 0.689, 0.416, 0.260, 0.122, 0.058, 0.034, 0.008, 0.002 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, and 15 respectively. The samples of brinjal when extracted with acetonitrile the residues of monocrotophos was detected 0.690, 0.417, 0.261, 0.128, 0.058, 0.039, 0.009 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, and 15 respectively (Table 4.21).

When a brinjal crop was treated at dose of 300 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically, extraction carried out with ethyl acetate. Residues of monocrotophos was detected 0.889, 0.518, 0.295, 0.145, 0.068, 0.032, 0.017, 0.008, 0.004 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15, and 17 respectively. The samples of brinjal when extracted with acetonitrile the residues of monocrotophos was detected 0.891, 0.521, 0.297, 0.149, 0.068, 0.032, 0.018, 0.004 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15, and 17 respectively (Table 4.21).
Table 4.22: Extraction of chlorpyrifos residue using different solvent system in okra samples collected from supervised field sprayed with 100, 200 and 300 g a.i. ha\(^{-1}\)

<table>
<thead>
<tr>
<th>Days after treatment</th>
<th>Recovery of residues (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample extracted with ethyl acetate</td>
</tr>
<tr>
<td></td>
<td>residues%</td>
</tr>
<tr>
<td></td>
<td>dose (100 g a.i. ha(^{-1}))</td>
</tr>
<tr>
<td>0 (2hr)</td>
<td>0.385</td>
</tr>
<tr>
<td>1</td>
<td>0.254</td>
</tr>
<tr>
<td>3</td>
<td>0.152</td>
</tr>
<tr>
<td>5</td>
<td>0.073</td>
</tr>
<tr>
<td>7</td>
<td>0.061</td>
</tr>
<tr>
<td>9</td>
<td>0.029</td>
</tr>
<tr>
<td>11</td>
<td>0.013</td>
</tr>
<tr>
<td>13</td>
<td>0.008</td>
</tr>
<tr>
<td>15</td>
<td>BDL</td>
</tr>
<tr>
<td>17</td>
<td>BDL</td>
</tr>
<tr>
<td>19</td>
<td>BDL</td>
</tr>
</tbody>
</table>

When a okra crop was treated with chlorpyrifos at dose of 100 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically from the experimental field, extraction carried out with ethyl acetate. Residues of chlorpyrifos was detected 0.385, 0.254, 0.152, 0.073, 0.061, 0.029, 0.013, 0.008 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13 and 15 respectively. The samples of okra when extracted with acetonitrile the residues of chlorpyrifos was detected 0.389, 0.258, 0.155, 0.078, 0.062, 0.025, 0.012, 0.006 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13 and 15 respectively (Table 4.22).

When a okra crop was treated at dose of 200 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically, extraction carried out with ethyl acetate. Residues of chlorpyrifos was detected 0.695, 0.432, 0.272, 0.129, 0.070, 0.030, 0.023, 0.014, 0.007 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment
of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15 and 17 respectively. The samples of okra when extracted with acetonitrile the residues of chlorpyrifos was detected 0.696, 0.432, 0.275, 0.129, 0.075, 0.036, 0.025, 0.016, 0.009 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15 and 17 respectively (Table 4.22).

When a okra crop was treated at dose of 300 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically, extraction carried out with ethyl acetate. Residues of chlorpyrifos was detected 0.874, 0.520, 0.292, 0.156, 0.072, 0.044, 0.034, 0.026, 0.011, 0.007 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15, 17 and 19 respectively. The samples of okra when extracted with acetonitrile the residues of chlorpyrifos was detected 0.879, 0.525, 0.299, 0.156, 0.074, 0.044, 0.035, 0.024, 0.011, 0.008 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15, 17 and 19 respectively(Table 4.22).

Table 4.23: Extraction of cypermethrin residue using different solvent system in okra samples collected from supervised field sprayed with 100, 200 and 300g a.i. ha\(^{-1}\)

<table>
<thead>
<tr>
<th>Days after treatment</th>
<th>Recovery of residues (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample extracted with ethyl acetate residues%</td>
</tr>
<tr>
<td></td>
<td>dose (100 g a.i. ha(^{-1}))</td>
</tr>
<tr>
<td>0 (2hr)</td>
<td>0.374</td>
</tr>
<tr>
<td>1</td>
<td>0.235</td>
</tr>
<tr>
<td>3</td>
<td>0.140</td>
</tr>
<tr>
<td>5</td>
<td>0.062</td>
</tr>
<tr>
<td>7</td>
<td>0.049</td>
</tr>
<tr>
<td>9</td>
<td>0.020</td>
</tr>
<tr>
<td>11</td>
<td>0.008</td>
</tr>
<tr>
<td>13</td>
<td>0.004</td>
</tr>
<tr>
<td>15</td>
<td>BDL</td>
</tr>
<tr>
<td>17</td>
<td>BDL</td>
</tr>
<tr>
<td>19</td>
<td>BDL</td>
</tr>
</tbody>
</table>
A okra crop was treated with cypermethrin at dose of 100 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically from the experimental field, extraction carried out with ethyl acetate. Residues of cypermethrin was detected 0.374, 0.235, 0.140, 0.062, 0.049, 0.020, 0.008, 0.004 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13 and15 respectively. The samples of okra when extracted with acetonitrile the residues of cypermethrin was detected 0.378, 0.236, 0.143, 0.065, 0.050, 0.024, 0.008, 0.004 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13 and 15 respectively (Table 4.23).

When a okra crop was treated with cypermethrin at dose of 200 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically, extraction carried out with ethyl acetate. Residues of cypermethrin was detected 0.682, 0.421, 0.260, 0.119, 0.062, 0.025, 0.017, 0.009, 0.002 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15 and 17 respectively. The samples of okra when extracted with acetonitrile the residues of cypermethrin was detected 0.685, 0.424, 0.260, 0.120, 0.064, 0.025, 0.018, 0.010, 0.004 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15 and 17 respectively (Table 4.23).

When an okra crop was treated at dose of 300 g a.i. ha\(^{-1}\) and the samples of vegetable were collected periodically, extraction carried out with ethyl acetate. Residues of cypermethrin was detected 0.862, 0.509, 0.281, 0.144, 0.061, 0.032, 0.025, 0.015, 0.008, 0.003 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15, 17 and 19 respectively. The samples of okra when extracted with acetonitrile the residues of cypermethrin was detected 0.862, 0.515, 0.290, 0.146, 0.065, 0.032, 0.025, 0.016, 0.008, 0.005mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13,15,17 and 19 respectively.
Table 4.24: Extraction of monocrotophos residue using different solvent system in okra samples collected from supervised field sprayed with 100, 200 and 300 g a.i. ha\(^{-1}\)

<table>
<thead>
<tr>
<th>Days after treatment</th>
<th>Sample extracted with ethyl acetate residues%</th>
<th>Sample extracted with acetonitrile residues%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dose (100 g a.i. ha(^{-1}))</td>
<td>dose (200 g a.i. ha(^{-1}))</td>
</tr>
<tr>
<td>0 (2hr)</td>
<td>0.389</td>
<td>0.695</td>
</tr>
<tr>
<td>1</td>
<td>0.254</td>
<td>0.432</td>
</tr>
<tr>
<td>3</td>
<td>0.149</td>
<td>0.271</td>
</tr>
<tr>
<td>5</td>
<td>0.080</td>
<td>0.131</td>
</tr>
<tr>
<td>7</td>
<td>0.049</td>
<td>0.068</td>
</tr>
<tr>
<td>9</td>
<td>0.035</td>
<td>0.042</td>
</tr>
<tr>
<td>11</td>
<td>0.019</td>
<td>0.032</td>
</tr>
<tr>
<td>13</td>
<td>0.007</td>
<td>0.018</td>
</tr>
<tr>
<td>15</td>
<td>BDL</td>
<td>0.005</td>
</tr>
<tr>
<td>17</td>
<td>BDL</td>
<td>0.004</td>
</tr>
<tr>
<td>19</td>
<td>BDL</td>
<td>BDL</td>
</tr>
</tbody>
</table>

A okra crop was treated with monocrotophos at dose of 100 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically from the experimental field, extraction carried out with ethyl acetate. Residues of monocrotophos was detected 0.389, 0.254, 0.149, 0.080, 0.049, 0.035, 0.019, 0.007 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11 and 13 respectively. The samples of okra when extracted with acetonitrile the residues of cypermethrin was detected 0.391, 0.256, 0.150, 0.081, 0.049, 0.039, 0.019, 0.007 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13 and 15 respectively (Table 4.24).

When a okra crop was treated with monocrotophos at dose of 200 g a.i. ha\(^{-1}\) and the samples of vegetable was collected periodically, extraction carried out with ethyl acetate. Residues of monocrotophos was detected 0.695, 0.432, 0.271, 0.131, 0.068, 0.042, 0.032, 0.018, 0.005 mg kg\(^{-1}\) and BDL respectively in samples which were
collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15 and 17 respectively. The samples of okra when extracted with acetonitrile the residues of monocrotophos was detected 0.698, 0.435, 0.270, 0.131, 0.073, 0.045, 0.034, 0.018, 0.007 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15 and 17 respectively (Table 4.24).

When a brinjal crop was treated at dose of 300 g a.i. ha\(^{-1}\) and the samples of vegetable were collected periodically, extraction carried out with ethyl acetate. Residues of monocrotophos was detected 0.898, 0.529, 0.312, 0.152, 0.078, 0.054, 0.045, 0.023, 0.012, 0.004 mg kg\(^{-1}\) and BDL respectively in samples which were collected after treatment of pesticide on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15, 17 and 19 respectively. The samples of brinjal when extracted with acetonitrile the residues of monocrotophos was detected 0.898, 0.533, 0.318, 0.156, 0.086, 0.056, 0.046, 0.028, 0.014, 0.004 mg kg\(^{-1}\) and BDL on the days 0(2hr), 1, 3, 5, 7, 9, 11, 13, 15, 17 and 19 respectively (Table 4.24).

In this study, it was evaluated the suitability of two solvent extraction cleanup method for GC analysis of pesticide residues in vegetables. Between the extraction methods ethyl acetate extraction was found time consuming and least suitable for isolation of multiclass pesticide residues from samples whereas MeCN offers advantages in extraction selectivity and compatibility with more diverse analytical techniques. In comparison to cleanup of the samples with selection of an optimal solvent for GC analysis depends on several factors including the type of GC injection technique and the range of analytes.

On comparison of analysis data obtained extraction of pesticide residues carried out using acetonitrile was found to be the most suitable solvent for extraction of a wide polarity range of pesticide residues from vegetables. Better recovery was obtained when the samples extracted with this solution and cleanup with PSA in comparison to ethyl acetate and cleanup with Florisil and charcoal. To conclude, acetonitrile is the most suitable solvent for extraction of a wide polarity range of pesticide residues from produce.

It can be concluded that extraction using acetonitrile giving more recovery that ethyl acetate. A critical review of literature showed that solvents such as acetonitrile and
ethyl acetate are extraction solvents most commonly used for isolation of multiple pesticide residues from produce and each of them has been demonstrated to give acceptably high recoveries of a wide range of pesticides. (Schenck et al., 2008; Lahotay et al., 2007; Lahotay et al., 2010). Samples of brinjal and okra collected from experimental field.

4.4 Dissipation and persistence period of pesticides residues in brinjal and okra

This study revealed that under laboratory conditions the initial deposits of chlorpyrifos, 0.362, 0.679 and 0.876 mg kg$^{-1}$ when applied 100, 200 and 300 g a.i.h$^{-1}$ on first day declined to 0.229, 0.409 and 0.501 mg kg$^{-1}$ showing 36.7, 39.7 and 41.9% dissipation, respectively (table 1). The initial deposits of cypermethrin 0.340, 0.661 and 0.858 mg kg$^{-1}$ when applied 100, 200 and 300 g a.i.h$^{-1}$ on first day declined to 0.207, 0.382 and 0.488 mg kg$^{-1}$ showing 39.1, 42.2 and 43.1% (table 2), respectively whereas the initial deposits of monocrotophos 0.388, 0.689 and 0.891 mg kg$^{-1}$ when applied 100, 200 and 300 g a.i.h$^{-1}$ on first day declined to 0.236, 0.419 and 0.521 mg kg$^{-1}$ showing 39.2, 39.2 and 43.1%, respectively (table 3). Residues of chlorpyrifos, cypermethrin and monocrotophos reached below detection limit (BDL) showing complete dissipation on 11, 13, 15 days, 11, 13, 15 days and 13, 15, 17 days respectively when it was applied 100, 200 and 300 a.i.h$^{-1}$, on brinjal.
Table 4.25: Persistence of chlorpyrifos residues at different intervals from the day of application in brinjal samples collected from supervised field sprayed with 100, 200 and 300 g a.i. ha\(^{-1}\).

<table>
<thead>
<tr>
<th>Days after treatment</th>
<th>Residue mg kg(^{-1}) (% of Dissipation)</th>
<th>Residue mg kg(^{-1}) (% of Dissipation)</th>
<th>Residue mg kg(^{-1}) (% of Dissipation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (2hr)</td>
<td>0.362 (-)</td>
<td>0.679 (-)</td>
<td>0.876 (-)</td>
</tr>
<tr>
<td>1</td>
<td>0.229 36.7</td>
<td>0.409 39.7</td>
<td>0.509 41.9</td>
</tr>
<tr>
<td>3</td>
<td>0.129 64.3</td>
<td>0.240 64.5</td>
<td>0.288 67.1</td>
</tr>
<tr>
<td>5</td>
<td>0.051 85.9</td>
<td>0.104 84.7</td>
<td>0.139 84.1</td>
</tr>
<tr>
<td>7</td>
<td>0.035 90.3</td>
<td>0.047 93.1</td>
<td>0.059 93.3</td>
</tr>
<tr>
<td>9</td>
<td>0.009 97.5</td>
<td>0.018 97.3</td>
<td>0.026 97.0</td>
</tr>
<tr>
<td>11</td>
<td>0.002 99.4</td>
<td>0.010 98.5</td>
<td>0.012 98.6</td>
</tr>
<tr>
<td>13</td>
<td>BDL -</td>
<td>0.002 99.7</td>
<td>0.007 99.2</td>
</tr>
<tr>
<td>15</td>
<td>- -</td>
<td>BDL -</td>
<td>0.004 99.5</td>
</tr>
<tr>
<td>17</td>
<td>- -</td>
<td>- -</td>
<td>BDL -</td>
</tr>
</tbody>
</table>

Persistence of chlorpyrifos residues at different intervals from the day of application in brinjal samples collected from supervised field sprayed with 100, 200 and 300 g a.i. ha\(^{-1}\). Brinjal crop treated with chlorpyrifos at dose of 100 g a.i. ha\(^{-1}\) was dissipated 36.7, 64.3, 85.9, 90.3, 97.5 and 99.4%, on the days 1, 3, 5, 7, 9 and 11 respectively. Brinjal crop treated with chlorpyrifos at dose of 200 g a.i. ha\(^{-1}\) was dissipated 39.7, 64.5, 84.7, 93.1, 97.3, 98.5 and 99.7%, on the days 1, 3, 5, 7, 9, 11 and 13 respectively. Brinjal crop treated with chlorpyrifos at dose of 300 g a.i. ha\(^{-1}\) was dissipated 41.9, 67.1, 84.1, 93.3, 97.3, 98.6, 99.2 and 99.5%, on the days 1, 3, 5, 7, 9, 11, 13 and 15 respectively (Table 4.25).
Table 4.26: Persistence of cypermethrin residues at different intervals from the day of application in brinjal samples collected from supervised field sprayed with 100, 200 and 300 g a.i. ha\(^{-1}\)

<table>
<thead>
<tr>
<th>Days after treatment</th>
<th>Residue mg kg(^{-1}) (% of Dissipation)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dose (100 g a.i. ha(^{-1}))</td>
</tr>
<tr>
<td>0 (2hr)</td>
<td>0.340</td>
</tr>
<tr>
<td>1</td>
<td>0.207</td>
</tr>
<tr>
<td>3</td>
<td>0.106</td>
</tr>
<tr>
<td>5</td>
<td>0.029</td>
</tr>
<tr>
<td>7</td>
<td>0.015</td>
</tr>
<tr>
<td>9</td>
<td>0.005</td>
</tr>
<tr>
<td>11</td>
<td>BDL</td>
</tr>
<tr>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>17</td>
<td>-</td>
</tr>
</tbody>
</table>

Persistence of cypermethrin residues at different intervals from the day of application in brinjal samples collected from supervised field sprayed with 100, 200 and 300 g a.i. ha\(^{-1}\). Brinjal crop treated with cypermethrin at dose of 100 g a.i. ha\(^{-1}\) was dissipated 39.1, 68.8, 91.5, 95.6 and 98.5%, on the days 1, 3, 5, 7 and 9 respectively. Brinjal crop treated with cypermethrin at dose of 200 g a.i. ha\(^{-1}\) was dissipated 42.2, 66.1, 88.2, 95.5, 98.3 and 99.4%, on the days 1, 3, 5, 7, 9 and 11 respectively. Brinjal crop treated with cypermethrin at dose of 300 g a.i. ha\(^{-1}\) was dissipated 43.1, 68.9, 87.5, 95.6, 97.3, 98.7 and 99.5, on the days 1, 3, 5, 7, 9, 11 and 13 respectively (Table 4.26).
Table 4.27: Persistence of monocrotophos residues at different intervals from the day of application in brinjal samples collected from supervised field sprayed with 100, 200 and 300g a.i. ha\(^{-1}\).

<table>
<thead>
<tr>
<th>Days after treatment</th>
<th>Residue mg kg(^{-1}) (% of Dissipation)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dose (100 a.i. ha(^{-1})) % of Dissipation</td>
</tr>
<tr>
<td>0 (2hr)</td>
<td>0.388 -</td>
</tr>
<tr>
<td>1</td>
<td>0.236 39.2</td>
</tr>
<tr>
<td>3</td>
<td>0.148 61.8</td>
</tr>
<tr>
<td>5</td>
<td>0.073 81.2</td>
</tr>
<tr>
<td>7</td>
<td>0.038 90.2</td>
</tr>
<tr>
<td>9</td>
<td>0.024 93.8</td>
</tr>
<tr>
<td>11</td>
<td>0.006 98.5</td>
</tr>
<tr>
<td>13</td>
<td>BDL -</td>
</tr>
<tr>
<td>15</td>
<td>- -</td>
</tr>
<tr>
<td>17</td>
<td>- -</td>
</tr>
</tbody>
</table>

Persistence of monocrotophos residues at different intervals from the day of application in brinjal samples collected from supervised field sprayed with 100, 200 and 300g a.i. ha\(^{-1}\). Brinjal crop treated with cypermethrin at dose of 100 g a.i. ha\(^{-1}\) was dissipated 39.2, 61.8, 81.2, 90.2, 93.8 and 98.5%, on the days 1, 3, 5, 7, 9 and 11 respectively. Brinjal crop treated with monocrotophos at dose of 200 g a.i. ha\(^{-1}\) was dissipated 39.6, 62.2, 81.4, 91.6, 94.3, 98.7 and 99.4%, on the days 1, 3, 5, 7, 9, 11 and 13 respectively. Brinjal crop treated with monocrotophos at dose of 300 g a.i. ha\(^{-1}\) was dissipated 41.5, 66.7, 83.3, 92.4, 96.4, 98.0 and 99.5%, on the days 1, 3, 5, 7, 9, 11, 13 and 15 respectively (Table 4.27).

Persistence of chlorpyrifos, cypermethrin and monocrotophos on okra was studied following application at dose of 100, 200, 300g a.i.h\(^{-1}\) to work out the safe preharvest waiting period. Samples of okra fruits were collected on 0, 1, 3, 5, 7, 9, 11, 13, 15, 17 and 19 days at harvest after treatment of pesticide. A typical multi-residue extraction procedure was carried out using acetonitrile containing 1% acetic acid and cleaned up...
with PSA and magnesium sulphate extract analysed by GC-MS. The initial residues were in the range of 0.362, 0.679 and 0.876 mg kg\(^{-1}\) for chlorpyrifos, 0.340, 0.661 and 0.858 mg kg\(^{-1}\) for cypermethrin, 0.388, 0.698 and 0.891 mg kg\(^{-1}\) for monocrotophos, respectively for the dose of 100, 200, 300 g a.i.h\(^{-1}\). The residues of pesticides fell below detection in the 15, 17 and 19 days for chlorpyrifos, cypermethrin and monocrotophos, respectively.

The persistence of cypermethrin on okra fruits observed in our study is partly agreement with the results reported by Prasad et al. (1993), who found that the residues of cypermethrin reduced below detectable concentration by 10 days after treatment. Moreover, cypermethrin on okra persisted for a shorter time than on cauliflower (Awasthi and Lalitha, 1983). Rai et al. (1986) observed that residues of cypermethrin though persisted for 15 days after treatment, were below the prescribed maximum residue limit within 8 days on cauliflower, is in good agreement with our results.

Raina and Raina (2008) were studied on dissipation of chlorpyrifos on cauliflower. Chlorpyrifos applied at dose of 500 and 1000 g a.i. ha\(^{-1}\) in the year 2004 and 2005 to work out safe preharvest waiting period. It was found that the average initial deposits varied from 0.56-.086 and 1.29-1.43 mg kg\(^{-1}\) respectively. The residues reached below the MRL of 0.05 mg kg\(^{-1}\) in 5.0-6.3 and 7.1-7.3 days at dose 500 and 1000 g a.i. ha\(^{-1}\) respectively.

The study was designed to determine the residual persistence and dissipation behavior of pesticides in brinjal and okra at experimental field at Goa, thereby to suggest waiting period for safe consumption of vegetables because most of the farmers do not take care about the waiting period between the spray of pesticides and crop harvesting.

### 4.5 Effect of normal/hot water washing on pesticide residues vegetables

Effect of washing on residue of chlorpyrifos and monocrotophos in capsicum and cauliflower was determined. The washing processes were carried out with normal and hot water with different span of time. The vegetables samples were washed with normal water, hot water (~50°C) and analysed by gas chromatography electron capture detection. The highest chlorpyrifos residue was found at raw stage in
cauliflower (0.116 mg kg\(^{-1}\)) followed by capsicum (0.160 mg kg\(^{-1}\)), and residue of monocrotophos was recorded in cauliflower (0.260 mg kg\(^{-1}\)) and in capsicum (0.178 mg kg\(^{-1}\)). The chlorpyrifos residue reduced in capsicum and cauliflower from 25 to 42% after normal water washing, and 36-74% reduced with hot water washing. Whereas monocrotophos residue was reduced in capsicum and cauliflower 23 to 39% after normal water washing and 35-72% reduced after hot water washing. The vegetable samples collected from the local market contained detectable residues representing approximate 80% rate of contamination. There were some of the vegetables samples contained chlorpyrifos and monocrotophos residues above maximum residue limits (MRLs). However, washing of vegetable reduced some extent of the pesticide residues. The samples were extracted with 1% acetic acid in acetonitrile mixture and cleaned up with primary secondary amine (PSA) and magnesium sulphate.

Table 4.28: Effect of normal water washing on chlorpyrifos residue in capsicum and cauliflower

<table>
<thead>
<tr>
<th>Vegetable</th>
<th>Initial residue mg kg(^{-1})</th>
<th>Periods of washing in min</th>
<th>% Reduction of pesticide</th>
<th>% Reduction of pesticide</th>
<th>% Reduction of pesticide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5min washing</td>
<td>10min washing</td>
<td>15 min washing</td>
<td></td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.160</td>
<td>0.119</td>
<td>25.6</td>
<td>0.109</td>
<td>25.6</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.094</td>
<td>0.070</td>
<td>26.1</td>
<td>0.064</td>
<td>26.1</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.024</td>
<td>0.017</td>
<td>29.2</td>
<td>0.016</td>
<td>29.2</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.048</td>
<td>0.036</td>
<td>25.0</td>
<td>0.030</td>
<td>25.0</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.027</td>
<td>0.020</td>
<td>25.9</td>
<td>0.017</td>
<td>25.9</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.009</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.116</td>
<td>0.087</td>
<td>25.0</td>
<td>0.077</td>
<td>25.0</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

The samples of capsicum and cauliflower analysed for the detection of chlorpyrifos and simultaneously study the effect of normal water washing on pesticides residues in vegetables. The initial residues of chlorpyrifos were detected the capsicum samples
0.160 mg kg\(^{-1}\), 0.094 mg kg\(^{-1}\), 0.024 mg kg\(^{-1}\) and 0.048 mg kg\(^{-1}\) respectively. Residues of chlorpyrifos reduced 25.6, 26.1, 29.2 and 25.0% in 5 min washing, 31.8, 31.9, 33.3 and 37.5% in 10 min washing and 42.5, 41.4, 41.6, 43.7% in 15 min of washing. The initial residues of chlorpyrifos were detected the cauliflower samples 0.027 mg kg\(^{-1}\), 0.009 mg kg\(^{-1}\) and 0.116 mg kg\(^{-1}\) respectively. Residues of chlorpyrifos reduced 25.9, ND and 25.0% in 5 min washing, 37.0, ND and 33.6% in 10 min washing and 40.7%, ND, 41.3% in 15 min of washing (Table 4.28).

Table 4.29: Effect of normal water washing on monocrotophos residue in capsicum and cauliflower

<table>
<thead>
<tr>
<th>Vegetable</th>
<th>Initial residue (mg/kg)</th>
<th>Periods of washing in min</th>
<th>% Reduction of pesticide</th>
<th>% Reduction of pesticide</th>
<th>% Reduction of pesticide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capsicum</td>
<td>0.094</td>
<td>5 min washing</td>
<td>0.073</td>
<td>22.3</td>
<td>0.063</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.128</td>
<td>10 min washing</td>
<td>0.099</td>
<td>22.6</td>
<td>0.088</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.178</td>
<td>15 min washing</td>
<td>0.134</td>
<td>24.7</td>
<td>0.122</td>
</tr>
<tr>
<td>Capsicum</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.096</td>
<td>5 min washing</td>
<td>0.072</td>
<td>25.5</td>
<td>0.066</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.260</td>
<td>10 min washing</td>
<td>0.196</td>
<td>24.6</td>
<td>0.177</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>ND</td>
<td>15 min washing</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.042</td>
<td>%</td>
<td>0.032</td>
<td>23.8</td>
<td>0.029</td>
</tr>
</tbody>
</table>

The samples of capsicum and cauliflower analysed for the detection of monocrotophos and simultaneously study the effect of normal water washing on pesticides residues in vegetables. The initial residues of monocrotophos were detected the capsicum samples 0.094 mg kg\(^{-1}\), 0.128 mg kg\(^{-1}\) and 0.178 mg kg\(^{-1}\) respectively. Residues of chlorpyrifos reduced 22.3, 22.6 and 24.70% in 5 min washing, 32.9, 31.2 and 31.9% in 10 min washing and 38.3, 37.5 and 38.7% in 15 min of washing. The initial residues of monocrotophos were detected the cauliflower samples 0.096 mg kg\(^{-1}\), 0.260 mg kg\(^{-1}\) and 0.042 mg kg\(^{-1}\) respectively. Residues of monocrotophos reduced
25.5, 24.6 and 23.8% in 5min washing, 31.2, 31.9 and 30.9% in 10min washing and 38.5, 37.7 and 35.7% in 15 min of washing (Table 4.29).

Table 4.30: Effect of hot water washing on chlorpyrifos residue in capsicum and cauliflower

<table>
<thead>
<tr>
<th>Vegetable</th>
<th>Initial residue mg kg(^{-1})</th>
<th>5 min washing</th>
<th>10 min washing</th>
<th>15 min washing</th>
<th>% Reduction of pesticide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capsicum</td>
<td>0.046</td>
<td>0.337</td>
<td>0.029</td>
<td>0.012</td>
<td>36.9</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.108</td>
<td>0.067</td>
<td>0.050</td>
<td>0.030</td>
<td>37.9</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.028</td>
<td>0.018</td>
<td>0.012</td>
<td>0.008</td>
<td>35.7</td>
</tr>
<tr>
<td>Capsicum</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.088</td>
<td>0.056</td>
<td>0.042</td>
<td>0.023</td>
<td>36.3</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.112</td>
<td>0.070</td>
<td>0.053</td>
<td>0.029</td>
<td>37.5</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.008</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.110</td>
<td>0.072</td>
<td>0.052</td>
<td>0.031</td>
<td>34.5</td>
</tr>
</tbody>
</table>

The samples of capsicum and cauliflower analysed for the detection of chlorpyrifos and simultaneously study the effect of hot water washing on pesticides residues in vegetables. The initial residues of chlorpyrifos were detected the capsicum samples 0.046 mg kg\(^{-1}\), 0.108 mg kg\(^{-1}\) and 0.028 mg kg\(^{-1}\) respectively. Residues of chlorpyrifos reduced 36.9, 37.9 and 35.7% in 5min washing, 52.2, 53.7 and 57.1% in 10min washing and 73.9, 72.2 and 71.4% in 15 min of washing. The initial residues of chlorpyrifos were detected the cauliflower samples 0.0112 mg kg\(^{-1}\), 0.008 mg kg\(^{-1}\) and 0.110 respectively. Residues of chlorpyrifos reduced 36.3, 37.5, ND and 34.5% in 5min washing, 52.2, 59.0, ND and 52.7% in 10min washing and 73.8, 74.1, ND and 71.8% in 15 min of washing (Table 4.30).
Table 4.31: Effect of hot water washing on monocrotophos residue in capsicum and cauliflower

<table>
<thead>
<tr>
<th>Vegetable</th>
<th>Initial residue mg kg(^{-1}) in unwashed samples</th>
<th>Periods of washing in min</th>
<th>Reduction of pesticide</th>
<th>Reduction of pesticide</th>
<th>Reduction of pesticide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5 min washing %</td>
<td>10 min washing %</td>
<td>15 min washing %</td>
<td></td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.150</td>
<td>0.098</td>
<td>34.7</td>
<td>0.068</td>
<td>54.7</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.068</td>
<td>0.043</td>
<td>36.8</td>
<td>0.032</td>
<td>52.9</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.008</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.098</td>
<td>0.061</td>
<td>37.0</td>
<td>0.047</td>
<td>51.0</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.210</td>
<td>0.137</td>
<td>34.7</td>
<td>0.093</td>
<td>55.7</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.074</td>
<td>0.045</td>
<td>39.2</td>
<td>0.035</td>
<td>52.7</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cauliflower</td>
<td>0.004</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

The samples of capsicum and cauliflower analysed for the detection of monocrotophos simultaneously study the effect of hot water washing on pesticides residues in vegetables. The initial residues of monocrotophos were detected the capsicum samples 0.150 mg kg\(^{-1}\), 0.068 mg kg\(^{-1}\), 0.008 mg kg\(^{-1}\) and 0.098 mg kg\(^{-1}\) respectively. Residues of monocrotophos was reduced to 34.7, 36.8, ND, and 37.0% in 5 min washing, 54.7, 52.9, ND and 51.0% in 10 min washing and 71.3, 70.6, ND and 71.4% in 15 min of washing. The initial residues of monocrotophos was detected the cauliflower samples 0.210 mg kg\(^{-1}\), 0.074 mg kg\(^{-1}\) and 0.004 mg kg\(^{-1}\) respectively. Residues of monocrotophos was reduced 34.7, ND and 39.2% in 5 min washing, 55.7, 52.7, ND and 52.7% in 10 min washing and 72.3, 71.6%, ND, ND, in 15 min of washing (Table 4.31).
4.6 Effect of household washing/processing on pesticides residues in vegetables

The study was conducted to investigate the effects of washing/household processing on removal of organophosphate (chlorpyrifos and monocrotophos) and pyrethroid (cypermethrin) residues in brinjal and okra. The household washing/processesing included washing separately with water, 2.0% NaCl, 1.0 % NaHCO3, 0.5 % acetic acid and boiling in water. Samples of brinjal and okra were collected from experimental field which were spiked with different concentration of pesticide. In the household washing/processesing of brinjal samples, residues of chlorpyrifos, cypermethrin and monocrotophos reduced by 29.5-99.2%, 30.2-92.1% and 65.6-99.7%, respectively. Whereas household washing/processesing of okra, residues of chlorpyrifos, cypermethrin and monocrotophos reduced by 24.5-98.9%, 29.5-92.2% and 65.5 -99.5%, respectively. Maximum residues were reduced by boiling (99.7%). Boiling was found comparatively more effective than washing in dislodging the residues.

Table 4.32: Reduction (%) of pesticide residues (mg kg\(^{-1}\)) on brinjal after washing with different washing solutions

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Sample</th>
<th>Initial residue (mg kg(^{-1}))</th>
<th>Water</th>
<th>1% NaHCO(_3)</th>
<th>2% NaCl</th>
<th>0.5% Acetic Acid</th>
<th>Boiling in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorpyrifos</td>
<td>1</td>
<td>0.362</td>
<td>29.5±2</td>
<td>62.5±2</td>
<td>59.8±1</td>
<td>65.6±3</td>
<td>98.5±1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.679</td>
<td>31.2±2</td>
<td>62.4±2</td>
<td>61.8±1</td>
<td>68.5±3</td>
<td>98.9±1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.876</td>
<td>32.5±2</td>
<td>65.6±2</td>
<td>61.2±1</td>
<td>67.3±3</td>
<td>99.2±1</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>1</td>
<td>0.340</td>
<td>30.2±2</td>
<td>61.9±2</td>
<td>62.2±1</td>
<td>68.5±3</td>
<td>90.1±1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.661</td>
<td>32.0±2</td>
<td>60.4±2</td>
<td>61.9±1</td>
<td>67.9±3</td>
<td>90.4±1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.858</td>
<td>31.4±2</td>
<td>62.9±2</td>
<td>62.8±1</td>
<td>68.1±3</td>
<td>92.1±1</td>
</tr>
<tr>
<td>Monocrotophos</td>
<td>1</td>
<td>0.388</td>
<td>65.6±2</td>
<td>71.1±2</td>
<td>81.2±1</td>
<td>78.9±3</td>
<td>98.5±1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.690</td>
<td>66.4±2</td>
<td>72.2±2</td>
<td>82.2±1</td>
<td>78.8±3</td>
<td>99.7±1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.891</td>
<td>65.8±2</td>
<td>72.8±2</td>
<td>80.8±1</td>
<td>79.2±3</td>
<td>99.1±1</td>
</tr>
</tbody>
</table>
Brinjal sample contained different concentration of pesticides residues, were taken for washing/houseprocessing. The residues of chlorpyrifos was reduced by washing/household processing to 29.5 to 32.5%, 62.5 to 65.6 %, 59.8 to 62.2 %, 65.6 to 68.5% and 98.5 to 99.2% when washing with water, 1%NaHCO3, 2% NaCl, 0.5% acetic acid and boiling water respectively. The residues of cypermethrin was reduced by washing/household processing to 30.2 to 32.0%, 60.4 to 62.9%, 61.9 to 62.8 %, 67.9 to 68.5% and 90.1 to 92.1% when washing with with water, 1%NaHCO3, 2% NaCl, 0.5% acetic acid and boiling water respectively. The residues of monocrotophos was reduced by washing/household processing to 65.6 to 66.4%, 71.1 to 72.8%, 80.8 to 82.2 %, 78.8 to 79.2% and 98.5 to 99.7% when washing with with water, 1%NaHCO3, 2% NaCl, 0.5% acetic acid and boiling water respectively (Table 4.32).
Table 4.33: Reduction (%) of pesticide residues (mg kg\(^{-1}\)) on okra after washing with different washing solutions

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Sample</th>
<th>Initial residue (mg kg(^{-1}))</th>
<th>Water</th>
<th>1% NaHCO(_3)</th>
<th>2% NaCl</th>
<th>0.5% Acetic Acid</th>
<th>Boiling in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorpyrifos</td>
<td>1</td>
<td>0.389</td>
<td>24.5±2</td>
<td>68.0±2</td>
<td>62.0±1</td>
<td>65.6±3</td>
<td>98.2±1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.696</td>
<td>28.2±2</td>
<td>68.2±2</td>
<td>64.8±1</td>
<td>69.6±3</td>
<td>97.9±1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.874</td>
<td>29.1±2</td>
<td>69.4±2</td>
<td>64.2±1</td>
<td>69.8±3</td>
<td>98.9±1</td>
</tr>
<tr>
<td>Cypermethrin</td>
<td>1</td>
<td>0.378</td>
<td>27.2±2</td>
<td>64.9±2</td>
<td>62.8±1</td>
<td>65.2±3</td>
<td>90.1±1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.685</td>
<td>28.3±2</td>
<td>67.4±2</td>
<td>65.8±1</td>
<td>68.4±3</td>
<td>89.9±1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.862</td>
<td>29.3±2</td>
<td>67.2±2</td>
<td>65.6±1</td>
<td>69.4±3</td>
<td>92.2±1</td>
</tr>
<tr>
<td>Monocrotophos</td>
<td>1</td>
<td>0.391</td>
<td>65.5±2</td>
<td>75.7±2</td>
<td>80.1±1</td>
<td>74.6±3</td>
<td>98.8±1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.698</td>
<td>62.4±2</td>
<td>76.9±2</td>
<td>84.3±1</td>
<td>78.0±3</td>
<td>99.1±1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.898</td>
<td>63.7±2</td>
<td>75.6±2</td>
<td>81.4±1</td>
<td>77.6±3</td>
<td>99.5±1</td>
</tr>
</tbody>
</table>
Figure 4.12: Reduction (%) of pesticide residues (mg kg\(^{-1}\)) on okra after washing with different washing solutions

Okra sample contained different concentration of pesticides residues, were taken for washing/household processing. The residues of chlorpyrifos was reduced by washing/household processing to 24.5 to 29.1%, 68.0 to 69.4 %, 62.0 to 64.8 %, 65.6 to 69.8% and 97.9 to 98.9% after washing with water, 1%NaHCO\(_3\), 2% NaCl, 0.5% acetic acid and boiling water respectively. The residues of cypermethrin was reduced by washing/household processing to  27.2 to 29.3%, 64.9 to 67.4%, 65.2 to 69.8 %, 67.9 to 68.5% and 89.9 9.2.2% when washing with with water, 1%NaHCO\(_3\), 2% NaCl, 0.5% acetic acid and boiling water respectively. The residues of monocrotophos was reduced by washing/household processing to 62.4 to 65.5%, 75.6 to 76.9%, 80.1 to 84.3 %, 74.6 to 78.0% and 98.8 to 99.5% when washing with with water, 1%NaHCO\(_3\), 2% NaCl, 0.5% acetic acid and boiling water respectively (Table 4.33).
Among the household processes using water, 2.0% NaCl, 1.0% NaHCO₃, 0.5% acetic acid and boiling in water chlorpyrifos residues reduced by 29.5-32.5%, 62.5-65.6%, 59.8-61.8%, 65.6-68.5% and 98.5-99.2%, cypermethrin residues reduced by 30.2-32.0%, 60.04-62.9%, 61.9-62.8%, 67.9-68.5% and 90.1-92.1%, monocrotophos residues reduced by 65.6-66.4%, 71.1-72.8%, 80.8-82.2%, 78.8-79.2% and 98.5-99.7% respectively in brinjal. The chlorpyrifos residues reduced by 24.5-29.1%, 68.0-69.4%, 62.0-64.8%, 65.6-69.8% and 97.9-98.9%, cypermethrin residues reduced by 27.2-29.3%, 64.9-67.4%, 62.8-65.8%, 65.2-69.4% and 89.2-92.2%, monocrotophos residues reduced by 62.4-65.5%, 75.6-76.9%, 80.1-84.3%, 74.6-78.0% and 98.8-99.5% respectively in okra (Table 4.33).

The results obtained in this study were in agreement as earlier research work conducted by Beena Kumari (2008) as it was observed that washing process reduced the OC residues by 27-44 percent in brinjal, 34-36 percent in cauliflower and 20-38 percent in okra. Whereas the residues of synthetic pyrethroid insecticides in brinjal, cauliflower and okra were reduced to 26, 29 and 31 percent, respectively.

Dhiman, N. et al. (2006) studied the effect of washing on cauliflower treated with chlorpyrifos, quinalphos, endosulfan, fenvalerate and deltamethrin reduced 28.92 %–78.64 % residues of these insecticides. Tomatoes contaminated at level of 1 mg kg⁻¹ upon washing with 10 % NaCl solution gave 42.90, 46.10, 27.20, 90.80, 82.40 and 91.40 per cent loss in HCB, lindane, p,p-DDT, dimethoate, profenophos and pirimiphos-methyl, respectively.

Liang et al. (2012) reported that 63.40, 60.00, 50.00, 31.10 and 66.70 per cent reduction in the residues of trichlorfon, dimethoate, dichlorvos, fenitrothion and chlorpyrifos respectively, were observed in cucumber when dipped in 2 % sodium chloride solution for 20 min. These results agree with those obtained by Zohair (2001) who reported that soaking of contaminated potatoes in neutral (NaCl) solution (5 and 10 %) for 10 min resulted in 100 percent removal of pirimiphos methyl residues. The cause and effect of the reduction in 2 % NaCl washing solutions is still not known and needs further investigation.

The effects of household processing on removal of residues of malathion, fenitrothion, formothion, parathion, methyl parathion and chlorpyrifos in tomato, bean, okra, eggplant, cauliflower and capsicum were studied. The processes included
washing water, 0.9 % NaCl, 0.1 % NaHCO₃, and 0.1 % acetic acid, 0.001 % KMnO₄, 0.1 % ascorbic acid, 0.1 % malic acid and 0.1 % oxalic acid and 2 % aqueous solution of raw Spondias pinnata (SP)) and boiling. In all of the vegetables, washing with different household chemicals reduced the residues by 20-89 % and boiling reduced the residues by 52-100 %. Boiling of vegetables was found to be more effective than washing in dislodging the residues (Gouri Satpathy et al., 2012). Residues of monochrotophos, fenitrothion and fenvalerate were removed to an extent of 41.81%, 100% and 100% by dipping in lemon juice, dipping in 2% tamarind solution for 5 min followed by wash tap water and steam cooking for 10 min respectively (Gardenmo.net, 2013).

In the earlier studies it was found that washing effective in dislodging the residues as it depends on a number of factors like location of residues, age of residues, water solubility and temperature and type of washing. Current results are in consistent with some earlier reports where reduction (10-30%) of alphamethrin residues in tomato and brinjal and cauliflower by Gill et al. (2001) and Malik et al. (1999). Rinsing of various vegetable was found very effective (Krol et al. 2000).

Smriti et al. (2011) observed that processing (washing and washing followed by boiling/cooking) was found very effective in reducing the levels of chlorpyrifos residues in okra fruits. Maximum reduction (64-77%) was observed by washing + boiling followed by washing (13-35%).

Anil Duhan et al. (2010) studied effect of household processing on fenazaquin residues in okra. Residue levels were determined in unprocessed and processed okra fruits and evaluated the effect of different processes (washing, boiling and washing followed by boiling) in reduction of residues of this pesticide. The pesticide was applied at dose of 125 g a.i. ha⁻¹ (Single Dose, T1) and 250 g a.i. ha⁻¹ (Double Dose, T2). Samples of okra fruits were collected on 0, 3, 7, 15 days after treatment and at harvest (30 days). It was found that the processing showed to be very effective in reducing the levels of fenazaquin residues in okra fruits. Maximum reduction (60–61%) was observed by washing + boiling followed by boiling/cooking (38–40%) and then by washing (31–32%).
In present study the household washing/processesing included washing separately with water, 2.0% NaCl, 1.0 % NaHCO3, 0.5 % acetic acid and boiling in water. The washing with water only found least effective in dislodging the pesticides residues and boiling was found more effective for removal of residues. The 2% NaCl solution reduced about 60% residues, if the vegetables and fruits eaten in the raw state washing with this solution best for house hold methods as the salt was found available in every houses.