INSECTICIDE RESIDUES IN MARKET SAMPLES OF VEGETABLES AND METHODS OF THEIR DECONTAMINATION

By

SANTHOSH KUMAR, S. R.

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COLLEGE OF AGRICULTURE
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DECLARATION

I hereby declare that this thesis entitled "***Insecticide residues in market samples of vegetables and methods of their decontamination***" is a bonafide record of research work done by me during the course of research and that the thesis has not previously formed the basis for the award of any degree, diploma, associateship, fellowship or other similar title, of any other university or society.

Vellayani,
19- 7 - 1997

19.7.97

SANTHOSH KUMAR, S. R.

CERTIFICATE

Certified that this thesis entitled "***Insecticide residues in market samples of vegetables and methods of their decontamination***" is a record of research work done independently by Mr. Santhosh Kumar, S. R, under my guidance and supervision and that it has not previously formed the basis for the award of any degree, fellowship or associateship to him.

Vellayani,
19-7 - 1997

Dr. Thomas Biju Mathew,
Assistant Professor,
Department of Agricultural Entomology,
College of Agriculture,
Vellayani.

APPROVED BY

Chairman

Dr. THOMAS BIJU MATHEW

Members

Dr. A. VISALAKSHI 16/1/98

Dr. S. NASEEMA BEEVI

Dr. P. RAJENDRAN 16-1-98

External Examinar

16.01.98

(M.S. PALANISWAMI)

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INTRODUCTION

INTRODUCTION

The goal of food monitoring programmes is to prevent excessive intake of pesticide residues by man through his food. Unintentional residues of pesticides in foods of plant origin, whether demonstrably harmful or not are universally condemned. Their significance lies not only in their direct toxicity, but also in their still unknown long term effects, notably the biological concentration of certain compounds which are trapped by lipids and stored in the fatty tissues of consuming organisms.

The discovery that lipophilic chlorinated pesticide residues exist in almost every living creature, food commodity and environmental samples throughout the world, mobilised the attention of scientists and layman alike. With the introduction of synthetic organic pesticides, organochlorines were gradually replaced by organophosphates, carbamates and synthetic pyrethroids, among which organophosphates still dominate the other groups. Banning or restrictions in the use of organochlorines owing to their ubiquitous contamination in food and environment might be a major reason for the sharp increase in the use of OP compounds for pest control.

The world wide interest in residues in foods, having a primary base in health aspects, is of commendable concern, because of economic implications in international trade. The adoption and enforcement of international tolerance or Maximum Residue Limits (MRL) based on successfully established safety protocols, good agricultural practices and on other environmental substrates still appear to be goals beyond reach for developing countries. However continuing research in the field of insecticide residues is required to perfect surveillance as well as compliance. systems for food commodities in the country. A few scattered surveys carried out by different workers in different parts of the country mostly on academic interest were the pioneer works on monitoring of insecticide residues in India.

Establishment of Maximum Residue Limits for insecticides under Provisions of Food Adulterations Act (PFA) 1954 or provisions even for banning the commodities if found contaminated with residues above MRL under the Insecticide Act of 1968 did not yet entrust any enforcement agencies for legal tolerances. Thus the observations and reports on 'illegal' residues detected in monitoring porgrammes carried out during 60's to 80's received only academic and public interest until the start of an organised network for monitoring insecticide residues in India. In 1988, ICAR established 18 centers of All India Co-ordinated Research Projects on pesticide residues for monitoring. Data obtained from regular monitoring of food commodities from 1988 to 1993 and subsequent monitoring of farmgate samples started from 1994 generated the base line data on the status of pesticide residues in Indian food. The data are submitted to the government and are officially utilised for planning and for making policy decisions regarding pest control and pesticide use.

The results of monitoring studies carried out in different food commodities in India were reviewed from 1964 to 1979 (Kalra and Chawla, 1981) and from 1970 to 1990 (Kathpal and Beenakumari, 1993). Widespread occurrence of organochlorine insecticides like BHC, DDT, endosulfan and cyclodienes was established from the reports reviewed by them.

The extent of insecticide contamination in Indian foods is probably maximum in the world when our data were compared with those of temperate countries. According to a rough estimate, about 20 to 25 per cent of Indian food commodities have been found to contain mainly residues of HCH and DDT and some other organochlorine compounds to a little extent, above the MRL fixed under PFA of 1954 (Kathpal and Beenakumari, 1993). They further reported that of the 2694 vegetable samples analysed all over India during the period from 1965 to 1991, 51 per cent (1377 samples) were contaminated with insecticides and about 20 per cent of them exceeded MRL. In contrast, out of 1,00,000 market basket surveys undertaken by official bodies in developed countries of the world, 80 per cent of the samples were free from residues, about 18 to 19 per cent contained traces well below the legal limits and only 1 to 2 per cent exceeded MRL (Buchel, 1983).

In Kerala, the first report on monitoring of pesticide residues in vegetables was published by Rajendran *et al.* (1991). The study revealed the presence of carbofuran, that too far above MRL of 0.2 ppm in vegetables like amaranthus, bhindi, brinjal, bittergourd and cucumber collected from markets and farmers fields in Kannur district. Another study conducted on market samples of vegetables in Thiruvananthapuram under AICRP on Pesticide Residues showed that the samples were contaminated with HCH that too below detectable level (Anon., 1990 ; Mathew *et al.*, 1993).

The first report on monitoring of farmgate samples of vegetables conducted under the AICRP on pesticide residues, Vellayani centre showed that cowpea and bittergoud samples contained high residues of monocrotophos while bhindi fruits carried high residues of phosphamidon and the residue levels were far above the MRL of 0.2 ppm (Mathew *et al.*, 1995). Thus wide variations were seen among the residue levels observed in vegetable samples collected from market and farmgates in Kerala.

Pesticide residues sticking on the surface of food commodities can be substantially removed by some normal food processing procedures. Specific studies (Farrow *et al.*, 1969) on the removal of residues showed that organochlorine and organophosphate pesticides in fruits and vegetables could be removed substantially ranging from 20 per cent by washing to more than 90 per cent through peeling, cooking etc.

Though the problem of insecticide contamination of vegetable samples assumes importance, it has not been studied systematically in Kerala so far. A few random studies were conducted by Rajendran *et al.* (1991) and Mathew *et al.* (1995). These studies indicated the existence of high level of organophosphates and carbamates insecticides residue problems in vegetables cultivated in Kerala.

In this context, the present study was conducted with the following objectives :-

1. To assess the insecticide residues in vegetables collected from different markets in Thiruvananthapuram district

2. To study the effect of different decontamination techniques on the removal of residues in vegetables

REVIEW OF LITERATURE

2. REVIEW OF LITERATURE

A brief review of literature related to the different aspects covered in the present investigations is given below.

2.1 Monitoring of insecticide residues in market samples

2.1.1 Bhindi

Bhalla *et al.* 1970 reported that of the ten samples of bhindi collected from markets of Hyderabad and analysed for insecticide residues, five of them were contaminated with DDT (1 ppm) and two of them with endrin (0.2 ppm). In the same year they reported that of the eight okra samples collected from Ludhiana six were contaminated with endrin (0.06 - 0.38 ppm).

In 1974 Agnihotri *et al.* found that 10 samples of bhindi collected from Delhi and tested for insecticide residue all the ten samples were invariably contaminated with residue of DDT ranging from non detectable to 9 ppm. Jadhav (1986) observed that when 31 samples of okra were analysed 20 samples were contaminated with DDT (0.01 - 4.12 ppm) and HCH (trace- 3.35 ppm) with percentage incidence of 69.5.

2.1.2 Brinjal

Jaglan and Chopra (1970) observed that ten brinjal samples collected from Ludhiana were analysed for residues of insecticides, four of them were contaminated with DDT with a range of 0.08 to 8 ppm. Jadhav

(1986) reported that of the 42 brinjal samples analysed 24 samples were found contaminated with DDT (0.25 to 2.42 ppm) and HCH (trace - 5.42 ppm) with a percentage incidence of 57.14. When 21 samples of brinjal collected at farm gate from Delhi were analysed for insecticide residues, three samples were contaminated with monocrotophos above MRL, 3 samples with endosulfan, four samples each with fluvalinate, and fenvalerate and two samples with cypermethrin (Anon, 1996d).

2.1.3 **Bittergourd**

A study conducted under AICRP on pesticide residues, Hariyana Agricultural University, showed that when seven bitter gourd samples monitored for insecticide residues, five of the samples were contaminated with monocrotophos and none of them was not above MRL. Two samples were found to be contaminated with quinalphos also. In the same year a study conducted under AICRP on pesticide residue, Rajasthan Agricultural University showed that, when eleven farm gate samples of bittergourd were collected from Jaipur village, three of them were contaminated with monocrotophos (Anon, 1996a)

2.1.4 **Beans**

Lekshminarayana and Menon (1975) reported the occurrence of DDT residues invariably in all the six samples of beans analysed from Hyderabad. When 42 french bean samples were collected from Bombay, five of them were contaminated with lindane in the range of 0.2 to 7.6 ppm (Noronha, 1978).

2.1.5 **Carrot**

Of the eight carrot samples collected from Hyderabad and analysed for residues of insecticides, four of them have been found contaminated with residues of lindane (2 ppm) and two of them with Aldrin (0.5, 0.1 ppm). (Lekshminarayana and Menon, 1975). When carrot samples collected from Maharashtra and analysed, they were contaminated with dieldrin in the range of 0.2 to 1.4ppm (Noronha, 1978).

2.1.6 **Cowpea**

In 1974, Agnihotri *et al.*,detected BHC and DDT residues in samples of cowpea collected from Delhi, the range being non detectable to 0.30 ppm.

In a study conducted on monitoring of farmgate samples of vegetables for pesticide residue under AICRP in Dr. YSPU Agrl. & Forestry, Solan it was found that all the twelve samples of cowpea collected from Delhi were contaminated with monocrotophos above MRL. They also observed that three samples were contaminated with cypermethrin, two samples with lindane and one sample each with fenvalarate, fluvalinate, quinalphos and phorate (Anon, 1996b). In another study conducted in Assam Agricultural University under AICRP on pesticide residue it was found that among six samples of cowpea analysed for insecticide residue three of them were contaminated with malathion, chlorpyriphos and endosulfan. But the level of residues in all the samples were below maximum residue limit (Anon, 1996c).

2.1.7 **Cabbage**

Agnihotri *et al*,(1974) reported that when 30 samples of cabbage collected from markets of Delhi were analysed for residue of insecticides, all of them were contaminated with residues of DDT (ND to 0.5 ppm.). They also found that when 10 sample of cabbage were analysed, five of them were contaminated with high levels of DDT (ND to 10 ppm.) and BHC (ND to 50 ppm.). Khandekar *et al* (1982) reported that when twenty five samples collected from Bombay markets eight were contaminated with DDT in the range of 1.00 to 2.10 ppm.

2.1.8 **Cauliflower**

Jadhav (1986) observed that of the 25 samples of cauliflower collected from different markets in Parbhani, 16 samples were contaminated with DDT (trace - 3.64 ppm) and HCH (trace - 3.92 ppm) with a percentage incidence of 64. Khandekar *et al* (1982) observed that out of 25 samples collected from Bombay twelve samples were contaminated with HCH (0.03 to 0.09), lindane (0.3 to 1.46) heptachlor (0.11 to 0.80) aldrin (0.44 to 0.60) and dieldrin 0.31 to 3.2ppm respectively.

2.1.9 **Chilli**

Lekshminarayana and Menon (1975) found that all the samples of chillies collected from markets of Hyderabad were free from insecticide residue.

2.1.10 **Leafy Vegetable**

Viswashwaraiah and Jayaram (1972) reported that when 300 samples of leafy vegetables collected from markets of Karnataka were analysed for insecticide residue, all the 300 samples were contaminated with BHC with a range of 10.5 ppm. to 20 ppm. While Lekshminarayana and Menon (1975) observed that of the 35 samples of leafy vegetables collected from Hyderabad 10 samples were contaminated with organochlorine residues. The level of HCH and endrin ranged from trace to 0.2 ppm, DDT trace to 2 ppm., and heptachlor in traces. When 60 samples of green vegetable collected from Delhi market analysed 40 were contaminated with DDT and HCH which ranged from traces to 35 and 0.2 to 60ppm respectively (Anon, 1988). And of the 195 green vegetables collected from Haryana 63 were contaminated with residues of HCH (0.87 to 6.03ppm) endosulfan (0.61 to 1.01ppm) dieldrin (0.2 to 1.ppm) and endrin 1.1 to 2.5ppm. (Anon, 1988).

2.1.11 **Mixed Vegetables**

Lekshminarayana and Menon (1975) found that of the 442 samples of vegetables collected from Hyderabad 208 samples were contaminated with BHC (trace - 0 5 ppm.), DDT (trace - 7 ppm), endosulfan (trace) and endrin (trace - 0.8 ppm.). Lekhminarayana (1980) found that when 847 samples of vegetables analysed 286 samples contained residues of BHC (traces to 4ppm), DDT (traces to 10ppm), endosulfan (traces), heptachlor, lindane and endrin in the range of trace to 2, 0.5 to 1.0 and trace to 1.5ppm respectively. When 61 mixed vegetables viz., cucurbit, brinjal, okra, tomato and radish were analysed, 12 of them were found contaminated with BHC (traces to 3.5), 25 with DDT (0.2 to 1ppm) and 5 samples with endosulfan in the range of 0.5 to 2.5ppm (Verma, 1980). Of 195 samples of green vegetables collected from Haryana, 59 were found contaminated with residues of HCH (0.87 - 6.03 ppm.), endosulfan 0.61 - 1.01 ppm.) and DDT (tr - 1.52 ppm.) with percentage incidence of 30.25 (Anon., 1988).

2.1.12 **Potato**

Khandekar *et al*, (1982) found that of the 30 potato samples collected from different locations in Bombay, 21 were contaminated with residues of DDT (0.2 - 10.2 ppm.) and dieldrin (0.4 - 1.4 ppm.) with percentage incidence of 70. Majumdar (1973) reported that of the ten samples of potato collected from Mysore all of them were contaminated with DDT in the range of 0.1 to 169ppm. In another study, Noronha, (1978) observed that of the 145 samples of potatoes collected from Bombay 45 samples contained DDT (0.3 to 7.04ppm). While Kalra and Chawla (1978) observed that of the 40 samples analysed all of them contained residues of DDT (trace to 1.11, BHC (trace to 0.05), aldrin (trace to 0.130 and heptachlor trace to 0.05ppm. Jadhav (1986) reported that of the 29 samples collected, fifteen were contaminated with DDT and HCH in the range of 0.05 to 3.79 and traces to 2.12 ppm respectively.

2.1.13 **Seasonal Vegetables**

Verma (1980) reported that of the 66 summer vegetables viz. okra, cucurbit, brinjal, cabage, carrot, cauliflower and chillies, 12 were contaminated with BHC (0.84 to 6.03ppm) and 12 samples with endosulfan (0.61 to 1.01ppm). He also reported that out of 68 winter vegetables viz. knolkhol, methi, spinach, peas, radish, mustard, tomatoes and turnip, 9 samples contained BHC residues in the range of 1.31 to 3.8ppm, 4 samples with DDT (0.4 to 1.5ppm) and 3 with endosulfan (0.75 to 1.01ppm). Banerji (1989) reported that when 313 samples of seasonal vegetables collected from Bombay were analysed, 153 of them contained residues of organochlorine with percentage incidence of 48.8. While Rajendran *et al.*, (1991) reported that when 21 samples representing the major summer vegetables like amaranthus, bhindi, bittergourd, brinjal, cowpea and cucumber, high levels of carbofuran residues (0.82 to 1.67 ppm.) above safe limits were observed in many of the samples.

Similarly in 1996 Madan and Beenakumari reported that when forty six farm gate samples of seasonal vegetables namely cauliflower, cabbage, pea, brinjal, okra, tomato, bittergourd, smoothgourd and chilli were monitored for residues of insecticides, monocrotophos, quinalphos, BHC isomers, DDT analogue and endosulfan were found in cauliflower, cabbage and pea peel samples. Whereas pea grain samples were found to contain monocrotophos and quinalphos. Only one sample out of six analysed contained 0.25 $mg.kg^{-1}$ of monocrotophos which was above MRL. Residues of monocrotophos and endosulfan were found in one sample of brinjal. Samples of green and red chillies were contaminated with aldrin and dimethoate. Phosphamidon and malathion residues were found in tomato. In twelve samples of summer vegetables viz., bhindi, bittergourd and smooth gourd, monocrotophos residue were below detectable level.

2.1.14 **Starchy Vegetables**

Lekshminarayana and Menon in 1975 found that when 192 starchy vegetables collected from Hyderabad were analysed for insecticide residues, 111 samples were found contaminated with residues of aldrin (trace - 2 ppm.), BHC (trace - 6.6 ppm.), DDT (trace 5 ppm.) dieldrin and endrin (traces).

2.1.15 **Radish**

Agnihotri *et al.* 1974 observed cent per cent contamination when 10 samples of radish top were analysed for residues of insecticides. The level of residues of DDT and BHC ranged from ND to 0.1 ppm. and ND to 50 ppm. respectively.

2.1.16 Tomato

Jaglan and Chopra (1970) reported that only one out of 10 samples of tomato collected from markets of Ludhiana was contaminated with DDT (0.08 ppm.). Lekshminarayana and Menon (1975) found that when 10 samples collected from Hyderabad were analysed four samples were found contaminated with DDT. Noronha (1978) observed that tomoto samples collected from Bombay were found contaminated with endrin in the range of 1.1 to 2.5ppm. Khandekar *et al*,(1982) found that of the 25 samples of tomato collected from different locations in Bombay, 10 samples were found to be contaminated with DDT (0.3 to 4.3 ppm.) and lindane (0.9 to 2.4 ppm.). Jadav *et al* (1986) reported that out of the 38 samples collected from Parbhani 18 were contaminated with DDT to the tune of 0.03 to 3.32 ppm. and HCH trace to 3.59 ppm.

2.2 Monitoring of insecticide residue on farm gate vegetable/ market samples in Kerala.

Monitoring of pesticide residues in vegetables was initiated in Kerala since 1980. Widespread occurrence of alpha, beta, gama and delta isomers of HCH was noticed when market samples of vegetables namely cucumber, snakegourd, bhindi, cowpea and bittergourd collected from local markets of Trivandrum city were analysed. The mean residues of total HCH isomers ranged from 0.008 to 0.029. None of the samples showed presence of organophosphate or carbomate insecticide (Anon, 1989).

In another study on residues of insecticdes in vegetables conducted under AICRP on pesticide residue in Vellayani it was observed that out of the ten samples of bhindi collected from local markets of Trivandrum, eight samples were contaminated with HCH (0.001 to 0.01 ppm), out of the 10 cowpea and bittergourd samples seven each were contaminated with HCH residue (0.001 to 0.021 ppm) (Anon, 1990).

Mathew *et al.* (1995) found that when four farm gate samples each of bitter gourd and cowpea were analysed, two samples of bittergourd were contaminated with monocrotophos, one sample each with residues of methylparathion (0.172ppm.) and phosphamidon (0.872ppm.). While of the four cowpea samples, two of them were contaminated with monocrotophos (1.08 and 1.217 mg./kg.) and one sample each with methyl parathion (0.218 mg./kg.) and phosphamidon (1.12 mg./kg). At the same time out of the three snake gourd samples collected, all of them were contaminated with residues of monocrotophos (0.04 to 0.12mg/kg). Of the two samples each of brinjal and bhindi collected and analysed, brinjal samples were found contaminated with quinalphos (0.02 and 0.19 mg./kg.) and the bhindi samples with phosphamidon (0.44 and 0.87 mg/ kg) residue.

In another study conducted under AICRP on pesticide residues, Vellayani, when four major vegetables collected from four vegetable growing tracts in Trivandrum, the percentage of samples contaminated above MRL was maximum in Palappur (58.4%), followed by Karipur

(54%), Aralummood (45.9%) and Powdikonam (41.7%) The study also showed that among the four vegetables collected, 70 per cent of cowpea samples, 33.3 per cent of bittergourd, 33.3 per cent snakegourd and 66.6 per cent cucumber samples were contained with organophosphate residue above maximum residue limits. They also observed the insecticide usage pattern in the four vegetables and reported that methyl parathion and monocrotophos were most widely used in bittergourd, snakegourd and cow pea often exeeding the recommended dosage. Phorate was the only insecticide detected in cucumber (Anon, 1996e).

Among the 96 samples of vegetable collected from different vegetables growing tracts in Thiruvananthapuram, none of the samples had residues above MRL. It was also reported that when residue studies conducted in vegetables, cowpea showed the highest level of residue (1.43 mg./kg. of quinalphos) which was 7 times that of MRL. Meanwhile in bittergourd, methyl parathion residue ranged from 0.03 to 0.65 mg./kg. and quinalphos 0.14 to 0.29 mg./kg. In snakegourd methylparathion, monocrotophos and quinalphos residue were detected in the ranges of 0.06 to 0.14, 0.07 to 0.22 and 0.08 to 0.32 mg./kg. respectively. In cucumber phorate residue ranged from 0.01 to 0.24 mg/kg

2.3 Decontamination studies in different vegetables

2.3.1 Bhindi

Nath *et al.* (1974) reported that removal endosulfan residues in bhindi fruits varied from 35 to 44 per cent after washing for 30 seconds, 23 to 26 per cent after cooking for 10 minutes and 57 to 58 per cent after dehydration.

Washing with water reduced carbaryl residues up to 79.95 per cent (Deshmukh and Singh, 1975) and upto 68.7 to 71.2 per cent (Krishnaiah *et al.*, 1975).

In 1970 Bhalla *et al.* observed 60% reduction of residue due to dehydration. Jat and Srivastava (1973) reported that there was a reduction of malathion residue upto 89.1% and 91.86% due to washing and dehydration respectively. Nath *et al.*,(1975) reported that there was 66.12 per cent and 79.2 per cent reduction in the residue of carbaryl due to washing and dehydration respectively. They also found that there was reduction of endosulfan residue upto 34.6% due to washing and 57.5 per cent due to dehydration.

There was a reduction of 50 per cent of lindane from bhindi due to cooking when the samples were taken two hours after treatment while the reduction was 54.1 per cent in the samples taken five days after treatment. In the case of triazophos, it could be reduced by 74.14% by cooking on the same day of treatment and 57.5% in samples which are taken 5 days after treatment. (Anon, 1995).

2.3.2 **Brinjal**

Deshmukh and Ratanlal (1969) found that washing of brinjal fruits reduced carbaryl residues to a range of 86 to 95 per cent.

2.3.3 **Cowpea**

Dewan *et al.* (1969) reported that washing with water removed malathion residue from cowpea pods to a level below the tolerance limit. Washing of cowpea treated with carbaryl could reduce the residue up to 77.5 to 82.32 per cent, while open and steam cooking of pods brought the residue below detectable level.

Attri and Lal 1974b, observed a reduction of 47.15% of ethyl parathion due to washing and 65.8% due to cooking. They also reported that there was cent per cent reduction of malathion due to washing alone. Methyl parathion residue declined upto 42.7% due to washing and 69.2% due to cooking.

Beevi *et al.* (1997) studied the effect of washing and cooking on the removal of lindane residue in cowpea and found that washing alone could reduce 25.24 to 46.8% of the initial deposit whereas washing followed by cooking could reduce 20.90 to 59.38% of the initial residue.

2.3.4 **Cabbage**

Dewan *et al.* (1969) reported that malathion residue was reduced to a level below the tolerance limit by washing.

2.3.5 Cauliflower

In cauliflower water washing of leaves and curds reduced the residues by about 90 per cent of carbaryl (Dewan *et al.*, 1971) and Awasti *et al.* (1974) reported that there was a reduction of endosulfan residue upto 43.5 per cent due to dehydration.

Attri and Lal (1974a) reported 42 per cent reduction in the residue of ethyl parathion due to washing and upto 55 per cent due to cooking. Methylparathion residues declined upto 44.3% due to washing and 58.2% due to cooking. While Awasthi *et al.*, (1974) observed that washing of cauliflower leaves and curds reduced endosulfan residue to the extent of 29 to 100 percent whereas, cooking of curd for 15 to 20 minutes removed residues upto 50 to 100 per cent.

2.3.6 Tomato

Deshmukh *et al.* (1972) observed that washing of tomato removed about 97 per cent of carbaryl residue. Rajukannu *et al.*,(1976) reported that there was a reduction of carbaryl upto 50% due to washing and 64% due to cooking. They also found that there was a reduction of endrin upto 1 per cent due to cooking and parathion upto 11% due to washing and 37% due to cooking.

MATERIALS AND METHODS

3. MATERIALS AND METHODS

This chapter presents a brief description of the methods and procedures employed in conducting the study, the details of which are presented below.

Experiment 1

Monitoring of insecticide residues in vegetables viz., bittergourd, cowpea, cucumber and snakegourd collected from different sellers in major markets in Thiruvananthapuram district viz., Aralumoodu, Chalai, Nedumangdu and Powdikonam.

3.1 Selection of location and sample

Four major vegetable markets viz., Aralumoodu, Chalai, Powdikonam and Nedumangadu were selected in Thiruvananthapuram district as the locale of the study. Samples of four major vegetables viz., cow pea, bitter gourd, snake gourd and cucumber were collected periodically from these markets for analysis. The period of collection coincided with the major crop season viz., January-March 1995, April-May - 1995, and September-October - 1995.

3.2 Sampling

Six samples each of bittergourd, cowpea, cucumber and snakegourd were collected from six cultivator cum sellers from each of the locations. Samples were collected randomly from the lots brought for sale in the markets in such a way that they were representative samples. A quantity of 500 g each of cowpea, bittergourd, and one kg each of snakegourd and cucumber were collected from each cultivator after interviewing them on the spray history of samples. Along with these samples information regarding the insecticides sprayed/ applied, spray concentration, number of spray loads, area of cultivation, time gap between the last application and harvest etc. were also collected through a proforma (Appendix).

3.3 Sample preparation

As and when the samples were taken to the lab, they were prepared for analysis. In the case of bittergourd and snakegourd the seeds and fruit stalks were removed and discarded. For the preparation of cowpea and cucumber whole fruits were used as such.

3.4 Sample composition

3.4.1 Cowpea and Cucumber

Five hundred gram each of the market samples were chopped into two centimetre long pieces. They were mixed well, composited and quartered. The opposite quarters were mixed and the process was continued till 50 g of sample obtained. Two sets of 50 g samples were taken from each lot. One set was used for analysis and the other sample was kept as reserve.

3.4.2 Snakegourd and bittergourd

The fruits were cut lengthwise into four longitudinal slices. The alternate pieces discarded and seeds removed. The selected pieces were then cut into small pieces of two cm length. Two sets of 50 g samples were taken by following the quartering technique described as in 2.4.1. One set was used for analysis and the other set was kept as reserve.

3.5 Analytical procedure

3.5.1 Equipment

1. Beaker - 250 ml capacity
2. Conical flask - 250 ml capacity
3. Funnel - 11 cm diameter
4. Chromatographic column -plain 2.4 cm x 30 cm
5. Air condenser
6. Oil bath with thermometer
7. Ice bath
8. Graduated test tube 30 ml
9. Graduated micro pipette - 1 ml capacity
10. Hot air oven
11. Spectro photometer - Spectronic - 20

3.5.2 Reagents

1. Chloroform. AR
2. 4-4 para nitro benzyl pyridine
3. Cyclohexyl amine

4. Anhydrous sodium sulphate
5. Ethyl acetate
6. Propylene glycol

3.5.3 **Extraction**

The chopped sample (50 g) was taken in a 250 ml conical flask. To this 50 ml of chloroform was added and shaken vigorously for 15 minutes in a mechanical shaker. The extract was filtered through 30 g of anhydrous sodium sulphate packed in 11 cm diameter glass funnel. The extraction was repeated with two additions of 25 ml portions of chloroform. Then the extract was evaporated and reduced to 10 ml.

3.5.4 **Clean up**

Clean up was done using chromatographic column (2.4 x 30 cm). The column was plugged at the base with cotton and was packed up to 5 cm. length with anhydrous sodium sulphate. Above the sodium sulphate a packing mixture containing MgO, celite and activated charcoal in the ratio of 1: 1: 0.25 was loaded.

The packed column was eluted with 25 ml. of chloroform as pre-wash. When the last of the pre-wash chloroform reached the top of packing mixture, the sample extract was transferred carefully through the sides of the column. The column was eluted with 40 ml of chloroform in 2 x 20 ml portions which was collected in glass container. The elutent was concentrated to 10 ml and transferred carefully to a 30 ml graduated test tube; then two drops of propylene glycol was added. The test tubes were then kept for evaporation of the sample extract to near dryness.

3.6 Quantitative assessment of residues by colorimeteric estimation

The graduated tubes containing concentrated thin film of the sample were taken and 0.4 ml. each of 4-4 paranitrobenzyl pyridene and cyclohexyl amine were added. The air condensers were then fitted to the tubes and immersed into oil bath which was maintained at 175-180^{0} C for 3 minutes. After a period of 3 minutes, the tubes were taken out of the oil bath and suddenly placed in ice bath for 30 seconds. The condensers were removed from the tubes and 3 ml of ethyl acetate was added to the tubes. The colour intensity of the resulting complex was measured with the help of a spectrophotometer (Spectronic 20) at 540 nm.

3.7 Preparation of standard curve

Standard curves were prepared for methyl parathion, quinalphos, monocrotophos, phosphamidon and phorate.

Five graded concentration viz., 5, 10, 15, 20 and 25 ppm. each of these insecticides were taken in graduated test tubes. A tube with 3 ml. of chloroform alone was used as blank. Two drops of propylene glycol were added to each of the tubes. The solutions were then evaporated to dryness. On complete evaporation, 0.4 ml. of 2 per cent 4 - 4 paranitro benzyl pyridene and 0.4 ml. of Cyclohexyl amine (2%) were added to the test tube. The tubes with air condensors were placed in oil bath maintained at 180 - 185^{0}C for three minutes. At the expiry of 3 minutes the tubes were taken out and placed in ice bath for 30 seconds and 3 ml of ethyl acetate were added to the tubes. The colour intensity was recorded in a Spectrophotometer (Spectronic- 20) in terms of transmittance. The transmittance was converted to absorbance with an equation :

$$A = 2 - \log T.$$

The values of absorbance were plotted against the different concentrations of insecticide to obtain the standard curve, for estimating the concentration of insecticides in the samples.

Experiment 2

3.6 Effect of different decontamination techniques on the removal of monocrotophos and phosphamidon residues from cowpea pods and bittergourd fruits

From the result of experiment 1, two vegetable crops (cowpea and bittergourd) and two insecticides (monocrotophos and phosphamidon) were selected for studying the decontamination.

Cowpea and bittergourd crops were raised under controlled conditions for this purpose. Mechanical methods of control, trapping and bagging were followed to protect the fruit from pest attack and untreated pods / fruits were brought to laborotary for studies on decontamination.

Since application of precise quantity of insecticide directly on pods / fruits was not possible under field condition, spray application was done in the laboratory. Commercial insecticide formulation of monocrotophos (Nuvacron 36 SL) and phosphamidon (Dimecron 86 SL) were serially diluted to make 50 ppm solutions of the insecticide. Identical pods / fruits were selected for the experiment and their weights were recorded individually. Precise quantities of dilutions were prepared and directly applied on the pods / fruits with the help of a micro pipette so as to get samples carrying a uniform deposit of 50 ppm in each fruit. The treated fruits were then allowed to dry overnight. The treated samples were subjected to different decontamination techniques as detailed below and the residues were estimated as detailed under item 2.5 of experiment 1. The percentage removal of residues in each treatment was worked out.

T0 Control

T1 Dipping in tamarind water (2%) for one hour (*20 g of preserved tamarind fruit pulp extracted in one litre water*).

T2 Dipping in 2 per cent lime water for one hour (*20 g of hydrated lime in one litre water*)

T3 Dipping in 2 per cent salt water for one hour (*20 g of common salt dissolved in one litre water*)

T4 Dipping in vinegar (2%) for one hour (*20 ml vinegar made up to one litre with water*)

T5 Tap water washing coupled with gentle rubbing

T6 Open cooking for 25 minutes

T7 Closed cooking for 25 minutes

T8 Storage for three days in a refregarator

T9 Sun drying for two days (for bittergourd fruits)

RESULTS

4. RESULTS

4.1 Experiment I

Monitoring of Insecticide residues in four vegetables viz., bittergourd, cowpea, cucumber and snakegourd collected from different sellers in four major markets in Thiruvananthapuram district viz., Aralumoodu, Chalai, Nedumangadu, and Powdikonam.

The consolidated data relating to the experiment I are presented in the Tables 1 to 3. Mean residues observed in four vegetables samples collected from six sellers each from four markets during the season I (January - March, 1995) are presented in Table 1, season II (April - May, 1995) in Table 2 and season III (September - October, 1995) in Table 3 respectively.

4.1.1 Season I (January - March, 1995)

In Aralumoodu market during season I (vide Table 1), the mean OP residues found in different vegetables differed significantly and the highest residue level was in cowpea (0.32 ppm.) which was followed by cucumber (0.20 ppm.). The mean organophosphate residue in snakegourd and bittergourd samples were on par and it ranged from 0.15 to 0.16 ppm.

Table 1 **Insecticide residues in samples of four vegetables collected from different sellers in four major markets in Thiruvananthapuram district. Season I : January- March, 1995**

Market	Vegetable	Mean OP residues (ppm) in samples collected from six sellers						
		1	2	3	4	5	6	Mean
Aralumoodu	Bittergourd	MP 0.12	MP 0.14	QP 0.28	QP 0.14	QP 0.10	QP 0.20	0.16
	Cow pea	QP 0.81	QP 0.68	QP 0.21	QP 0.14	MP 0.04	MP 0.02	0.32
	Cucumber	PHOR 0.24	PHOR 0.20	PHOR 0.25	PHOR 0.20	PHOR 0.16	PHOR 0.14	0.20
	Snakegourd	MCP 0.08	MCP 0.12	MCP 0.32	MCP 0.11	MCP 0.15	MCP 0.09	0.15
	Mean							**0.21**
Chalai	Bittergourd	MCP 0.46	MCP 0.30	MCP 0.05	MP 0.30	MP 0.13	MP 0.01	0.21
	Cow pea	MP 0.14	MP 0.10	MP 0.09	MP 0.05	MP 0.05	MP 0.16	0.09
	Cucumber	PHOR 0.24	PHOR 0.31	PHOR 0.15	PHOR 0.02	PHOR 0.03	PHOR 0.02	0.13
	Snakegourd	MCP 0.19	MCP 0.08	MCP 0.08	MP 0.13	MP 0.04	MP 0.13	0.11
	Mean							**0.14**
Nedumangadu	Bittergourd	MP 0.18	MP 0.04	MP 0.22	MP 0.04	MP 0.03	MP 0.04	0.09
	Cow pea	MP 0.06	MP 0.56	MP 0.09	MP 0.18	MP 0.21	QP 0.17	0.21
	Cucumber	MCP 0.16	PHOR 0.17	PHOR 0.14	PHOR 0.01	PHOR 0.13	MP 0.13	0.13
	Snakegourd	MP 0.05	MP 0.10	MP 0.20	MP 0.20	MP 0.04	MP 0.04	0.10
	Mean							**0.14**
Powdikonam	Bittergourd	MCP 0.11	MCP 0.13	MCP 0.08	MCP 0.07	MCP 0.10	MCP 0.07	0.09
	Cow pea	MCP 0.32	MCP 0.12	MCP 0.33	MCP 0.32	MCP 0.22	MCP 0.21	0.26
	Cucumber	MP 0.21	MP 0.19	MP 0.22	PHOR 0.12	PHOR 0.12	PHOR 0.12	0.16
	Snakegourd	QP 0.29	QP 0.05	MP 0.05	MP 0.09	MP 0.05	MP 0.04	0.10
	Mean							**0.15**
CD (0.05) for comparison of vegetables								**0.04**
CD (0.05) for comparison of markets								**0.04**

MP : Methyl parathion
MCP : Monocrotophos
PHOR: Phorate
QP : Quinalphos
PHOS : Phosphamidon

In Chalai market during season I the mean organophosphate residue in cowpea (0.09 ppm.), cucumber (0.13 ppm.) and snakegourd (0.11 ppm.) did not significantly vary much among themselves. Whereas the organophosphorous insecticide residue (0.21 ppm.) observed in bittergourd was the highest.

In Nedumangadu market highest level of OP residue was found in cowpea (0.21 ppm.) and the residue levels in other three vegetables viz., bittergourd, snakegourd and cucumber was significantly lower than that in cowpea which ranged from 0.09 to 0.13 ppm.

In the case of Powdikonam market the mean organophosphate residue found in various vegetables showed statistically significant differences among themselves. The highest level of organophosphorous residues was observed in cowpea (0.26 ppm.) which was followed by that in cucumber (0.16 ppm.). The mean OP residue in snakegourd and bittergourd were on par (0.09 to 0.10 ppm.).

When the pooled means of insecticide residue observed in samples of all the four vegetables collected from each markets during the season I was examined, the highest organophosphate residue was observed in Aralumoodu market (0.21 ppm.). The relative level of OP insecticide residue in vegetable samples collected from the other three markets viz., Chalai, Nedumangadu and Powdikonam were statistically on par and the total organophosphate residue level in the three markets ranged from 0.14 to 0.15 ppm.

4.1.2 **Season II (April - May, 1995)**

The data relating to the monitoring carried out during the second season (April - May 1995) of the experiment are presented in Table 2.

In Aralumoodu market, the mean organophosphate residue found in bittergourd (0.11 ppm), cucumber (0.12 ppm.) and snakegourd (0.13 ppm.) did not vary much among themselves whereas the OP residue in cowpea varied significantly and it was the highest (0.18 ppm.).

In Chalai market, mean organophosphorous insecticide residues found in different vegetables varied significantly. The highest level of OP residue was observed in cowpea samples (0.51 ppm.) followed by snakegourd (0.38 ppm.). The mean organophosphate residue in cucumber and bittergourd were statistically on par (0.12 to 0.14 ppm.).

Table 2 **Insecticide residues in samples of four vegetables collected from different sellers in four major markets in Thiruvananthapuram district.**
Season II : April-May, 1995

Market	Vegetable	Mean OP residues (ppm) in samples collected from six sellers						
		1	2	3	4	5	6	Mean
Aralumoodu	Bittergourd	MP 0.11	QP 0.12	MP 0.12	MP 0.10	MP 0.08	QP 0.14	0.11
	Cow pea	MP 0.15	QP 0.25	MP 0.18	MP 0.19	MP 0.10	MCP 0.22	0.18
	Cucumber	PHOS 0.17	PHOR 0.11	PHOR 0.11	PHOR 0.16	PHOR 0.10	PHOR 0.07	0.12
	Snakegourd	MP 0.14	QP 0.12	MCP 0.21	QP 0.11	MP 0.10	QP 0.11	0.13
	Mean							**0.14**
Chalai	Bittergourd	PHOS 0.18	MP 0.12	MP 0.05	MP 0.29	MP 0.16	MP 0.05	0.14
	Cow pea	MP 0.65	QP 0.77	MP 0.35	MP 0.35	PHOS 0.44	MP 0.55	0.51
	Cucumber	PHOR 0.11	PHOS 0.23	PHOR 0.11	PHOR 0.18	PHOR 0.04	PHOS 0.15	0.12
	Snakegourd	MP 0.52	MCP 0.25	MP 0.45	MP 0.39	MCP 0.22	MP 0.46	0.38
	Mean							**0.29**
Nedumangadu	Bittergourd	MP 0.20	MP 0.14	MP 0.10	PHOS 0.18	PHOS 0.13	PHOS 0.13	0.15
	Cow pea	MP 0.13	MP 0.36	MP 0.16	MP 0.18	MP 0.10	MP 0.23	0.19
	Cucumber	MP 0.03	PHOR 0.14	PHOR 0.26	PHOR 0.03	MP 0.07	MP 0.09	0.10
	Snakegourd	MP 0.07	MP 0.07	PHOS 0.11	QP 0.16	MP 0.05	MP 0.10	0.09
	Mean							**0.13**
Powdikonam	Bittergourd	MP 0.17	MP 0.25	MP 0.21	MP 0.05	PHOS 0.10	MP 0.04	0.14
	Cow pea	MP 0.15	QP 0.26	QP 0.35	MP 0.09	PHOS 0.22	MP 0.05	0.19
	Cucumber	PHOR 0.15	PHOR 0.11	PHOR 0.07	PHOR 0.17	PHOR 0.23	PHOR 0.12	0.14
	Snakegourd	MP 0.10	MP 0.05	QP 0.31	MP 0.10	QP 0.04	MP 0.08	0.11
	Mean							**0.15**
CD (0.05) for comparison of vegetables								**0.03**
CD (0.05) for comparison of markets								**0.03**

MP : Methyl parathion
QP : Quinalphos
MCP : Monocrotophos
PHOS : Phosphamidon
PHOR: Phorate

In Nedumangadu market, the mean OP residue found in four vegetables collected showed statistically significant differences. The highest residue of organophosphates was observed in cowpea (0.19 ppm.) which was followed by bittergourd (0.15 ppm.). The mean organophosphate residue in other two vegetables viz., cucumber and snakegourd were statistically lower than that in bittergourd which ranged from 0.09 to 0.10 ppm.

In Powdikonam market, the average organophosphate residue in bittergourd (0.14 ppm.), cucumber (0.14 ppm.) and snakegourd (0.11 ppm.) showed no significant differences among themselves. Whereas the OP residue in cowpea was significantly different from the rest and it was the highest (0.19 ppm.).

Similarly when the pooled means of insecticide residue observed in samples of all the four vegetables collected from each market during the second season were compared, the highest level of organophosphorous insecticide residue was observed in Chalai market (0.29 ppm.). The relative level of OP residue in vegetable samples collected from other markets viz., Aralumoodu, Nedumangadu and Powdikonam were statistically on par and the total organophosphorus insecticide residue level ranged from 0.13 ppm. (Nedumangadu) to 0.15 ppm. (Powdikonam).

4.1.3 **Season III (September - October, 1995)**

The data relating to the third season (Sept. - Oct., 1995) of the experiment are presented in Table 3.

In Aralumoodu, the mean organophosphate residue found in different vegetables differed significantly and the highest OP residue was found in snakegourd (0.20 ppm.) and the lowest residue was observed in bittergourd (0.08 ppm.). The mean OP residue in cowpea and cucumber samples showed the same value (0.14 ppm. for both) which was significantly higher than the level observed in bittergourd.

In Chalai, the mean organophosphate residue in bittergourd (0.10 ppm.), cucumber (0.13 ppm.) and snakegourd (0.10 ppm.) did not vary much among themselves. Whereas the organophosphate residue in cowpea was oberved as the highest (0.23 ppm.).

In Nedumangadu market, the mean organophosphorous insecticide residue found in different vegetables showed statistically different values. The highest residue of 0.15 ppm was recorded from cowpea samples which was statistically different from other vegetables collected viz., bittergourd (0.11 ppm.), cucumber (0.09

Table 3 **Insecticide residues in samples of four vegetables collected from different sellers in four major markets in Thiruvananthapuram district.**
Season III : September- October, 1995

Market	Vegetable	Mean OP residues (ppm) in samples collected from six sellers						
		1	2	3	4	5	6	Mean
Aralumoodu	Bittergourd	MP 0.09	MP 0.07	MP 0.09	MP 0.05	MP 0.10	MP 0.11	0.08
	Cow pea	MP 0.15	MP 0.12	QP 0.35	MP 0.05	QP 0.19	MP 0.09	0.14
	Cucumber	MP 0.07	MP 0.03	PHOR 0.20	PHOR 0.25	PHOR 0.20	PHOR 0.08	0.14
	Snakegourd	PHOS 0.32	PHOS 0.15	PHOS 0.14	PHOS 0.06	PHOS 0.32	PHOS 0.24	0.20
	Mean							**0.14**
Chalai	Bittergourd	MP 0.05	MP 0.11	QP 0.07	MP 0.02	QP 0.20	QP 0.13	0.10
	Cow pea	MP 0.41	MP 0.22	QP 0.21	MP 0.28	QP 0.17	MP 0.16	0.23
	Cucumber	PHOS 0.10	PHOR 0.25	PHOS 0.02	PHOS 0.08	PHOR 0.12	PHOR 0.20	0.13
	Snakegourd	MP 0.07	MP 0.06	QP 0.07	MP 0.14	QP 0.21	MP 0.07	0.10
	Mean							**0.14**
Nedumangadu	Bittergourd	MP 0.11	QP 0.12	MP 0.16	MP 0.11	MP 0.10	QP 0.08	0.11
	Cow pea	MP 0.23	MP 0.13	MP 0.16	MP 0.14	MP 0.14	QP 0.10	0.15
	Cucumber	PHOR 0.06	PHOR 0.07	PHOR 0.10	PHOR 0.03	PHOR 0.17	PHOR 0.08	0.09
	Snakegourd	MCP 0.13	MCP 0.14	MCP 0.12	MCP 0.17	MP 0.07	MP 0.11	0.13
	Mean							**0.12**
Powdikonam	Bittergourd	MP 0.16	QP 0.15	MP 0.11	MP 0.10	MP 0.05	QP 0.20	0.13
	Cow pea	MP 0.13	MP 0.14	MP 0.11	QP 0.35	MP 0.34	QP 0.12	0.20
	Cucumber	MCP 0.08	MCP 0.12	MCP 0.20	PHOR 0.03	PHOR 0.14	PHOR 0.20	0.13
	Snakegourd	MP 0.04	MP 0.13	MP 0.05	MP 0.12	QP 0.18	MP 0.05	0.08
	Mean							**0.13**
CD (0.05) for comparison of vegetables								**0.03**
CD (0.05) for comparison of markets								**0.03**

MP : Methyl parathion
QP : Quinalphos
MCP : Monocrotophos
PHOS : Phosphamidon
PHOR: Phorate

ppm.) and snakegourd (0.13 ppm.). The relative residues of these vegetables were statistically on par.

In Powdikonam, the average residue of organophosphate insecticide in different vegetables collected differed significantly. The highest residue was observed in cowpea (0.20 ppm.) which was followed by that in bittergourd and cucumber (0.13 ppm. each). Lowest residue was observed in snakegourd (0.08 ppm.). The residue in bittergourd, cucumber and snakegourd were statistically on par.

When the pooled means of organophosphate residues observed in samples of all the four vegetables collected from Aralumoodu, Chalai, Nedumangadu and Powdikonam markets during the third season showed no significant differences among themselves.The total OP residue ranged from 0.12 (Nedumangadu) to 0.14 ppm. (Aralumoodu and Chalai).

4.1.4 Extent of insecticide contamination of different vegetables with reference to Maximum Residue Level (MRL) fixed by FAO/WHO

The data obtained in the above experiment (Table 1 to 3) was reclassified based on the type of insecticide detected in each sample.

The sample collected from four market during three season for each crop were taken as one unit for this purpose. The number and percentage of samples below or above the MRL fixed for each insecticide was worked out and the extent of contamination arrived are presented in Table 4.

In bittergourd, all the 72 samples collected from different markets during different season were contaminated with any one organophosphate insecticide viz., methyl parathion, quinalphos or monocrotophos. Of the 72 samples collected, quinalphos was the insecticide which showed highest percentage of contamination above MRL (30.7 %) which was followed by monocrotophos (22.3 %) and methyl parathion (13.4%).

With reference to magnitude of residues above MRL, monocrotophos stood highest which showed a mean level of 0.30 to 0.46 ppm. in bittergourd. The mean level of methyl parathion residue ranged from 0.20 to 0.30 ppm. which was followed by quinalphos (0.20 to 0.28 ppm.). With reference to the total number of bittergourd samples with OP residues above MRL, the contamination was found to the extent of 16.7 per cent.

Table 4 **Extent of cantamination of different vegetables with reference to Maximum Residue Limit (MRL) fixed by FAO / WHO.**

Crop	Insecticide	Samples analysed	Below MRL		Above MRL		Range of residue above MRL (ppm.)
			No.	%	No.	%	
bittergourd	Methyl parathion	45	39	86.7	6	13.4	0.20-0.30
	Quinalphos	13	9	69.2	4	30.7	0.20-0.28
	Monocrotophos	9	7	77.8	2	22.3	0.30-0.46
	Phosphamidon	5	5	100	0	0.0	0
	Phorate	-	-	-	-	-	-
	Total (O.P)	72	60	83.4	12	16.7	0.2-0.46
cowpea	Methyl parathion	47	34	72.3	13	27.6	0.22-0.65
	Quinalphos	16	6	37.5	10	62.3	0.21-0.81
	Monocrotophos	7	1	14.2	6	85.7	0.21-0.33
	Phosphamidon	2	0	0	2	100	0.22-0.44
	Phorate	-	-	-	-	-	-
	Total (O.P)	72	41	56.9	31	43.0	0.21-0.81
cucumber	Methyl parathion	9	7	77.8	2	22.3	0.21-0.22
	Quinalphos	-	-	-	-	-	-
	Monocrotophos	4	3	75.0	1	25.0	0.20
	Phosphamidon	6	5	83.4	1	16.7	0.23
	Phorate	53	39	73.5	14	26.4	0.20-0.26
	Total (O.P)	72	54	75.0	18	25.0	0.2-0.26
snakegourd	Methyl parathion	38	32	84.2	6	15.7	0.2-0.52
	Quinalphos	11	8	72.7	3	27.2	0.21-0.32
	Monocrotophos	16	12	75.0	4	25.0	0.21-0.32
	Phosphamidon	7	4	57.0	3	42.8	0.24-0.32
	Phorate	-	-	-	-	-	-
	Total (O.P)	72	56	77.8	16	22.3	0.2-0.52

In cowpea samples collected during the three seasons from four different vegetable markets, all the 72 samples were contaminated with one or other OP insecticide viz methyl parathion, quinalphos, phosphamidon or monocrotophos. Among the 72 samples, phosphamidon was the insecticide which showed the highest percentage of contamination above MRL (100%), which was followed by monocrotophos (85.7%), quinalphos (62.3%) and methyl parathion (27.6%). The mean level of phosphamidon residue above MRL detected in cowpea ranged from 0.22 to 0.44 ppm. The residue level of monocrotophos, quinalphos and methyl parathion in cowpea pods ranged from 0.21 to 0.33, 0.21 to 0.81 and 0.22 to 0.65 ppm respectively. The percentage of cowpea samples contaminated with total OP insecticide residue above MRL was 43 percent.

In cucumber samples (72) collected, methyl parathion, monocrotophos, phosphamidon and phorate are the insecticides detected. Out of 72 samples examined, the highest percentage of contamination above MRL was that of phorate (26.4 %) which was followed by monocrotophos (25 %), methyl parathion (22.3%) and phosphamidon (16.7 %). The mean level of phorate residue observed in cucumber samples contaminated above MRL ranged from 0.20 to 0.26 ppm. The residue level of monocrotophos and phosphamidon (one sample each) was 0.20 and 0.23 ppm respectively and the residue level of methyl parathion ranged from 0.21 to 0.22 ppm. The total percentage of cucumber samples contaminated with total organophosphate residues above MRL was found to the extent of 25%.

In snakegourd, all samples collected was contaminated with any one insecticide viz., methyl parathion, quinalphos, monocrotophos or phosphamidon. Among the 72 samples, the insecticide which showed the highest percentage of contamination above MRL was that of phosphamidon (42.8 %) which was followed by quinalphos (27.2 %), monocrotophos (25 %) and methyl parathion (15.7 %). The mean level of phosphamidon residue detected in snakegourd above MRL ranged from 0.24 to 0.32 ppm. The residue levels of quinalphos, monocrotophos and methyl parathion in snakegourd fruits contaminated above MRL ranged from 0.21 to 0.32, 0.21 to 0.32 and 0.20 to 0.52 ppm respectively. The total OP insecticide contamination above MRL in 72 snakegourd samples was observed to the extent of 22.3%.

The mean residue level for each insecticide in the contaminated crop samples was calculated separately and the data are presented in Fig 1. It clearly shows relatively higher values for all insecticides

Fig : 1

Mean level of insecticide residues in different vegetables collected from Trivandrum

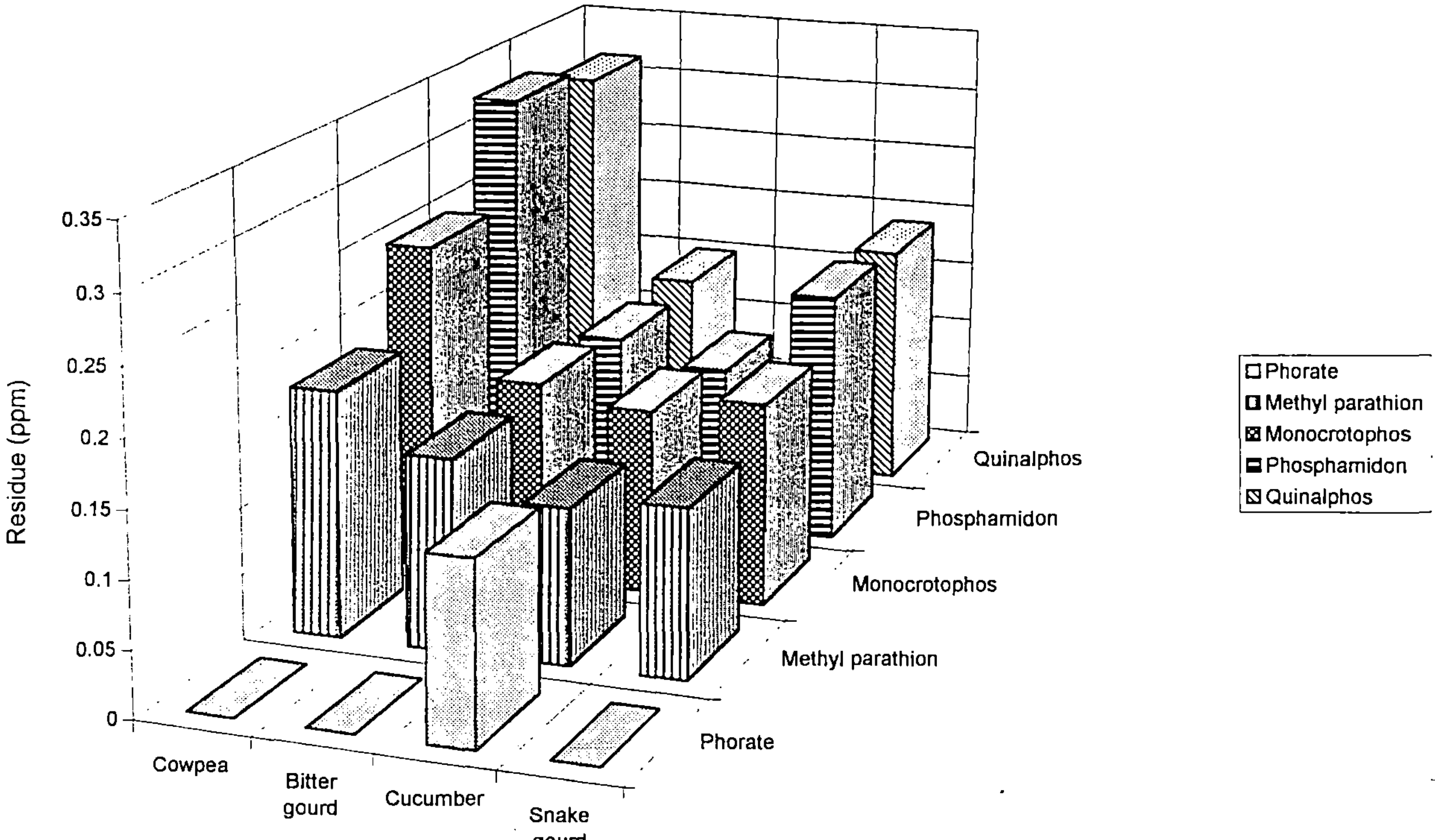


Fig: 2
Extent of insecticide contamination in market samples of different vegetables collected from Thiruvananthapuram

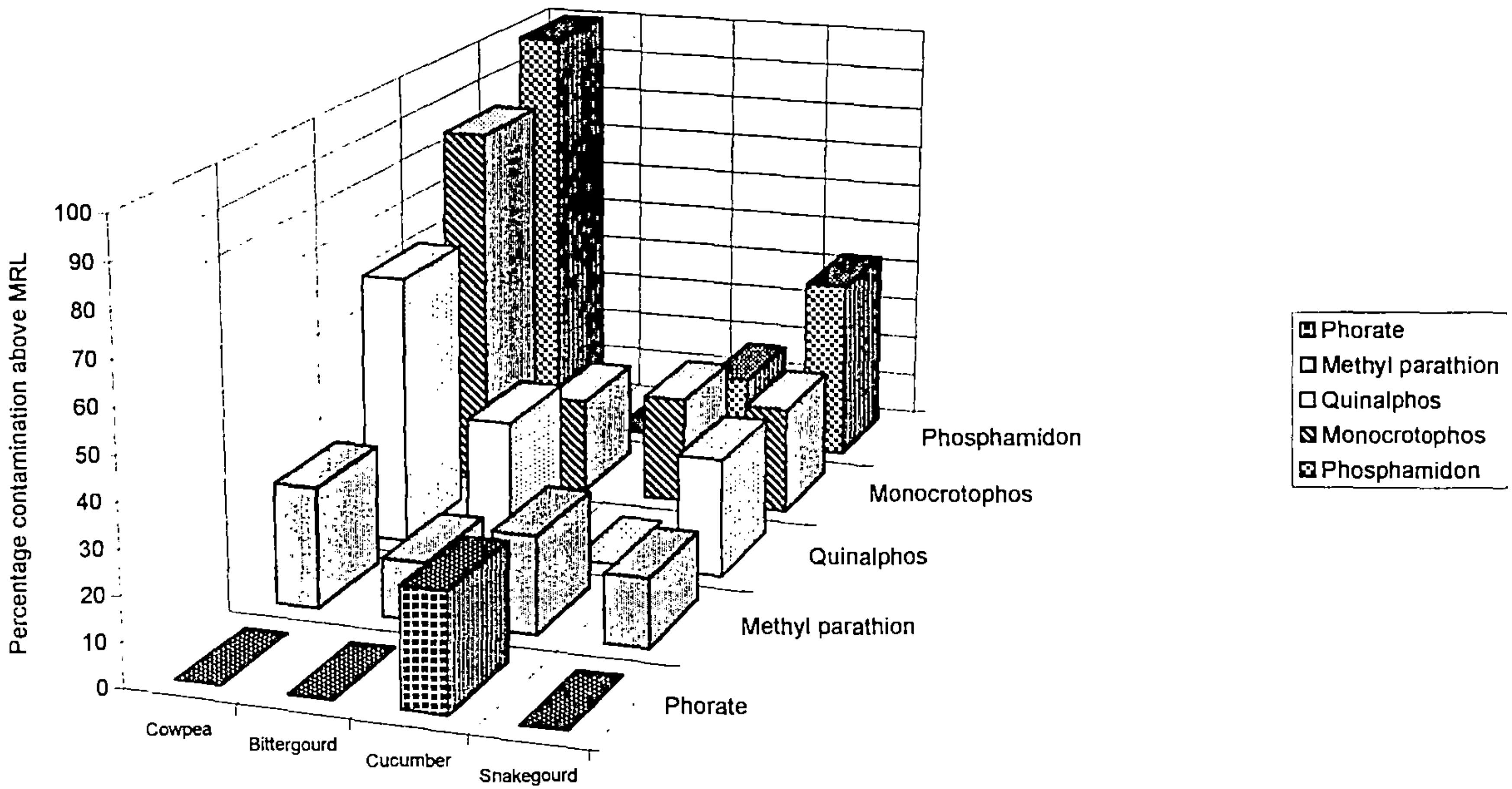
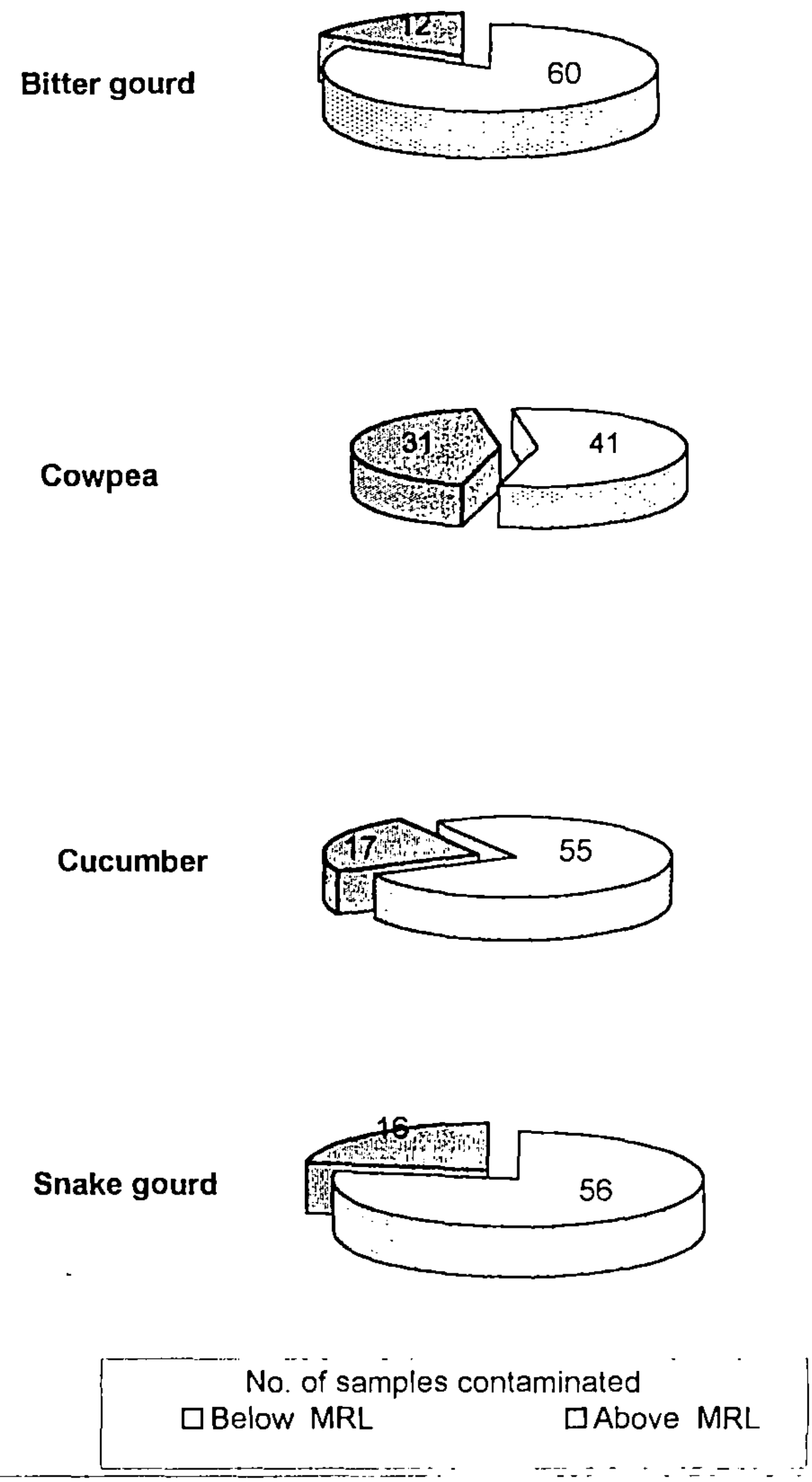


Fig: 3

Proportion of total number of vegetables contaminated with organophosphate residues



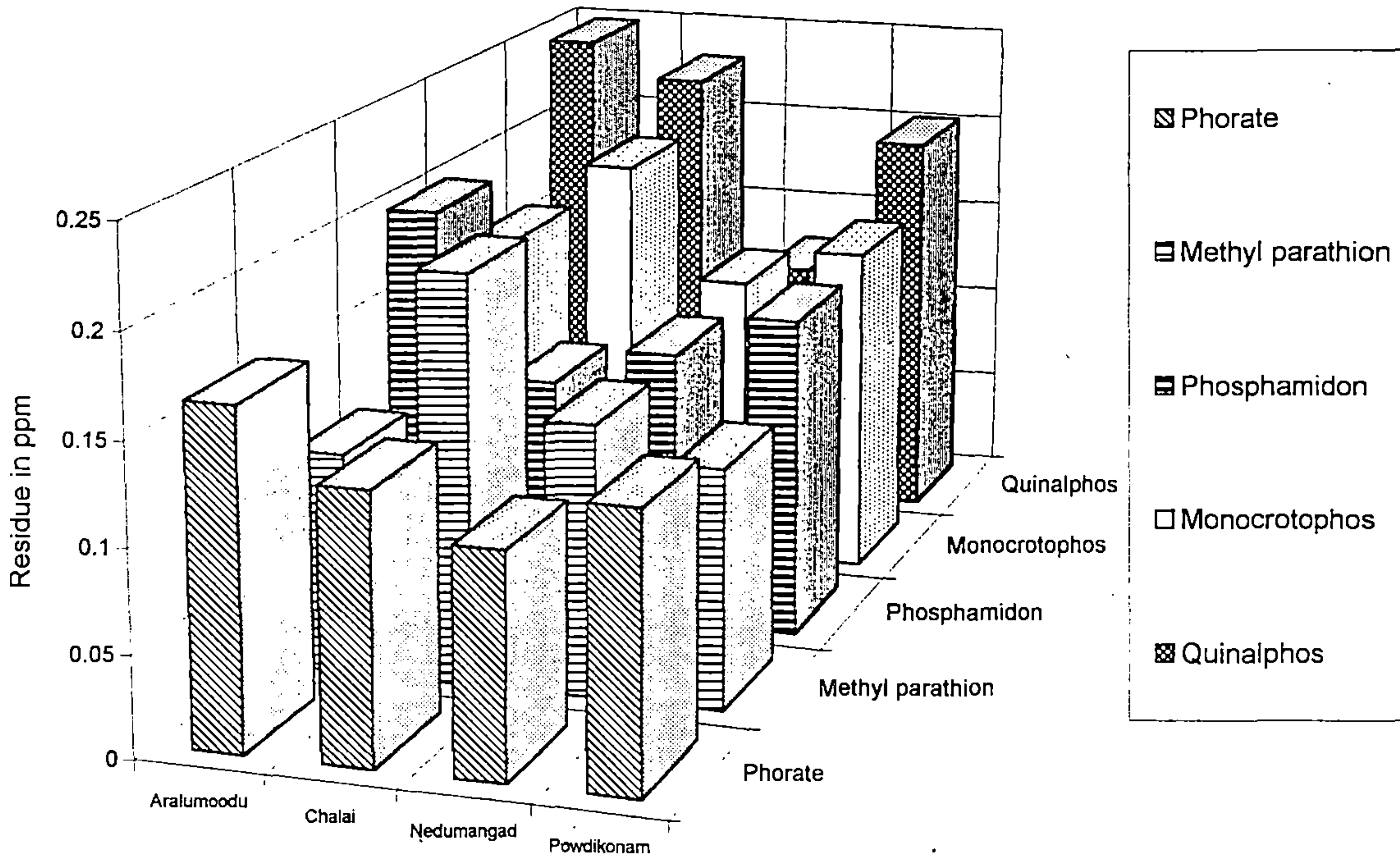
detected in cowpea except for phorate and the mean values for quinalphos, phosphamidon, monocrotophos and methyl parathion were 0.32, 0.33, 0.25 and 0.18 ppm respectively. Whereas in the case of other three crops, the mean residues observed were in a lower level.

Data on the extent of contamination above MRL for different insecticides in different vegetables collected during the survey are presented in Fig 2 and 3. As clearly shown in the histogram (Fig 2) the contamination with reference to the percentage above MRL was also higher in cowpea when compared with those in other crops. The total number of samples contaminated for each vegetable above or below MRL (data presented in Table 4) is represented as a pie chart in Fig 3 which also demonstrate higher proportion of contaminated samples in cowpea.

4.1.5 **Effect of markets and crop seasons on the mean insecticide residue in vegetable**

A marketwise and seasonwise comparison of the mean values of insecticide residue in vegetables are made and represented in Fig 4 and 5 respectively. With reference to the mean level of residue,

Fig. 4 Marketwise comparison of mean insecticide residue in vegetables



relatively higher values were recorded in samples collected from Chalai (0.11 to 0.23 ppm) and Aralumoodu (0.10 to 0.24 ppm). Whereas in samples collected from Nedumangadu and Powdikonam the corresponding values were 0.10 to 0.14 ppm and 0.11 to 0.20 ppm respectively.

When seasonwise comparison of the data was made with reference to the mean level of residue, relatively higher values were observed in crops raised during January-March 1995 (0.12 to 0.28 ppm). Whereas in the samples collected during second (April-May 1995) and third (September-October 1995) seasons, the corresponding values were 0.12 to 0.22 ppm and 0.12 to 0.16 ppm respectively.

4.2 **Insecticide preference by vegetable growers in Thiruvananthapuram district.**

The consolidated data on insecticide preference by vegetable growers in Thiruvananthapuram district are presented in Table5 and Fig. 6.

As clearly shown in Table 5 and Fig 6, maximum preference of O.P insecticide observed in bittergourd was for methyl parathion.

Fig. 5 Seasonwise comparison of mean insecticide residues observed in vegetables

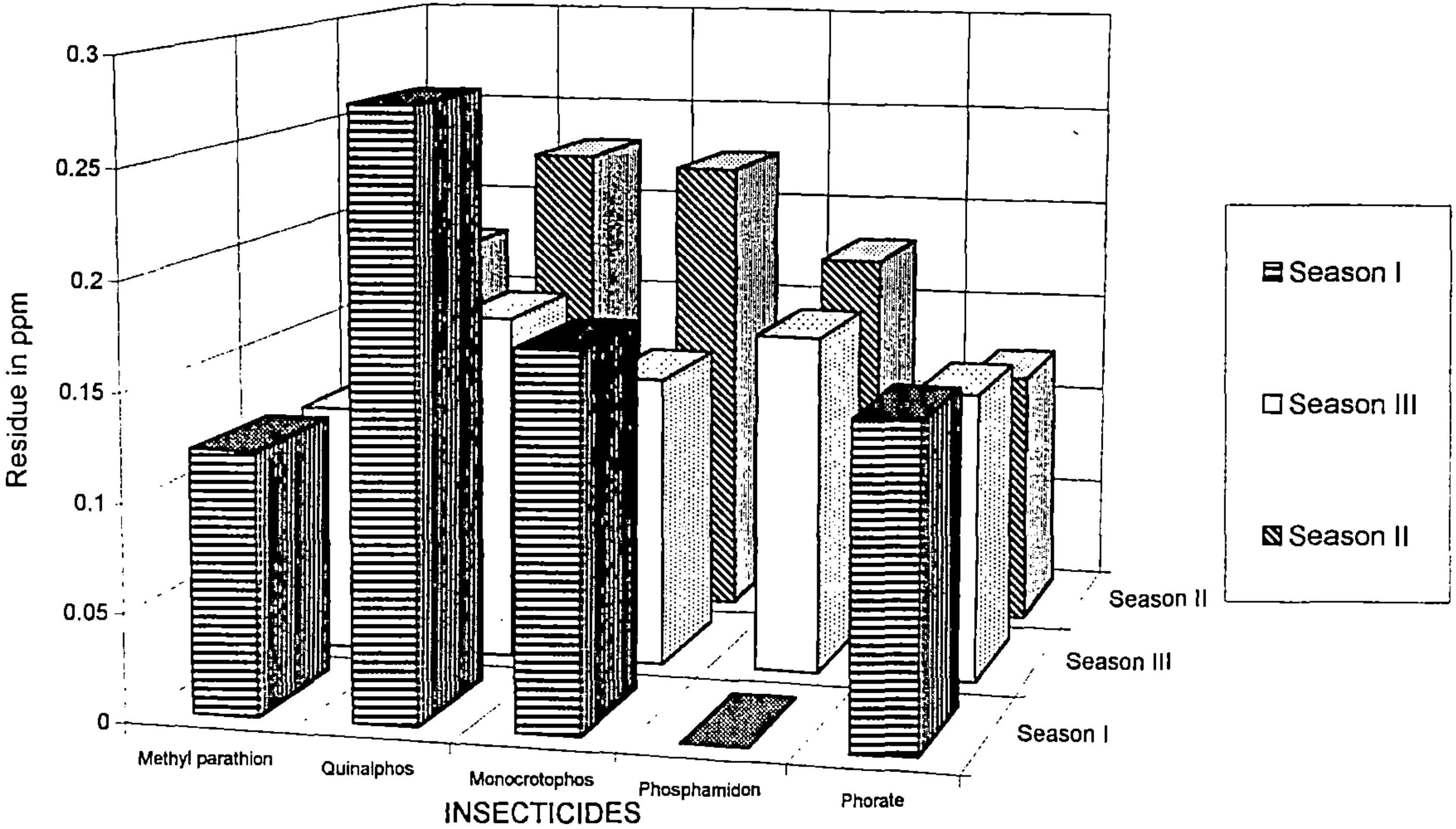
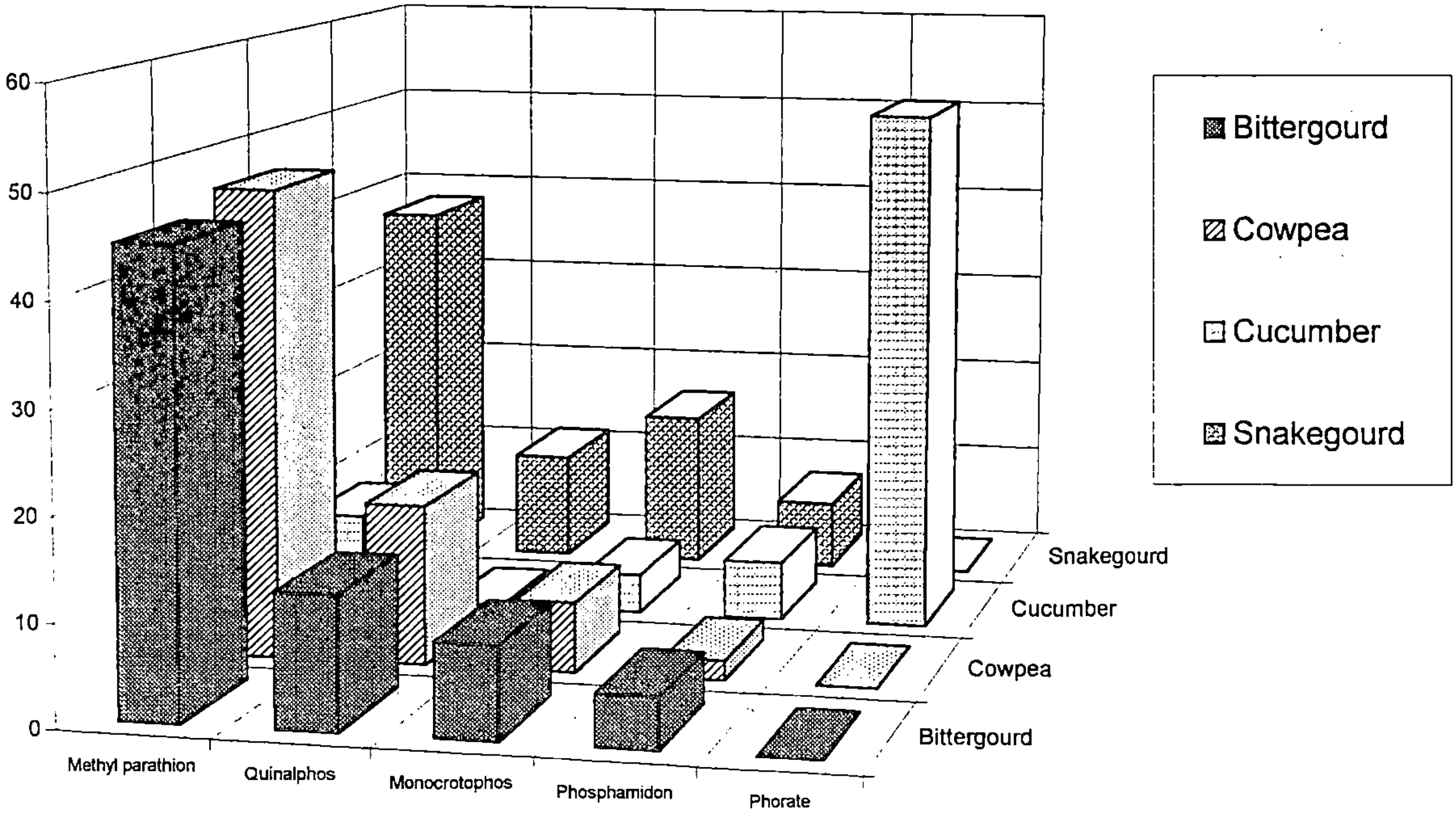


Table. 5 **Preference of vegetable growers in Thiruvananthapuram to different OP insecticides for pest control.**

Insecticide	Bittergourd		Cowpea		Cucumber		Snakegourd		Total out of 288 samples	
	Number	Percentage	Number	Percentage	Number	Percentage	Number	Percentage	Number	Percentage
Methyl parathion	45	62.25	47	65.20	9	12.50	38	52.70	139	48.20
Quinalphos	13	18.00	16	22.30	0	0.00	11	15.20	40	13.80
Monocrotophos	9	12.50	7	9.70	4	5.50	16	22.30	36	12.50
Phosphamidon	5	6.90	2	2.70	6	8.30	7	9.70	20	6.90
Phorate	0	0.00	0	0.00	53	73.60	0	0.00	53	18.40

Fig. 6 Relative preference of vegetable growers in Thiruvananthapuram to different organophoshate insecticides [72 respondents (6 sellers x 4 markets x 3 seasons) for each vegetable]



Out of 72 bittergourd growers 45 growers used methyl parathion (62.5 %), 13 farmers used quinalphos (18%), 9 used monocrotophos (12.5 %) and 5 growers (6.9 %) used phosphamidon.

In the case of cowpea samples, out of 72 growers, 47 used methyl parathion (65.2 %), 16 used quinalphos (22.3 %), 7 growers used monocrotophos (9.7 %) and two (2.7 %) used phosphamidon.

The data observed from cucumber farmers showed that 73.6 % of the 72 growers used phorate and only 12.5 % used methyl parathion. Monocrotophos was used by 4 growers and phosphamidon used by 6 farmers.

In snakegourd it was observed that 38 growers (52.8%) preferred methyl parathion which was followed by monocrotophos (22.3 %). Quinalphos and phosphamidon were preferred by 15.2 and 9.7 per cent growers respectively.

When the pooled data shown in Table 5 was examined, it was observed that out of 288 vegetable growers surveyed, 139 growers preferred methyl parathion (48.20 %) for pest control in vegetables. Phorate was the next insecticide in preference used by 53 growers (18.4 %). It was also observed that phorate was extensively used only by cucumber growers and it was not used by any other vegetable growers viz., bittergourd, cowpea or snakegourd. Quinalphos was used by 40 farmers (13.8 %) out of the total 288 growers and monocrotophos was used by 36 growers (12.5 %). The lowest preference was recorded for phosphamidon. A total of only 20 growers (6.9) used this insecticide out of the 288 growers surveyed in Thiruvananthapuram district.

4.3 The pattern of insecticide usage with reference to the spray concentration / dose (ai / ha) among vegetable growers in Thiruvananthapuram.

The pooled data on pattern of insecticide usage with respect to spray concentration / dose (ai / ha) obtained from 288 respondents surveyed during the experiment are presented in Table 6. The number and percentage of farmers who used the insecticide at a spray concentration below or above the recommended rate are calculated and presented in the table. The data showed that in bittergourd, 90.3 per cent of farmers used insecticides at concentrations higher than the recommended. Whereas 5.6 per cent of the farmers used the insecticides at concentration which are lower than the normally recommended. Only 4.2 per cent of farmers were found to use the insecticides at their recommended concentration.

In the case of cowpea, when 72 farmers were surveyed, only one farmer used the insecticide at recommended concentration with a

Table. 6 **Pattern of insecticide usage with reference to spray concentration / dose (ai / ha) among vegetable growers in Thiruvananthapuram**

Category of farmer w.r.t. insecticide usage	Respondents in each category of vegetable									
	Bittergourd		Cowpea		Cucumber		Snakegourd		Total	
	Number	Percentage	Number	Percentage	Number	Percentage	Number	Percentage	Number	Percentage
Spray concentration										
1. Recommended	3/72	4.16	1/72	1.30	2/72	2.70	0/72	0	6/288	2.00
2. Below recommended	4/72	5.60	0/72	0	0/72	0	4/72	5.60	8/288	2.70
3. Above recommended	65/72	90.30	71/72	98.60	70/72	97.20	68/72	94.40	274/288	95.13
Volume of spray fluid										
1. Recommended	0/72	0	0/72	0	0/19	0	0/72	0	0/235	0
2. Below recommended	72/72	100	72/72	100	19/19	100	72/72	100	235/235	100
3. Above recommended	0/72	0	0/72	0	0/19	0	0/72	0	0/235	0
Average volume of spray fluid used 378.38 litres / ha										

percent usage of 1.3, while there was no farmer who used the insecticides below the normal recommendation. But a very high proportion of the farmers (98.6%) were using the insecticide at levels above their recommended concentration.

In the case of cucumber growers, out of the 19 farmers who used the insecticide spray, 17 of them used levels above recommended concentration with a percent usage of 98.4 and the rest of the farmers (53) used granular insecticide (phorate) at a dose which were higher than the normal recommendation. Thus among the 72 growers who used the insecticide as spray or as granules for pest control in cucumber, 97.2 per cent of farmers used higher concentrations / dose than the recommended and only 2.7 per cent farmers used recommended dose, while none of the farmers used below the recommended concentration / dose.

In the case of snakegourd, there were 68 farmers out of 72 who used the insecticide spray at concentrations higher than the normal with a mean percent usage of 94.4. The number of growers who used the insecticides at below the recommended concentration in snakegourd was observed only to the tune of 5.6 per cent and there was no farmers used the insecticides at recommended concentration.

The consolidated data presented in Table 6 revealed that of the 288 vegetable growers in Thiruvananthapuram district, only 2 per cent of them used insecticides at recommended concentration, and 2.7 per cent used at suboptimum level of spray concentration. While a large majority of the vegetable growers (upto 95.13%) in Thiruvananthapuram used the insecticides at concentration higher than the normal recommendation.

The usage pattern of insecticide spray volume (vide Table 6) by 235 vegetable growers surveyed during three seasons of 1995 in Thiruvananthapuram district showed that all the 235 farmers who used the insecticides as sprays adopted a spray volume below that recommended for vegetables. The average spray volume used by them was 378.38 litres per hectare, whereas an optimum volume of 550 to 750 litres per hectares would be required for better coverage of the crop plants.

Experiment II

4.4 Effect of different decontamination techniques on vegetables to remove residues of monocrotophos and phosphamidon from cowpea pods and bittergourd fruits.

4.4.1 Cowpea

Data relating to this experiment and the effect of variours techniques tried to remove monocrotophos and phosphamidon residues from cowpeapods are presented in Table 7a and 7b respectively.

4.4.1.1 **Decontamination of monocrotophos**

The highest percentage removal of monocrotophos (93.6%) was observed in the case of treatment 2 viz., dipping in 2% lime water for one hour. Washing and dipping in two per cent vineger for one hour (Treatment 4) showed 93.10 per cent removal of monocrotophos. A percentage removal of 92.55 was observed where the pods dipped in two per cent tamarind water for one hour (Treatment 1).

A dip in two percentage solution of salt water for one hour (Treatment 3) removed 89.7 per cent of monocrotophos residue in cowpea pods. A mere washing with tap water coupled with gentle rubbing (Treatment 5) could remove 16.83 per cent monocrotophos. The cooking of cowpea pods in closed container for 25 minutes (Treatment 7) removed 61.05 per cent monocrotophos, whereas open cooking for 25 minutes (Treatment 6) removed the residue to the extent of 51.76 per cent.

The storage of cowpea pods in a refrigerator for three days (Treatment 8) removed monocrotophos to the tune of 17.84 per cent.

Table. 7a **Effect of decontamination techniques on the removal of residues from cow pea pods treated with monocrotophos.**

Sl. No.	Decontamination techniques	Mean per cent removal of residue (ppm.) from pods	
		Treated	% removal
T0	Control	50 ppm	5.00
T1	Dipping in tamarind water(2%)for 1 hour	50 ppm.	92.55
T2	Dipping in 2% lime water for 1 hour	50 ppm.	93.60
T3	Dipping in 2% salt water for 1 hour	50 ppm.	89.70
T4	Dipping in 2% vinegar for 1 hour	50 ppm.	93.10
T5	Tap water washing	50 ppm.	16.83
T6	Open cooking	50 ppm.	51.76
T7	Closed cooking	50 ppm.	61.05
T8	Storage for 3 days in refrigerator	50 ppm.	17.84

Table. 7b **Effect of decontamination techniques on the removal of residues from Cow pea pods treated with Phosphamidon**

Sl. No.	Decontamination techniques	Mean per cent removal of residue (ppm.) from pods	
		Treated	% removal
T0	Control	50 ppm	7.00
T1	Dipping in tamarind water (2%) for 1 hour	50 ppm.	92.36
T2	Dipping in 2% lime water for 1 hour	50 ppm.	97.28
T3	Dipping in 2% salt water for 1 hour	50 ppm.	84.90
T4	Dipping in 2% vinegar for 1 hour	50 ppm.	94.60
T5	Tap water washing	50 ppm.	11.55
T6	Open cooking	50 ppm.	48.36
T7	Closed cooking	50 ppm.	49.41
T8	Storage for 3 days in a refrigerator	50 ppm.	14.97

4.4.1.2 **Decontamination of phosphamidon**

The highest percentage removal of phosphamidon (97.28) was observed in the case of treatment 2 viz., dipping in two per cent lime water for one hour. Washing and dipping in two per cent vinegar for one hour (Treatment 4) showed 94.6 per cent removal of phosphamidon residue. A per cent removal of phosphamidon to the extent of 92.36 was observed when the pods were dipped in two per cent tamarind water for one hour (Treatment 1)

A dip in two per cent solution of salt water for one hour (Treatment 3) removed 84.9 per cent phosphamidon residue in cowpea pods. A mere washing with tap water coupled with gentle rubbing (Treatment 5) could remove 11.55 per cent phosphamidon. Cooking of cowpea pods in closed container for 25 minutes (Treatment 7) removed 49.41 per cent phosphamidon, whereas open cooking for 25 minutes (Treatment 6) removed 48.36 per cent of phosphamidon residue.

A storage of cowpea pods in a refrigerator for three days removeed phosphamidon to an extent of 14.7 per cent.

Fig. 7a Effect of decontamination techniques on the removal of residues from cowpea pods treated with monocrotophos

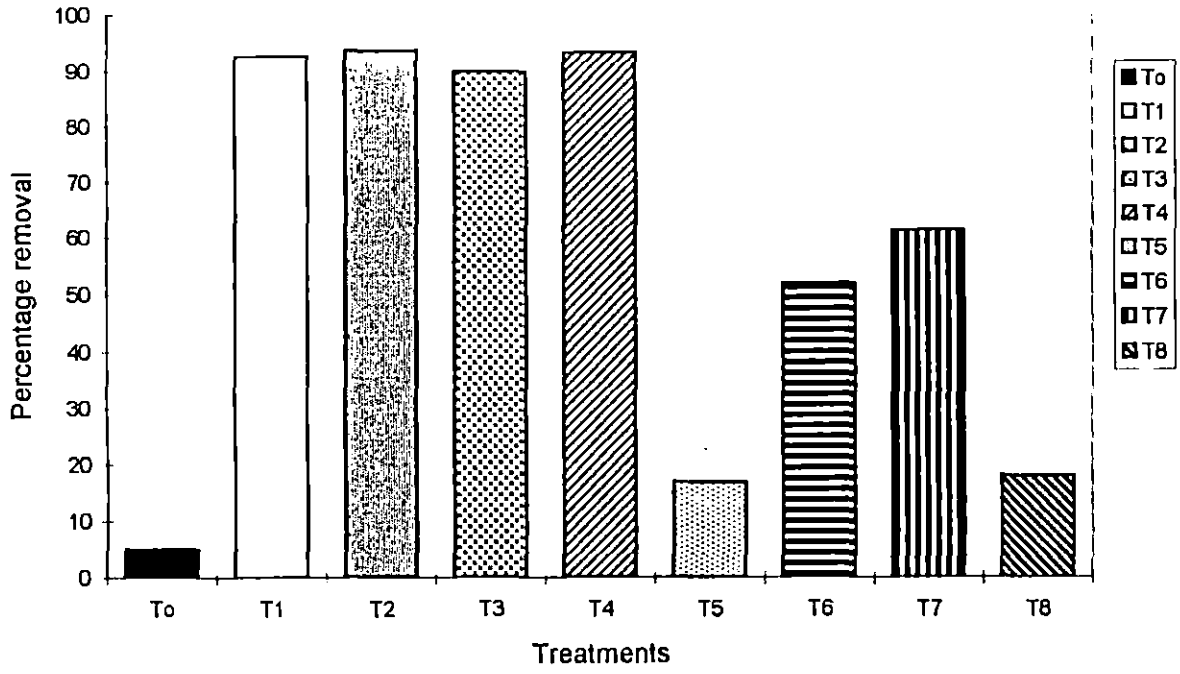
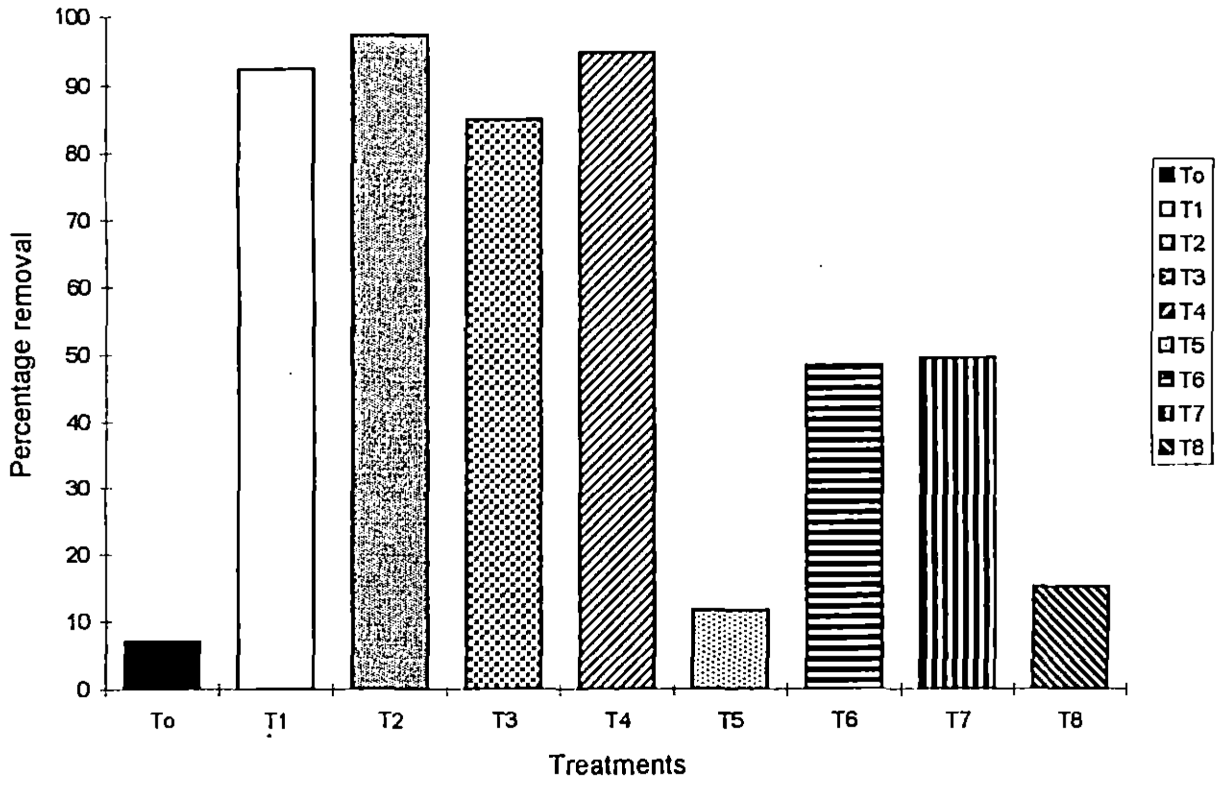


Fig. 7b Effect of decontamination techniques on the removal of residues from cowpea pods treated with phosphamidon



4.4.2 Bittergourd

The percentage removal of monocrotophos and phosphamidon in bittergourd fruits by the different decondamination treatments are presented in Table 8a and 8b respectively.

4.4.2.1 Decontamination of monocrotophos

The bittergourd fruits dipped in two per cent salt solution for one hour (Treatment 3) removed 91.65 per cent of monocrotophos residue. Similarly dipping in two per cent lime water for one hour (Treatment 2) showed a percentage removal 89.4 of monocrotophos residue.

A dip in two percentage tamarind water for one hour (Treatment 1) could remove 90.55 per cent monocrotophos and 84.05 per cent of phosphamidon residue. Soaking for an hour in two per cent vinegar solution (Treatment 4) removed monocrotophos to the ture of 82.21per cent.

A mere washing of bittergourd fruits in tap water coupled with gentle hand rubbing could remove 6.66 per cent monocrotophos. Cooking of sliced bittergourd fruit in closed container for 25 minutes

Table. 8a **Effect of decontamination techniques on the removal of residues from bittergourd fruits treated with Monocrotophos.**

Sl. No.	Decontamination techniques	Mean per cent removal of residue (ppm.) from fruits	
		Treated	% removal
T0	Control	50 ppm	10.00
T1	Dipping in tamarind water (2%) for 1 hour	50 ppm.	90.55
T2	Dipping in 2% lime water for 1 hour	50 ppm.	89.40
T3	Dipping in 2% salt water for 1 hour	50 ppm.	91.65
T4	Dipping in 2% vinegar for 1 hour	50 ppm.	82.21
T5	Tap water washing	50 ppm.	6.60
T6	Open cooking	50 ppm.	52.20
T7	Closed cooking	50 ppm.	54.44
T8	Storage for 3 days in a refrigerator	50 ppm.	8.33
T9	Sun drying for 2 days	50 ppm.	43.30

(Treatment 7) removed 54.44 per cent monocrotophos, whereas open cooking for 25 minutes (Treatment 6) could remove 52.2 per cent of the residue.

The storage of bittergourd fruits in a refrigetor for three days (Treatment 8) removed monocrotophos residue to the tune of 8.33 per cent.

Sun drying of bittergourd fruit chips for two days (Treatment 9) could remove monocrotophos residue to the extent of of 43.3 per cent.

4.4.2.2 **Decontamination of phosphamidon**

The bittergourd fruits dipped in two per cent salt solution for one hour (Treatment 3) removed 95 per cent of phosphamidon residue. Similarly dipping in two per cent lime water solution for one hour (Treatment 2) showed a percentage removal of 88.3 of phosphamidon residue.

A dip in tamarind water for one hour (Treatment 1) could remove 84.05 per cent of phosphamidon. Soaking for an hour in two per cent vinegar solution (Treatment 4) removed 94.35 per cent phosphamidon.

Table. 8b **Effect of decontamination techniques on the removal of residues from bitter gourd fruits treated with Phosphamidon.**

Sl. No.	Decontamination techniques	Mean per cent removal of residue (ppm.) from fruits	
		Treated	% removal
T0	Control	50 ppm	8.00
T1	Dipping in tamarind water (2%) for 1 hour	50 ppm.	84.05
T2	Dipping in 2% lime water for 1 hour	50 ppm.	88.30
T3	Dipping in 2% salt water for 1 hour	50 ppm.	95.05
T4	Dipping in 2% vinegar for 1 hour	50 ppm.	94.35
T5	Tap water washing	50 ppm.	8.78
T6	Open cooking	50 ppm.	45.05
T7	Closed cooking	50 ppm.	56.04
T8	Storage for 3 days in a refrigerator	50 ppm.	16.00
T9	Sun drying for 2 days	50 ppm	24.17

Fig. 8a Effect of decontamination techniques on the removal of residues from bittergourd fruits treated with monocrotophos

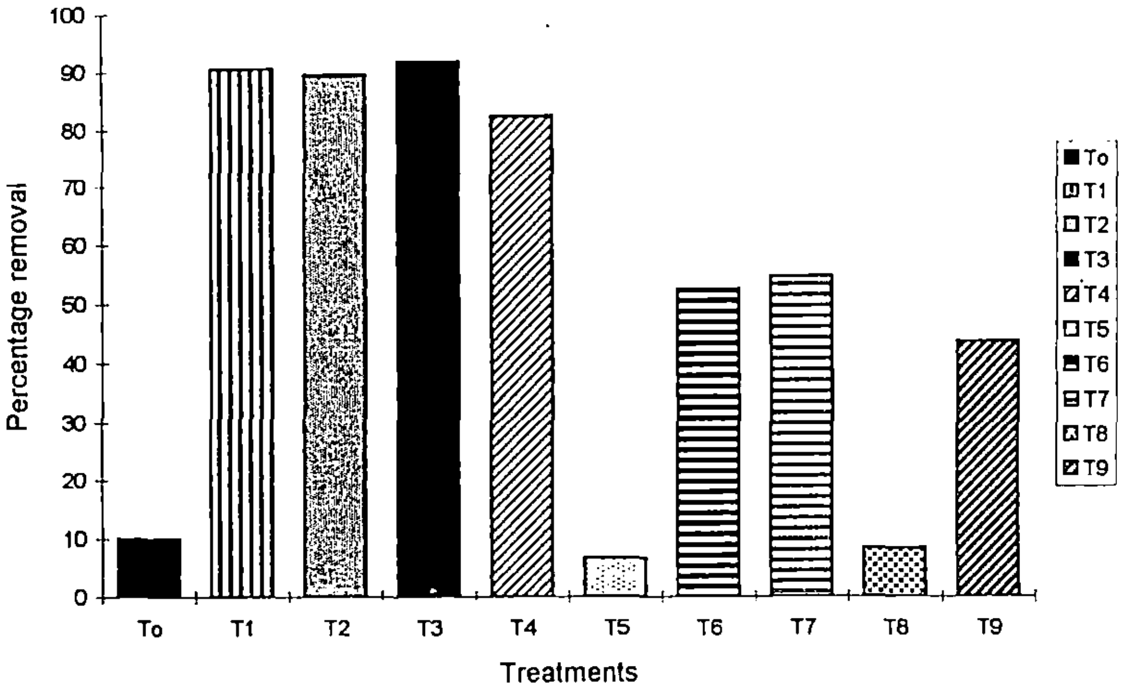
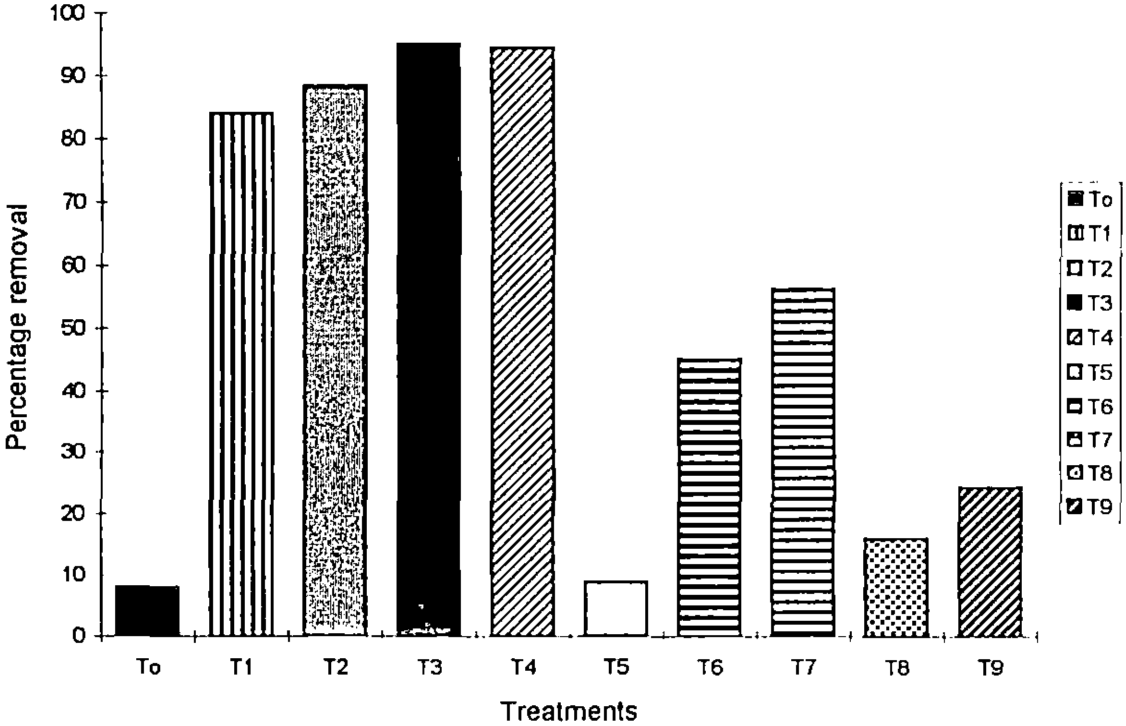


Fig. 8b Effect of decontamination techniques on the removal of residues from bittergourd fruits treated with phosphamidon



A mere washing of bittergourd fruits in tap water coupled with gentle rubbing (Treatment 5) could remove only 8.78 per cent of phosphamidon residue. Cooking of sliced bittergourd in closed container for 25 minutes (Treatment 7) removed 56.04 per cent phosphamidon, whereas open cooking for 25 minutes (Treatment 6) could remove 45.05 per cent of the residue.

Storage of bittergourd fruits in a refrigetor for three days (Treatment 8) removed phosphamidon to an extent of 16 per cent.

Sun drying of bittergourd fruit chips for two days (Treatment 9) could remove 24.17 per cent phosphamidon.

DISCUSSION

5. DISCUSSION

Insecticide residues in market samples of vegetables collected from different sellers in four major markets in Thiruvananthapuram.

Monitoring of insecticide residues in market samples of vegetables was started in 1995 covering four major vegetable markets in Thiruvananthapuram viz., Aralumoodu, Chalai, Nedumangadu and Powdikonam. Four major vegetable crops cultivated extensively in Kerala viz., bittergourd, cowpea, cucumber and snakegourd were selected for the study. A large share of vegetables arriving in the markets of Kerala are coming from neighbouring states of Tamilnadu and Karnataka. The collection of information on the pesticide usage or type and frequency of their application is not possible since they are produced elsewhere. But in the four crops selected for the study cultivator cum sellers could be identified in each market from whom the information on spray history of the samples could also be collected directly.

In Thiruvananthapuram 19 markets of which four major markets located near the vegetable growing pockets viz., Aralumoodu market (vegetable fields in Aralumoodu and Kalliyoor), Chalai market (Palappur, Papanchani and Kalliyoor), Nedumangadu market (Karippur and Anad) and Powdikonam (Powdikonam, Kattumpuram) were selected. In each market, six cultivator cum sellers were selected for each crop for collection of samples. This sampling procedure was targeted to the actual producer who supply the vegetables to the markets inorder to collect all available information on the history of samples. This helped the estimation of insecticides of known identity easier and relatively quicker when compared to the routine procedure followed for the screening of unidentified contaminants.

In Thiruvananthapuram district, majority of vegetable cultivation is done in reclaimed paddy fields and uplands where the crops are raised in succession(Kerala Land Use Board 1997) Since year round cultivation is made, no definite cropping season exist. However for assessing the influence of cropping season on the pest build up and its consequent influence on pesticide usage, three peak harvest season for vegetables were identified which were January - March, April - May and September - October, 1995.

Number of studies have been conducted on the extent of contamination on different food commodities with pesticide residues in India during the last three decades (1960 to 1990). Studies for this purpose were conducted on surveillance and compliance basis. In surveillance, samples are taken at random to measure the residues resulting from a specific pest control without suspicion that they contain illegal pesticide residue or in other words they are routine studies involving analysis of objective samples. While in compliance, samples are collected subjectively when other evidences indicate the likelihood of violation of recommended plant protection practices and consequent illegal residues. However under Indian conditions, practically no such regular surveillance or compliance studies have been carried out. Whatever data are available on monitoring of pesticide residue have been generated in sporadic studies conducted in various Agricultural Universities and some National institutes.

The first review report on contamination in vegetables and fruits with insecticides in India came in 1981 (Kalra and Chawla) and they reviewed the reports published during the period from 1964 to 1979. Residues of only organochlorine insecticides like DDT, BHC, endosulfan, aldrin, dieldrin, lindane, heptachlor etc. were reported in these references. A residue level upto 60 ppm of DDT was detected in vegetable samples collected Delhi (Agnihotri *et al.*, 1974). A residue level as high as 169 ppm of DDT in potatoes collected from Mysore (Majumdar, 1973) and a level of 8 to 20 ppm of BHC in leafy vegetables collected from Karnataka (Visweswaraiah and Jayaram, 1972) and from Hyderabad (Lakshminarayana, 1980) were also reported in this review. However, the general level of organochlorine residue reported in these references varied from traces to 8 ppm.

The second review paper on pesticide residue in market samples of vegetables collected during the period from 1970 to 1980 in different states of the country, was published in 1993 (Kathpal and Beenakumari). The reports covered under this review also did not bring out any additional information other than the wide spread occurrence of organochlorine insecticide like BHC, DDT, endosulfan, aldrin, dieldrin, heptachlor etc. (traces to 8 ppm). It is only with the starting of All India Co-ordinated Research Project on pesticide residue from the year 1984, monitoring of different food commodities has been taken up as a regular work by various centers of the project. But the protocol issued for monitoring insecticide residues in vegetables was mainly aimed to estimate the organochlorine insecticides because the methodology for multiresidue determination of organochlorines was relatively easy and quick than that for other groups of pesticides. However the concept of farmgate samples which are the samples collected at 'farmgate' (the stage at which the harvested fruits are just ready for transportation to the markets) facilitated subjective investigation of the residues by knowing the spray history. Systematic monitoring of farmgate samples was started from the year 1993 under AICRP on pesticide residue.

In Kerala the first report on monitoring of insecticide residue in market samples of vegetables was from Rajendran and his team in 1991 from RARS, Pilicode which was a typical compliance study for monitoring residues of carbofuran. It showed that samples of amaranthus, bhindi, brinjal, bittergourd and cucumber collected from local markets of Thaliparamba, Kannur and Panniyur showed higher levels of carbofuran residue (0.82 to 1.67 ppm) whereas the maximum residue limit fixed was only 0.2 ppm (Rajendran *et al.*, 1991). However the samples of different vegetables (cucumber, snakegourd, bhindi, cowpea and bittergourd) collected from local markets of Thiruvananthapuram were contaminated only with HCH that too far below the MRL (Mathew *et al.*, 1993). In the former case carbofuran residues were estimated in a subjective manner and in the latter only organochlorine residues could be measured. The first report on monitoring of farmgate samples of vegetables conducted under the AICRP on pesticide residues, Vellayani centre showed that cowpea and bittergourd samples contained very high residues of monocrotophos (0.93 to 1.32 ppm) while bhindi fruits carried high residue of phosphamidon (0.68 to 1.12 ppm) and residue level were far above 0.2 ppm (Mathew *et al.*, 1995). Thus wide variation were seen among the residue levels observed in markets and farmgate samples of vegetables collected from different locations in Kerala. The general observation on pesticide usage evident from these studies was that vegetable growers in Kerala often violate recommended plant protection practices. Thus compliance type of residue investigation was highly essential in the vegetable growing sector of Kerala to identify the chief contaminants, their level, extent of contamination with reference to MRL and to investigate the pesticide application practices followed by the farmers which lead to the illegal residues. Thus a series of sampling, residue analysis and investigation on the history of residues were started in the southern part of Kerala to begin the state wide monitoring studies during 1995.

The results presented in para 4.1 to 4.8.9 and Table 1 to 3 showed that organophosphate insecticide viz., methyl parathion, quinalphos, monocrotophos, phosphamidon and phorate were the only insecticide contaminant detected in the study. A total number of 288 samples (6 sellers x 4 vegetables x 4 markets x 3 seasons) were analysed of which not a single sample was found free from insecticide residue.

During the first season (Jan. - March 1995), the highest level of OP residue detected was in a cowpea sample (0.81 ppm of quinalphos) collected from Aralumoodu market and the level was four times more than that of the MRL fixed for quinalphos (0.2 ppm). The lowest residue observed during the first season was in a cucumber sample (0.01 ppm phorate) collected from Nedumangadu. Variation among the mean residue values of four vegetables and four markets was statistically significant. The Aralumoodu market ranked first with reference to the mean residue level (0.21 ppm), and among the vegetables, cowpea was ranked top (0.81 ppm).

During the second season (April - May 1995) the highest level of OP residue was observed in samples collected from Chalai market (0.29 ppm) and the crop carrying the highest OP residue was cowpea itself (0.51 ppm). Considering the individual sample collected from different sellers during the second season, peak level of OP residue detected was in cowpea (0.77 ppm quinalphos) which was also about four times the MRL value.

During the survey conducted in Sept. - Oct 1995 the general residue levels noticed were relatively lower and the highest residue level observed among 72 samples collected during the period was 0.41 ppm of methyl parathion in a cowpea sample collected from Chalai market which was twice the MRL fixed for the insecticide. The variation among the different market was insignificant but the variation among the different crop was significant with cowpea carrying the maximum pesticide residue levels. The result obtained from the study for three season with reference to MRL presented in Table.4 showed that methyl parathion (60 %) is the major contaminant identified in cowpea, bittergourd and in snakegourd whereas phorate (74 %) was the major contaminant in cucumber, which was not detected in the former three vegetables. The result obtained in the present study is in tune with the findings of Mathew et al. 1995. Quinalphos and monocrotophos came next in rank among the organophosphate with 14 and 13 per cent contamination of total samples collected. Maximum per cent contamination below the MRL values was observed in bittergourd samples(83.4 %) followed by snakegourd (77.8 %), cucumber (75 %) and cowpea (57 %). In contrast, the proportion of sample contaminated above MRL was highest in cowpea(43%) followed by cucumber (25%), snakegourd (22.3 %) and bittergourd (17 %). Considering the insecticide wise contamination methyl parathion stood first (48 % of total samples analysed) followed by phorate (18 %), quinalphos (14%), monocrotophos (12.5 %) and phosphamidon (7 %).

The number of different vegetables carrying illegal residues falling in different ranges above MRL are presented in Table 9a to 9e.

Table 9a. Frequency table showing illegal residue ranges of organophosphate in vegetables -- Methyl parathion

Range	Bittergourd	Cowpea	Cucumber	Snakegourd	Total
0.20-0.40	6	8	2	4	20
0.41-0.60	-	3	-	2	5
0.61-0.80	-	1	-	-	1
0.81-1.00	-	-	-	-	-
Total	6	12	2	6	26

Methyl parathion was identified as the chief contaminants with highest number of violative samples (26 / 77) closely followed by quinalphos (18 / 77). However earlier studies showed that monocrotophos and phosphamidon are the chief contaminants (Mathew et al., 1995). Of the 26 violative samples contaminated with methyl parathion, 77 per cent were carrying residues twice the MRL, 19 per cent with residues thrice the MRL and 3.8 per cent with residues 4 times the MRL.

Table 9b. Frequency table showing illegal residue ranges of organophosphate in vegetables -- Quinalphos

Range	Bittergourd	Cowpea	Cucumber	Snakegourd	Total
0.20-0.40	4	7	-	3	14
0.41-0.60	-	-	-	-	-
0.61-0.80	-	3	-	-	3
0.81-1.00	-	1	-	-	1
Total	4	11	-	3	18

In the case of violative samples containing illegal residues of quinalphos, one samples exceeded 4 times the MRL, three samples were contaminated with 3 to 4 times MRL and 14 samples with double the safe limit for quinalphos.

Table 9c. Frequency table showing illegal residue ranges of organophosphate in vegetables -- Monocrotophos

Range	Bittergourd	Cowpea	Cucumber	Snakegourd	Total
0.20-0.40	1	6	1	3	11
0.41-0.60	1	-	-	1	2
0.61-0.80	-	-	-	-	-
0.81-1.00	-	-	-	-	-
Total	2	6	1	4	13

In the case of violative samples of monocrotophos, phosphamidon and phorate, highest frequency of illegal residues fell in the range of 0.20 to 0.40 which was twice the MRL value fixed for these insecticides and none of them exceeded thrice the MRL value.

Table 9d. Frequency table showing illegal residue ranges of organophosphate in vegetables -- Phosphamidon

Range	Bittergourd	Cowpea	Cucumber	Snakegourd	Total
0.20-0.40	-	1	1	3	5
0.41-0.60	-	1	-	-	1
0.61-0.80	-	-	-	-	-
0.81-1.00	-	-	-	-	-
Total	-	2	1	3	6

Table 9e. Frequency table showing illegal residue ranges of organophosphate in vegetables -- Phorate

Range	Bittergourd	Cowpea	Cucumber	Snakegourd	Total
0.20-0.40	-	-	14	-	14
0.41-0.60	-	-	-	-	-
0.61-0.80	-	-	-	-	-
0.81-1.00	-	-	-	-	-
Total	-	-	14	-	14

The overall analysis of the per cent contamination of vegetable samples (Fig. 3), also showed cowpea as the most contaminated vegetables.

The market-wise and season-wise comparison of the data in Fig. 4 and 5 showed that samples collected from Chalai and Aralumoodu markets and those collected during January-March 1995, had relatively higher levels of residue.

The overall observation on the per cent usage of different OP insecticides by the vegetable growers revealed that methyl parathion was preferred most (48.2 %) followed by phorate (18.0 %), monocrotophos (12.5 %), phosphamidon (6.9 %) and quinalphos (13.8 %). The results obtained in the present study is in agreement with the findings of Mathew et al. (1995).

The overall findings on the adoption of recommended spray concentration revealed that 95.13 % of farmers used the insecticides at higher concentrations whereas 2.7 per cent of farmers adopted lower levels of spray concentrations and only 2 per cent of growers used recommended spray concentration. The results in the present investigation is also in conformity with the findings of Mathew et al. (1995).

The observation regarding the spray volume of insecticide used by farmers in the present study revealed that cent per cent of the farmers used volumes below the recommendation, which further intensified the problem of overdosage.

The decontamination of insecticide residue on cowpea showed that dipping the pods in locally available solutions such as two per cent solution of tamarind extracts, salt, lime, vinegar could remove the residues of monocrotophos to the tune of 90 per cent whereas the treatment could remove phosphamidon in the range of 84.9 to 94 per cent.

A mere tap water washing was found to remove 11.5 per cent phosphamidon and 16.83 per cent of monocrotophos residue. Cooking the samples for 25 minutes in open and closed containers removed the residues of monocrotophos and phosphamidon to the tune of 48.36 to 61.05 and 45.05 to 56.04 per cent respectively.

Refrigeration of the fruits/pods for three days removed the residues of monocrotophos and phosphamidon to the extent of 14.97 to 17.84 per cent in cowpea whereas in bittergourd it ranged between 8.33 to 16 per cent.

SUMMARY

SUMMARY

An investigation was undertaken to assess the insecticide residues in market samples of vegetables, viz., bittergourd, cowpea, cucumber and snakegourd from four markets of Thiruvananthapuram during three seasons of 1995. The effect of certain decontamination techniques which can be practiced at consumer level to remove the residues of insecticide was also studied.

The study revealed that organophosphate insecticides, viz., methyl parathion, quinalphos, monocrotophos, phosphamidon and phorate were the contaminants present in the vegetable samples. Invariably all the 288 samples collected from the four vegetable markets (Aralumoodu, Chalai, Neduamangadu and Powdikonam) were contaminated with one or other OP insecticides. The samples collected from Aralumoodu market during the first season (January-March) and from Chalai market during the second season (April-May) were found contaminated to a significantly higher extent than those collected from the other three markets. It was observed from the study that cowpea was the most contaminated vegetables. Forty three per cent of the cowpea samples were contaminated with OP insecticides above MRL followed by cucumber (25.0 %), snakegourd (22.3 %) and bittergourd (16.7 %). Among the five OP insecticides detected

during the survey, methyl parathion was identified as the chief contaminant in cowpea (0.22 to 0.65 ppm), bittergourd (0.01 to 0.29 ppm) and in snakegourd (0.04 to 0.52 ppm) whereas phorate was the major contaminant in cucumber (0.02 to 0.26 ppm). Phorate was found only in cucumber.

The mean residue level for each insecticide in the contaminated samples showed relatively high values for all insecticides detected in cowpea except for phorate. The mean values for quinalphos, phosphamidon, monocrotophos and methyl parathion were 0.32, 0.33, 0.25 and 0.18 ppm respectively whereas in other three crops, the mean residues observed were in a lower level (0.08 - 0.38 ppm).

A marketwise comparison of mean values of insecticide residues in vegetables are made and it revealed that with reference to the mean level of residue, relatively higher values were observed in samples collected from Chalai (0.14 - 0.29 ppm) and Aralumoodu (0.14 - 0.21 ppm). Whereas in the samples collected from Nedumangadu and Powdikonam, the corresponding values were 0.12 - 0.14 ppm and 0.13 - 0.15 ppm respectively.

The overall observation on the insecticide preference of vegetable growers indicated that methyl parathion was the most preferred insecticide (48.2 %) followed by phorate (18.4 %). The preference for monocrotophos, phosphamidon and quinalphos were 12.5, 6.9 and 13.8 per cent respectively.

The pesticide usage data collected from the growers showed that 95.13 per cent of farmers were using the insecticide at concentrations higher than the normal, whereas 2.7 per cent of farmers used sub-optimal concentration, and only two per cent of farmers used the insecticides at their recommended concentrations. The study also showed that 100 per cent of the farmers used the spray volumes below the recommended rates (mean volume of 378 liters / ha as against an optimum volume of 550 to 750 liters / ha). Thus over use of OP insecticides was found to be the main reason for higher extent of violative residues detected in the study. Besides frequent application of insecticides and harvesting at shorter intervals was identified as the reason for higher insecticide contamination in vegetable cowpea.

The decontamination of the insecticide residue on cowpea showed that dipping the pods with a 2 per cent solution of salt, tamarind extract, lime or vinegar could remove the phosphamidon residue in the range of 84.9 to 94 per cent and monocrotophos to the tune of 90 per cent. Whereas mere tap water washing could remove 11.5 per cent of the phosphamidon residue and 16.83 per cent of monocrotophos.

Cooking the cowpea pods for 25 minutes (open and closed cooking) could remove monocrotophos residue in the range of 51.76 to 61.05 per cent and phosphamidon residue in the range of 48.36 to 49.41. While refrigeration could remove the monocrotophos to the extent of 17.84 per cent and phosphamidon to the tune of 14.97 per cent.

In bittergourd, dipping the fruit in 2 per cent solution of tamarind extract, lime, salt or in vinegar for one hour could remove the monocrotophos residue to an extent of 90 per cent and phosphamidon to 95 per cent. At the same time washing the fruit could remove 6.6 per cent monocrotophos and 8.78 per cent phosphamidon.

Cooking bittergourd fruits for 25 minutes (open and closed cooking) removed residues of monocrotophos in the range of 52.2 to 54.44 per cent and phosphamidon in the range of 45.05 to 56.04 per cent whereas sun drying fruit chips for 2 days removed monocrotophos to the tune of 43.3 and phosphamidon to 24.17 per cent.

Refrigeration of fruits could remove 8.33 per cent of monocrotophos and 16 per cent of phosphamidon residues.

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APPENDIX

APPENDIX

Proforma for the details on spray history of vegetables collected

Name & Address	Vegetable	season	Area (cent)	No. of fruits	First harvest	Last harvest	Harvest interval	Formulation	Doze / Pump	No. of Pump	No. of spray	Pump capacity	Time b / w harvest &spray	Marketed date	a i / ha	Spray vol / ha

INSECTICIDE RESIDUES IN MARKET SAMPLES OF VEGETABLES AND METHODS OF THEIR DECONTAMINATION

By

SANTHOSH KUMAR, S. R.

ABSTRACT OF THESIS
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DEPARTMENT OF AGRICULTURAL ENTOMOLOGY
COLLEGE OF AGRICULTURE
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ABSTRACT

An investigation was undertaken to assess the insecticide residues in market samples of vegetables, viz., bittergourd, cowpea, cucumber and snakegourd from four markets of Thiruvananthapuram during three seasons of 1995. The effect of certain decontamination practices on vegetables to remove residues of insecticides was also assessed.

The study revealed that organophosphate insecticides, viz., methyl parathion, quinalphos, monocrotophos, phosphamidon and phorate were the contaminants present in the vegetable samples. It was observed that invariably all the 288 samples collected from the four vegetable markets (Aralumoodu, Chalai, Neduamangadu and Powdikonam) were contaminated with one or other OP insecticides. The samples collected from Aralumoodu market during the first season (January-March) and from Chalai market during the second season (Apri-May) were found contaminated to a significantly higher extent than those collected from the other three markets. The overall analysis of the data on the extent of contamination revealed that cowpea was the most contaminated vegetable. Forty three per cent of the cowpea samples were contaminated with OP insecticides above MRL followed by cucumber (25.0 %), snakegourd (22.3 %) and bittergourd (16.7 %). Among the five OP insecticides detected during the

survey, methyl parathion was identified as the chief contaminant in cowpea (0.22 to 0.65 ppm), bittergourd (0.01- to 0.21 ppm) and in snakegourd (0.04 to 0.52 ppm) whereas phorate was the major contaminant in cucumber (0.02 to 0.26 ppm).

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